Ionic liquids are organic salts that are liquid at low temperatures (<100 °C) and consist of large organic cations and anions such as tetrafluoroborate, chloride, etc. The application of ionic liquids for extraction processes is promising because of their non-volatile nature. The ionic liquid [mebupy]BF$_4$ is suitable as an extractant for aromatic hydrocarbons from aliphatic hydrocarbons and was selected for tests in a pilot scale Rotating Disc Contactor (RDC). The pilot plant RDC provided good results: small droplets and a high column capacity.

An economic evaluation was made for the separation of toluene from a mixed toluene/heptane stream with [mebupy]BF$_4$ and compared to the extraction with sulfolane. The total investment costs in the sulfolane process were about M€ 86 for a naphtha feed of 300 ton/hr, containing about 10% aromatic hydrocarbons. The process with the ionic liquid was estimated to be M€ 56, including an ionic liquid inventory of M€ 20. The main conclusion of the process evaluation is that development of ionic liquids which show a high aromatic distribution coefficient with a reasonable aromatic/aliphatic selectivity could reduce the investment costs of the aromatic/aliphatic separation to about M€ 25 to 30.

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Extraction of Aromatics from Naphtha with Ionic Liquids **Geert Wytze Meindersma**

From Solvent Development
to Pilot RDC Evaluation

Extraction of Aromatics from Naphtha with **Ionic Liquids**

Geert Wytze Meindersma

Uitnodiging

Hierbij wil ik u van harte uitnodigen
voor het bijwonen van de openbare
verdediging van mijn proefschrift,
getiteld

Extraction of
Aromatics from
Naphtha with
Ionic Liquids

op vrijdag 9 september 2005
om 15:00 uur
in zaal 2 van gebouw de Spiegel
van de Universiteit Twente.

Voorafgaande aan de verdediging zal ik
om 14:45 uur een korte inleiding geven
over de inhoud van dit proefschrift.

Na afloop van de promotie is er een
receptie op dezelfde lokatie.

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STELLINGEN

behorende bij het proefschrift

EXTRACTION OF AROMATICS FROM NAPHTHA WITH IONIC LIQUIDS
FROM SOLVENT DEVELOPMENT TO PILOT RDC EVALUATION

Geert Wytze Meindersma, Universiteit Twente (09-09-2005)

1. Het gebruik van activiteitscoëfficiënten bij oneindige verdunning om de verdelingscoefficiënt en de selectiviteit voor extractie te bepalen, geeft bij normale concentraties geen exact beeld van de waarden van deze parameters, hooguit een indicatie.
   Dit proefschrift, hoofdstuk 4.

2. Door de bijna oneindige variatie in kat- en anionen van ionische vloeistoffen zouden er theoretisch 10^{18} verschillende ionische vloeistoffen zijn. Deze enorme verscheidenheid heeft echter in de praktijk weinig nut.
   Dit proefschrift, hoofdstuk 4.

3. Aan het begin van elk project in toegepast onderzoek dient een ruwe economische evaluatie van mogelijke procesroutes plaats te vinden om aan te geven in welke richting het onderzoek dient te gaan.
   Dit proefschrift, hoofdstukken 1, 2 en 7.

4. Veel onderzoekers gaan uit van een “me-too” houding, zo ook bij onderzoek op het gebied van ionische vloeistoffen, waar velen nog steeds werken met PF_6^--houdende ionische vloeistoffen, terwijl aangetoond is dat hiermee HF-vorming kan plaatsvinden.
   Dit proefschrift, hoofdstuk 4.

5. Bij de selectie van een ionische vloeistof als extractant voor de aromaat/alifaat scheiding is de verdelingscoefficiënt van de aromaat veel belangrijker dan de aromaat/alifaat selectiviteit om tot redelijke apparaatdimensies te komen.
   Dit proefschrift, hoofdstuk 7.

6. Onderzoekers presenteren de resultaten van hun onderzoek naar nieuwe methoden dikwijls als positief, waar conventionele methoden betere, hetzij effectievere, hetzij economisch interessantere, resultaten opleveren.
   Dit proefschrift, hoofdstukken 4 en 6.

7. “Papier is geduldig” is een uitdrukking die ook in de wetenschap van toepassing is.

8. Veel Nederlandse politici hebben zich niet gerealiseerd dat de in de Londense Underground hoorbare waarschuwing “mind the gap between the train and the platform” volledig op hen van toepassing is.
   Opgetekend op 2 juni 2005, na de uitslag van het Europese Referendum.

9. Een minister van Onderwijs, Cultuur en Wetenschap, die terecht opmerkt dat met de huidige stand van de wetenschap niet alle vragen beantwoord kunnen worden, dient onafhankelijk fundamenteel onderzoek te bevorderen en geen populistisch debat over “intelligent design” aan te zwengelen.
   Opgetekend in mei 2005.

PROPOSITIONS
belonging to the thesis

EXTRACTION OF AROMATICS FROM NAPHTHA WITH IONIC LIQUIDS
FROM SOLVENT DEVELOPMENT TO PILOT RDC EVALUATION
Geert Wytze Meindersma, University of Twente (09-09-2005)

1. The use of activity coefficients at infinite dilution for the determination of distribution coefficients and the selectivity at extraction does not produce accurate values of these parameters at normal concentrations, but gives at most an indication thereof.
   This thesis, chapter 4.

2. There are claimed to be 10^{18} possible combinations in ionic liquids, because of the endless possible variation of the cations and anions, but this variety has little usefulness in practice.
   This thesis, chapter 4.

3. A crude economic evaluation of possible process routes in applied research should be carried out at the start of each project in order to indicate in which direction the research should go.
   This thesis, chapters 1, 2 and 7.

4. Many researchers have a “me-too” attitude, also true in the ionic liquid field, where a lot of them still use PF_6^--containing ionic liquids, while it has been shown that HF formation is quite probable with these ionic liquids.
   This thesis, chapter 4.

5. The aromatic distribution coefficient has a much larger impact than the aromatic/ aliphatic selectivity in selecting an ionic liquid for aromatic/aliphatic separations in order to arrive at reasonable dimensions for the equipment.
   This thesis, chapter 7.

6. Researchers often present the results of their project in a positive way, while conventional methods sometimes produce better results with respect to effectiveness or economics.
   This thesis, chapters 4 and 6.

7. “Paper won’t blush” is an expression which is also applicable in science.

8. Many Dutch politicians do not realise that the announcement in the London Underground “mind the gap between the train and the platform” completely applies to themselves.
   Written down on June 2, 2005, after the Dutch European Referendum.

9. A Secretary of Education, Culture and Science, who rightly remarks that with the current state of science not all questions can be answered, should promote fundamental research and should not initiate a popular debate on “intelligent design”.
   Written down in May 2005.

From Solvent Development
to Pilot RDC Evaluation

Extraction of Aromatics from Naphtha with **Ionic Liquids**

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EXTRACTION OF AROMATICS FROM NAPHTHA WITH **IONIC LIQUIDS**

FROM SOLVENT DEVELOPMENT TO PILOT RDC EVALUATION

PROEFSCHRIFT

ter verkrijging van
de graad van doctor aan de Universiteit Twente,
op gezag van de rector magnificus,
prof.dr. W.H.M. Zijm,
volgens besluit van het College van Promoties
in het openbaar te verdedigen
op vrijdag 9 september 2005 om 15.00 uur

door

Geert Wytze Meindersma
geboren op 4 augustus 1947
te Tilburg

Dit proefschrift met bijbehorende stellingen is goedgekeurd door de promotor
Prof. dr. ir. A.B. de Haan

en de assistent-promotor
Dr. ir. N.J.M. Kuipers

VOORWOORD

De klassieke openingszin luidt: “Het is af!!”. Dit proefschrift is nu, gelukkig, inderdaad af, maar het werk aan ionische vloeistoffen nog lang niet. Als alles gaat zoals we verwachten, wordt het onderzoek voortgezet.

Dit proefschrift was niet tot stand gekomen zonder hulp, aanwijzingen, raad en aansporingen van anderen. Allereerst wil ik mijn promotor André de Haan bedanken voor het feit dat hij voor mijn aanstelling aan de UT heeft gezorgd en voor de grote vrijheid van handelen die ik tijdens het promotieonderzoek heb genoten. Zijn kritiek was steeds opbouwend en stimulerend. Norbert Kuipers wil ik graag bedanken voor het kritisch doorlezen van diverse hoofdstukken, waarbij hij vele waardevolle suggesties heeft gedaan, die het geheel hebben verbeterd. De gehele vakgroep Scheidingstechnologie was en is heel gezellig: er heerst een goede en collegiale sfeer en ik hoop dit nog enige jaren te kunnen meemaken. Daarvoor bedank ik van harte de promovendi Karin, Fahong, Boris, Johan, Bart, Maartje, Jeroen (ook voor het beantwoorden van mijn vragen op computergebied), Thijs, Maksym, Daleen, Renze, Katarina, Paul, Lara, Tanja, Meritxell, Natasja, Marjette en Bernd en de vaste staf (en oud-vaste staf): Alfons, Anita, Annemiek, Annet, Bert, Hans, Henny, Imre, Louis en Rita.

Een speciaal woord van dank gaat naar onze technici: Anita heeft de analysemethode opgezet en een groot aantal evenwichtsmetingen uitgevoerd, Bert heeft de kolom opgebouwd en de experimenten daarin begeleid, Henny heeft adviezen gegeven voor de analyses en Alfons heeft de vele chemicaliën besteld en gezorgd voor de veiligheidstraining van alle stagiairs en afstudeerders. In het begin van dit project heb ik met behulp van Hanneke Becht van de bibliotheek een aantal uitgebreide literatuurrecherches uitgevoerd naar de verschillende methoden die geschikt zouden kunnen zijn voor deze scheiding.

Vooraf had ik niet kunnen weten dat ik met een extractie met ionische vloeistoffen zou eindigen. De opdracht luidde namelijk: ontwikkeling van een scheidingstechnologie voor de selectieve winning en zuivering van de aromatische koolwaterstoffen benzeen, tolueen, ethylbenzeen en xylenen uit de voeding van een naftakraker door middel van extractie, adsorptie/desorptie op zeolieten of een membraanscheiding met zeoliet membranen, of een combinatie van deze technologieën. Met mijn achtergrond in membraantechnologie had ik eigenlijk gedacht dat een membraanscheiding wel eens een goede oplossing zou kunnen zijn, maar na enig rekenwerk bleek dat het technisch wel, maar economisch niet haalbaar was. Daarom moest er een geheel nieuwe weg worden ingeslagen. Het doen van onderzoek en het uitvissen hoe iets in elkaar zit, heb ik altijd boeiend gevonden.

Bij DSM Research heb ik eens een stagiaire “geholpen” toen mijn assistent afwezig was. De gevolgen waren dusdanig dat hij mij naderhand heeft afgeraden om zelf nog werk in het laboratorium uit te voeren. Daarom kwam het goed uit dat ik, gezien mijn leeftijd, geen gewone promovendus was en het praktische onderzoekswerk door anderen kon laten uitvoeren. Daarvoor wil ik vooral Anita en Bert bedanken, maar ook een aantal anderen. Zo heeft Irene met Bert de kolom opgebouwd en is begonnen met een ionische vloeistof, die echter helaas niet zo “groen” bleek te zijn als men beweerde. Onze rvs roerders roestten met deze ionische vloeistof namelijk voor onze ogen weg. Daarom heeft Mireia met andere ionische vloeistoffen een groot aantal evenwichtsmetingen uitgevoerd. Tessa heeft de extractie met cyclodextrines onderzocht en haar afstudeerrapport vormde de basis van hoofdstuk 3. Marianne heeft de laatste evenwichtsmetingen gedaan en de extractie in de pilot plant RDC kolom samen met Bert uitgevoerd. Ard heeft nog wat ontbrekende gegevens verzameld en enkele metingen herhaald. Zijn verdere afstudeerwerk betreft het voorspellen van eigenschappen van ionische vloeistoffen m.b.v. een computerprogramma, maar de resultaten daarvan worden pas in een volgend project gebruikt.

Voor de financiering van dit onderzoek dank ik DSM Research, met name Sietse van der Sluis voor al zijn inspanningen om het geheel rond te krijgen, en SenterNovem. Met DSM Research, voornamelijk met Kees van Luijk, zijn er regelmatig voortgangsbijeenkomsten geweest.

Rolanda, ik ben je heel dankbaar voor jouw liefde, steun en geduld en een luisterend oor. Vooral in de laatste periode had ik bijna nergens anders aandacht voor.

Wytze

CONTENTS

SAMENVATTING

VERWIJDERING VAN AROMATEN UIT NAFTA

Het doel van deze studie was de ontwikkeling van een scheidingstechnologie voor de selectieve terugwinning en zuivering van de aromaten benzeen, tolueen, ethylbenzeen en xylenen uit de voeding van een naftakraker. De voeding van de meeste naftakrakers bevat 10 – 25% aromatische componenten, afhankelijk van de oorsprong van de voeding (nafta of gascondensaat). Deze aromatische koolwaterstoffen worden niet omgezet tot olefinen (etheen en propeen) en kleine hoeveelheden aromaten worden zelfs gevormd tijdens het kraakproces in de kraakovens. Daardoor verlagen zij de capaciteit van de kraakovens en geven een extra belasting aan de scheidingssectie van de C_5^+-stroom. Als een groot gedeelte van de aromatische koolwaterstoffen uit de krakervoeding zou kunnen worden verwijderd, zou dat een aantal voordelen met zich meebrengen: een hogere capaciteit, hogere thermische efficiency en minder vervuiling van de kraakovens en de nageschakelde warmtewisselaars.

De huidige processen om aromatische en alifatische koolwaterstoffen van elkaar te scheiden zijn ofwel alleen geschikt voor aromaatgehaltes van 20% en hoger, zoals extractie, extractieve en azeotropische destillatie, ofwel ze vertonen een lage aromaat/alifaat selectiviteit en/of hebben een lage capaciteit. In dit proefschrift werd daarom onderzocht of en op welke wijze de prestaties van adsorptie/desorptie, membraanscheidingen en extractie bij lage aromaatconcentraties drastisch konden worden verbeterd door het toepassen van nieuwe scheidingsmiddelen. Na een korte literatuurstudie werd adsorptie/desorptie uitgesloten van verder onderzoek, aangezien de potentieel geschikte zeoliet adsorbentia, bijvoorbeeld X en Y types, grote technische problemen bij de desorptie met zich mee zouden brengen en aangezien de opschaling naar grotere capaciteiten niet gunstig bleek te zijn.

MEMBRAANSCHEIDINGEN

Zeoliet membranen vertonen een hoge selectiviteit voor aromaten en hebben de voorkeur voor organisch/organische scheidingen vanwege hun robuustheid in organische oplosmiddelen en hun geschiktheid bij hogere temperaturen. Verder is de desorptie eenvoudiger dan bij adsorptie/desorptie, omdat een partieel drukverschil de drijvende kracht voor de desorptie is bij pervaporatie en damppermeatie. Uit de uitgevoerde haalbaarheidsstudie bleek dat, hoewel de benzeen/cyclohexaan selectiviteit hoog genoeg was ($S = 20 – 260$), de fluxwaarden veel te laag waren voor een praktische scheiding. De fluxwaarden moeten daarom met minimaal een factor 25 worden verhoogd ten opzichte van de huidige waarde om een redelijk membraanoppervlak te verkrijgen voor deze scheiding. De fluxstijging is in principe mogelijk, als de toplaag van het beschouwde zeolietmembraan teruggebracht zou kunnen worden van 30 μm tot 1,2 μm, die dan wel defectvrij moet zijn. Een ander probleem met zeolietmembranen is hun hoge prijs, die momenteel kan variëren van € 2.000 – 10.000/m^2. Zelfs wanneer een verhoging met een factor 25 van de flux kan worden gerealiseerd, zal de terugverdientijd voor dit proces met de huidige zeolietprijzen in de orde van 10 jaar of langer zijn. Gecombineerd met het feit dat defectvrije toplagen van 1,2 μm extreem moeilijk te maken zijn, is het duidelijk dat een membraanscheiding met zeolietmembranen momenteel geen haalbare optie is.

EXTRACTIE MET WATERIGE CYCLODEXTRINES

De enige manier om de economische haalbaarheid van extractie bij lage aromaatgehaltes te kunnen verbeteren is de ontwikkeling van nieuwe oplosmiddelsystemen die een drastische verhoging van de verdelingscoëfficiënt van aromaten en/of een hogere aromaat/alifaat selectiviteit vertonen dan de huidige bekende oplosmiddelen, zoals sulfolaan (D_{tol} = 0.31 en $S_{tol/hept}$ = 31). Waterige cyclodextrines (CD) leken een mogelijke oplossing om dit doel te kunnen bereiken, omdat cyclodextrines verscheidene organische componenten kunnen insluiten en omdat de scheiding van een waterige oplossing van cyclodextrine complexen en de organische voeding eenvoudig is. Cyclodextrines zijn niet oplosbaar in organische oplosmiddelen, maar cyclodextrine derivaten zijn zeer goed oplosbaar in water. Verschillende gesubstitueerde cyclodextrines werden onderzocht voor de scheiding van tolueen uit tolueen/heptaan mengsels en van o-xyleen uit o-xyleen/heptaan mengsels. Helaas waren de verdelings-coëfficiënten van de aromaten (D = 0.05 voor tolueen bij [m-β-CD (1,7)] = 0,22 mol/L en D = 0,023 voor o-xyleen bij [HP-β-CD (0,8)] = 0,25 mol/L) en de aromaat/alifaat selectiviteit erg laag (S = 6 voor tolueen/heptaan met m-β-CD (1,7)). Waterige oplossingen van cyclodextrines zijn daarom niet geschikt voor de extractie van aromatische stoffen uit alifatische koolwaterstoffen.

SELECTIE VAN IONISCHE VLOEISTOFFEN

Aangezien adsorptie, membraanpermeatie en extractie met cyclodextrines geen haalbare opties waren, moest er een extractieproces met andere oplosmiddelen worden gebruikt. Ionische vloeistoffen zijn organische zouten die bij lage temperaturen (< 100 °C) vloeibaar zijn en zij bestaan uit grote organische kationen gebaseerd op onder andere methylimidazolium [Rmim], N-butylpyridinium [R-N-bupy], quaternaire ammonium en fosfonium ionen, en anionen als hexafluorfosfaat, tetrafluorboraat, alkylsulfaten, alkylsulfonaten, chloride, enzovoort. De R-groep van het kation is variabel (methyl, ethyl, butyl, etc.). De verscheidenheid van de anionen en de R-groepen in de imidazolium, pyridinium, ammonium en fosfonium kationen kunnen worden gebruikt om de eigenschappen van de ionische vloeistoffen aan te passen. De toepassing van ionische vloeistoffen in extractieprocessen is veelbelovend vanwege hun niet-vluchtige aard. Dit maakt de terugwinning van het oplosmiddel gemakkelijk door gebruik te maken van eenvoudige technieken als flash destillatie of strippen.

In de literatuur wordt gemeld dat aromatische koolwaterstoffen lage activiteits-coëfficiënten bij oneindige verdunning hebben in verscheidene ionische vloeistoffen en dat alifatische koolwaterstoffen hoge activiteitscoëfficiënten hebben in dezelfde ionische vloeistoffen. Dit betekent dat ionische vloeistoffen inderdaad kunnen worden gebruikt als extractanten voor aromatische koolwaterstoffen uit alifatische koolwaterstoffen. Diverse ionische vloeistoffen werden gekozen op basis van activiteitscoëfficiënten bij oneindige verdunning en gegevens over oplosbaarheid en extractie. De gebruikte kationen waren meestal imidazolium en pyridinium, en de anionen waren waterstofsulfaat, methylsulfonaat, methylsulfaat, ethylsulfaat, dimethylfosfaat, diethylfosfaat en tetrafluorboraat. De scheiding van tolueen uit tolueen/n-heptaan mengsels werd gebruikt als een model voor de aromaat/alifaat scheiding. Op basis van initiële experimenten werden drie ionische vloeistoffen geselecteerd ([mmim]CH_3SO_4, [emim]$C_2H_5SO_4$ en [mebupy]BF_4) voor meer gedetailleerde evenwichtsmetingen, omdat de verdelingscoëfficiënt van tolueen en/of de tolueen/heptaan selectiviteit hoog was. De ionische vloeistof [mebupy]BF_4 was van deze drie de meest geschikte vanwege een combinatie van een hoge verdelingscoefficiënt van tolueen (D_{tol} = 0,44) en een hoge tolueen/heptaan selectiviteit ($S_{tol/hept}$ = 53). Daarom zijn met [mebupy]BF_4 ook extractie experimenten uitgevoerd met andere aromaat/alifaat mengsels (benzeen/n-hexaan, ethylbenzeen/n-octaan en m-xyleen/n-octaan).

De regeneratie van de ionische vloeistoffen kon eenvoudig worden uitgevoerd door de organische componenten te verdampen in een roterende verdamper bij 75 °C. Visuele beschouwing van NMR spectra van zowel de oorspronkelijke ionische vloeistof als van de geregenereerde ionische vloeistof toonde geen verschillen tussen beide monsters. Ook zijn een aantal ionische vloeistoffen gedurende 7,5 weken in een oven bij 150 °C verhit, waarbij er geen degradatie van de ionische vloeistof kon worden geconstateerd.

EVALUATIE VAN DE EXTRACTIEKOLOM

Aangezien de ionische vloeistof [mebupy]BF_4 zowel een hogere verdelingscoëfficiënt van tolueen (D_{tol} = 0,44) en een hogere tolueen/heptaan selectiviteit ($S_{tol/hept}$ = 53) vertoonde dan sulfolaan (D_{tol} = 0,31 en $S_{tol/hept}$ = 31), is deze ionische vloeistof uitgekozen voor verder onderzoek naar de extractieve verwijdering van tolueen uit een tolueen/heptaan mengsel in een semi-technische extractie kolom, uitgerust met roterende schijven (Rotating Disc Contactor, RDC). In de semi-technische RDC werden goede resultaten behaald voor de tolueen/heptaan scheiding: met de ionische vloeistof werden er kleine druppels gevormd en de kolomcapaciteit was hoog. De extractie met de ionische vloeistof was min of meer vergelijkbaar met die met sulfolaan in de RDC. Vanwege de hogere verdelingscoëfficiënt van tolueen waren lagere oplosmiddel/voeding verhoudingen (Solvent-to-Feed ratio, S/F) met de ionische vloeistof nodig om dezelfde hoeveelheid tolueen te extraheren, terwijl de flux (volumetrische doorzet) met [mebupy]BF_4 ongeveer 10% hoger was dan met sulfolaan en er een vergelijkbare efficiency in stoftransport werd waargenomen. De voedingsstroom met [mebupy]BF_4 was ook hoger (10 kg/u) dan met sulfolaan (5,8 kg/u) als oplosmiddel. De beste prestaties (hoogste extractie efficiency voor tolueen) werden gemeten bij de hoogste rotatiesnelheid (643 rpm) die in de kolom werd gebruikt. Bij een flux van 10 m^3/m^2.u werd een uitstekend hydrodynamisch gedrag waargenomen en bevatte de kolom ongeveer drie evenwichtstrappen over een actieve lengte van 1,8 m.

TERNAIRE VLOEISTOF-VLOEISTOF EVENWICHTEN

Ternaire gegevens van de systemen tolueen+n-heptaan+oplosmiddel werden verzameld voor de oplosmiddelen sulfolaan en de ionische vloeistoffen [mebupy]BF_4, [emim]$C_2H_5SO_4$ en [mmim]CH_3SO_4. Aangezien [mebupy]BF_4 was geselecteerd als de meest optimaal presterende ionische vloeistof, werden ternaire gegevens van de systemen aromaat+alifaat+[mebupy]BF_4 verzameld voor andere aromaat/alifaat combinaties, te weten benzeen/n-hexaan, ethylbenzeen/n-octaan en m-xyleen/n-octaan.

De binaire interactieparameters voor het NRTL model werden bepaald door regressie van de experimentele ternaire gegevens met ASPEN Plus 12.1. Vergelijking van de experimentele en gefitte waarden gaf aan dat er een uitstekende overeenkomst was tussen de berekende en de experimentele waarden met over het algemeen een gemiddelde afwijking van minder dan 0,01.

CONCEPTUEEL PROCES ONTWERP

Met de NRTL parameters die waren bepaald voor de diverse combinaties van aromatische en alifatische koolwaterstoffen met de ionische vloeistof [mebupy]BF_4, kon een procesmodel worden opgesteld met behulp van het flowsheeting programma van ASPEN Plus 12.1. Verscheidene simulaties van de extractie van tolueen uit een tolueen(10%)/heptaan mengsel werden uitgevoerd om het optimale aantal evenwichtstrappen in de kolom en de S/F verhouding te bepalen. Voor een opbrengst van tolueen van minimaal 98% en een zuiverheid van heptaan van meer dan 98% waren er twaalf trappen en een S/F verhouding van 2,3 nodig.

Een conceptueel scheidingsproces, bestaande uit alleen een extractiekolom en een verdamper, werd ontwikkeld voor een tolueen/heptaan mengsel. Het was niet mogelijk om een compleet proces te ontwikkelen, inclusief een extractiekolom, een extractieve stripper voor de verwijdering van heptaan uit het extract en een verdamper om tolueen van de ionische vloeistof [mebupy]BF_4 te verwijderen, vanwege ernstige fouten die in het ASPEN programma optraden.

Met de grove resultaten van de processimulaties van de scheiding van tolueen uit tolueen/heptaan mengsels werd een economische evaluatie van het proces gemaakt en vergeleken met het extractieproces met sulfolaan. De totale investeringskosten van het sulfolaanproces waren geschat door UOP, de leverancier van dit proces, op ongeveer M€ 86 voor een nafta voeding van 300 ton/u met 10% aromatische koolwaterstoffen. Het extractieproces met de ionische vloeistof [mebupy]BF_4 werd geschat op ongeveer M€ 56, inclusief een voorraad ionische vloeistof ter waarde van M€ 20.

Als de ionische vloeistoffen [mebupy]CH_3SO_4 of [emim]$AlCl_4$ worden gebruikt als extractant, die beiden een hogere verdelingscoëfficiënt van tolueen hebben dan [mebupy]BF_4, zouden de totale investeringkosten kunnen dalen naar respectievelijk M€ 47 of zelfs M€ 26. De ionische vloeistof [emim]$AlCl_4$ kan echter niet worden gebruikt in de industrie, aangezien deze heftig met water reageert.

De voornaamste conclusie van de procesevaluatie is dat de ontwikkeling van ionische vloeistoffen die een hoge verdelingscoëfficiënt van aromaten vertonen met een redelijke aromaat/alifaat selectiviteit, de investeringskosten zouden kunnen reduceren tot M€ 25 – 30. Een van de hulpmiddelen om dergelijke verbeterde ionische vloeistoffen te verkrijgen is het programma COSMO-RS, waarmee activiteitscoëfficiënten bij oneindige verdunning van ionische vloeistoffen kunnen worden voorspeld voor diverse combinaties van kat- en anionen.

Voor de acceptatie van ionische vloeistoffen in de industrie is het een absolute voorwaarde dat er genoeg toxicologische gegevens over de betreffende ionische vloeistoffen voorhanden zijn. Zonder deze gegevens zal er geen enkele ionische vloeistof worden toegepast in de industrie. Verder is de prijs van de ionische vloeistof, die nu varieert van € 200 – 3.000/kg, veel te hoog voor een industriële toepassing. Uiteraard zijn de huidige prijzen gebaseerd op gebruik op laboratoriumschaal en daarom vindt de productie ervan ook op kleine schaal plaats. Een aanvaardbare prijs is ongeveer € 10 – 25/kg. BASF, die een belangrijke producent is van imidazole, een van de grondstoffen voor ionische vloeistoffen, heeft aangegeven dat het inderdaad mogelijk is om dat prijsniveau te bereiken bij een grootschalige productie van ionische vloeistoffen.

SUMMARY

AROMATICS REMOVAL FROM NAPHTHA

The objective of this study was the development of a separation technology for the selective recovery and purification of aromatic compounds benzene, toluene, ethylbenzene and xylenes (BTEX) from liquid ethylene cracker feeds. Most ethylene cracker feeds contain 10 – 25% of aromatic components, depending on the source of the feed (naphtha or gas condensate). The aromatic compounds are not converted to olefins and even small amounts are formed during the cracking process in the cracker furnaces. Therefore, they occupy a part of the capacity of the furnaces and they put an extra load on the separation section of the C_5^+-aliphatic compounds. If a major part of the aromatic compounds present in the feed to the crackers could be separated up stream of the furnaces, it would offer several advantages: higher capacity, higher thermal efficiency and less fouling.

The current processes for the separation of aromatic and aliphatic hydrocarbons are either suitable for aromatic concentrations of 20% or more, such as extraction, extractive distillation and azeotropic distillation, or show low aromatic/aliphatic selectivities and/or have low capacities. Therefore, it was investigated, whether and how the performance of adsorption/desorption, membrane separation and extraction could be drastically improved at low aromatics content by using new separating agents. After a short literature study, adsorption/desorption was discarded for further work because potentially suitable zeolite adsorbents, for instance X and Y types, would result in tremendous technical problems during desorption and its scale up to large capacities appeared unfavourable.

MEMBRANE SEPARATION

Zeolite membranes exhibit high aromatic selectivities and are preferred for organic/organic separations because of their robustness in organic solvents and their application at higher temperatures. Furthermore, desorption is much less difficult as in adsorption/desorption, because a partial pressure difference is the driving force in pervaporation and in vapour permeation. The performed feasibility study indicated that, although benzene/cyclohexane selectivities are high enough (S = 20 – 260), the flux rates are far too low for a feasible separation. Therefore, the flux rates must be increased by at least a factor of 25 to obtain a reasonable membrane area for this separation. The increase in flux is, in principle, possible, if the used zeolite membrane top layer of 30 μm can be reduced to a defect-free thickness of 1.2 μm. Another problem for zeolite membrane permeation is their current price, which can vary from € 2,000 – 10,000/m^2. Even when a 25 times increase in membrane flux is considered, the pay back time for this process with these prices for zeolite membranes will be 10 years or more. Combined with the fact that a defect-free top layer of 1.2 μm is extremely difficult to manufacture, it is clear that zeolite membrane permeation is presently not a feasible option.

EXTRACTION WITH AQUEOUS CYCLODEXTRINS

The only way to improve the economic feasibility of extraction technology at low aromatics content is the development of new solvent systems that exhibit a dramatically higher aromatic distribution coefficient and/or a higher aromatic/aliphatic selectivity than the known solvents, such as sulfolane (D_{tol} = 0.31 and $S_{tol/hept}$ = 31). To achieve this objective, aqueous solutions of cyclodextrins (CD) seemed a possible solution, because cyclodextrins can incorporate several organic compounds and the separation of the aqueous solution of complexed cyclodextrins from the organic feed is simple. Cyclodextrins are not soluble in organic liquids, but cyclodextrin derivatives are highly soluble in water. Several substituted cyclodextrins were investigated for the separation of toluene from toluene/heptane mixtures and of o-xylene from o-xylene/heptane mixtures. Unfortunately, the aromatic distribution coefficients (D_{tol} = 0.05 at [m-ß-CD (1.7)] = 0.22 mole/L and $D_{o\text{-}x}$ = 0.023 at [HP-ß-CD (0.8)] = 0.25 mole/L) and the aromatic/aliphatic selectivity were low ($S_{tol/hept}$ = 6 with m-ß-CD (1.7)). Therefore, aqueous cyclodextrin solutions are not suitable for the extraction of aromatic compounds from aliphatic hydrocarbons.

SELECTION OF IONIC LIQUIDS

Since adsorption, membrane permeation and extraction with cyclodextrins were not viable, an extraction process with other solvents had to be used. Ionic liquids are organic salts that are liquid at low temperatures (<100 °C) and consist of large organic cations based on methylimidazolium [Rmim], N-butylpyridinium [R-N-bupy], quaternary ammonium or phosphonium ions and others, and anions such as hexafluorophosphate, tetrafluoroborate, alkylsulfates, alkylsulfonates, chloride, etc. The R group of the cation is variable (e.g. methyl, ethyl, butyl, etc.). The variability of the anion and R groups in the imidazolium, pyridinium, ammonium or phosphonium cations may be used to adjust the properties of the ionic liquids. The application of ionic liquids for extraction processes is promising because of their non-volatile nature. This facilitates solvent recovery using techniques as simple as flash distillation or stripping.

Aromatic hydrocarbons are reported to have low activity coefficients at infinite dilution in several ionic liquids, while aliphatic hydrocarbons show high activity coefficients in the same ionic liquids. This means that ionic liquids can indeed be used as extractants for aromatic hydrocarbons from aliphatic hydrocarbons. Several ionic liquids were screened on basis of activity coefficients at infinite dilution, solubility and extraction data. The cations were mostly imidazolium and pyridinium, and the anions were hydrogensulfate, methylsulfonate, methylsulfate, ethylsulfate, dimethylphoshate, diethylphosphate and tetrafluoroborate. The separation of toluene from toluene/n-heptane mixtures was used as a model for the aromatic/aliphatic separation. Based on initial screening results, three ionic liquids ([mmim]CH_3SO_4, [emim]$C_2H_5SO_4$ and [mebupy]BF_4) were chosen for more detailed equilibrium tests, because the toluene distribution coefficient and/or the toluene/heptane selectivity were high. Of these ionic liquids, [mebupy]BF_4

appeared to be the most suitable, because of a combination of a high toluene distribution coefficient (D_{tol} = 0.44) and a high toluene/heptane selectivity ($S_{tol/hept}$ = 53). Therefore, with [mebupy]BF_4 also extraction experiments with other aromatic/aliphatic combinations (benzene/n-hexane, ethylbenzene/n-octane and m-xylene/n-octane) were carried out.

Evaporating the organic compounds from the extract phase in a rotary evaporator at 75 °C could easily regenerate the ionic liquids used. Visible inspection of the NMR spectra of both the original ionic liquid and the regenerated product showed no differences between the two samples. Furthermore, several ionic liquids were continuously heated in an oven at 150 °C during 7.5 weeks and no degradation of the ionic liquid could be detected.

EVALUATION OF CONTACTOR PERFORMANCE

Since the ionic liquid [mebupy]BF_4 showed both a higher toluene distribution coefficient (D_{tol} = 0.44) and a higher toluene/heptane selectivity ($S_{tol/hept}$ = 53) than sulfolane (D_{tol} = 0.31 and $S_{tol/hept}$ = 31), this ionic liquid was selected for testing the extractive removal of toluene from a toluene/heptane mixture in a pilot scale Rotating Disc Contactor (RDC) extraction column. The pilot plant RDC provided good results for toluene/heptane separation: small droplets were formed with the ionic liquid and the column capacity was high. The extraction with the ionic liquid was more or less comparable to the extraction with sulfolane in the RDC. Due to the higher toluene distribution coefficient, lower Solvent-to-Feed (S/F) ratios were required to extract the same amount of toluene with the ionic liquid, while compared to sulfolane a 10% higher flux (volumetric throughput) and similar mass transfer efficiency were obtained. Also, the feed flow with [mebupy]BF_4 was higher (10 kg/hr) than with sulfolane (5.8 kg/hr) as the solvent. The best performance (highest toluene extraction efficiency) was obtained at the highest rotation speed used (643 rpm) in the extraction experiments in the RDC column. At a flux of 10 m^3/m^2.hr, excellent hydrodynamic behaviour was observed and about three equilibrium stages were contained in the 1.80 m high active section of the column.

TERNARY LIQUID-LIQUID EQUILIBRIA

Ternary data of the systems toluene+n-heptane+an solvent were collected for the solvents sulfolane and the ionic liquids [mebupy]BF_4, [emim]$C_2H_5SO_4$ and [mmim]CH_3SO_4. Since [mebupy]BF_4 was selected as the optimal performing ionic liquid, ternary data for the systems aromatic+aliphatic hydrocarbon+[mebupy]BF_4 were gathered for other aromatic/aliphatic combinations, notably benzene/n-hexane, ethylbenzene/ n-octane and m-xylene/n-octane.

The binary interaction parameters for the NRTL model were determined by regression of the experimental ternary data with ASPEN Plus 12.1. Comparison of the experimental and the fitted data demonstrated that excellent agreement between the calculated and experimental data is obtained with root mean square deviation values generally below 0.01.

CONCEPTUAL PROCESS DESIGN

With the NRTL interaction parameters determined for the combinations of aromatic and aliphatic hydrocarbons with the ionic liquid [mebupy]BF_4, a process model could be developed using the flow sheeting program of ASPEN Plus 12.1. Several simulations of the extraction of toluene from a toluene (10%)/heptane mixture with the flow sheeting program were carried out in order to determine the optimal number of stages and the S/F ratio. For a toluene recovery of at least 98% and a heptane purity of more than 98%, 12 stages and an S/F ratio of 2.3 were required.

A conceptual separation process, consisting of an extractor and an evaporator only, was developed using a toluene/heptane mixture. It was not possible to develop a complete process, including an extractor, an extractive stripper for the removal of heptane from the extract phase and an evaporator to remove toluene from the ionic liquid [mebupy]BF_4, due to severe errors occurring in the flow sheeting program.

With the crude results of the process simulation of the separation of toluene from a mixed toluene/heptane stream, an economic evaluation of the process was made and compared to the extraction process with sulfolane. The total investment costs in the sulfolane extraction were estimated by UOP, the supplier of this process, to be about M€ 86 for a naphtha feed of 300 ton/hr, containing 10% aromatic hydrocarbons. The extraction process with the ionic liquid [mebupy]BF_4 was estimated to be M€ 56, including an ionic liquid inventory of M€ 20.

If the ionic liquids [mebupy]CH_3SO_4 or [emim]$AlCl_4$ are used as a solvent, which both have a higher toluene distribution coefficient than [mebupy]BF_4, the total investment costs could decrease to M€ 47 or even M€ 26, respectively. However, the ionic liquid [emim]$AlCl_4$ cannot be used in industrial practice because it reacts violently with water.

The main conclusion of the process evaluation is that development of ionic liquids which show a high aromatic distribution coefficient with a reasonable aromatic/aliphatic selectivity could reduce the investment costs of the aromatic/aliphatic separation to about M€ 25 – 30. One of the tools to obtain such an improved ionic liquid is the use of the program COSMO-RS, which can predict activity coefficients at infinite dilution of ionic liquids with variations of the cation and the anion.

For the acceptance of ionic liquids in industrial practice, it is a prerequisite that enough toxicological data about ionic liquids are known. Without these data, no ionic liquid will be applied in industry. Furthermore, the current price of ionic liquids, ranging from € 200 – 3,000/kg, is too high for industrial use. Of course, the current prices are based on laboratory use and, hence, the scale of production is small. A reasonable price would be in the range of € 10 – 25/kg. BASF, who is a major producer of imidazole, one of the primary products for ionic liquids, has indicated that it is indeed possible to reach that level if ionic liquids are produced on a large scale.

1 AROMATICS REMOVAL FROM NAPHTHA

1.1 INTRODUCTION

In Figure 1.1, a simplified flow scheme of a naphtha cracker is depicted. Firstly, metal contaminants in the feed are hydrogenated and removed by molecular sieves (IFP-RAM process). The remaining feed stream is heated up to 60 °C and enters the furnace section where aliphatic hydrocarbons are converted by the high temperature (850 – 900 °C) into smaller molecules, preferably ethylene and propylene. After the furnace section the product stream has to be cooled down in several steps.

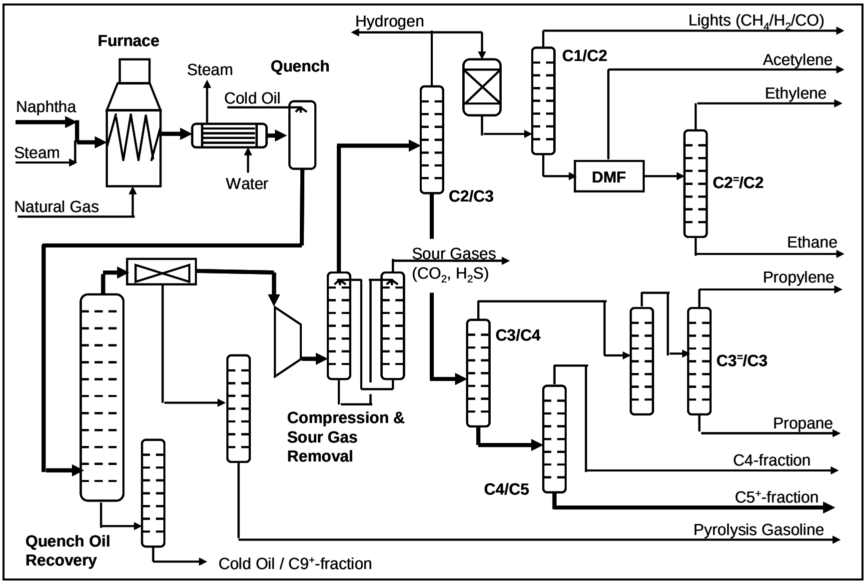

Figure 1.1. Simplified flow scheme of a naphtha cracker

Most ethylene cracker feeds contain 10 – 25% of aromatic components, depending on the source of the feed (naphtha or gas condensate). A typical naphtha feed composition is given in Table 1.1. The aromatic compounds present are not converted to olefins and even small amounts formed during the cracking process in the cracker furnaces [1]. Therefore, they occupy a large part of the capacity of the furnaces and they put an extra load on the separation section of the C_5^+-aliphatic compounds. This is illustrated by the bold line in the process scheme in Figure 1.1 the aromatic hydrocarbons follow. Moreover, the presence of aromatic compounds in the feed to the cracker also has a negative influence on the thermal efficiency. Aromatic compounds present in the feed tend to foul the radiation sections (coking of the coils) and the Transfer Line Exchangers.

Because the aliphatic hydrocarbons present in the feed and product streams form azeotropes with the aromatic compounds, the industrial separation of aromatic compounds and C_5^+ aliphatic hydrocarbons is currently carried out by extractive distillation using polar solvents such as sulfolane, N-methyl pyrrolidone (NMP), ethylene glycols or N-formyl morpholine (NFM). This involves additional separation and purification steps to recover the aromatics from the solvent and to purify the solvent, requiring additional investment costs and energy consumption.

Table 1.1. Typical composition of a naphtha feed containing 10 wt% aromatics [DSM]

Component	wt%	Component	wt%	Component	wt%
N-Butane	1.5	Cyclohexane	2.8	2,6-Dimethyl-heptane	1.9
I-Pentane	4.2	2-Methyl-hexane	2.8	Ethylbenzene	2.0
N-pentane	10.3	3-Methyl-hexane	3.8	P-xylene	1.9
Cyclopentane	1.5	N-heptane	4.4	3-Methyl-octane	2.7
2,3-Dimethyl-butane	0.8	Methyl-cyclohexane	4.8	O-xylene	1.0
2-Methyl-pentane	6.0	Toluene	3.0	N-nonane	2.6
3-Methyl-pentane	4.0	2-Methyl-heptane	2.4	N-decane	3.0
N-hexane	8.6	1,3-Dimecyclohexane	7.0	I-decanes	4.0
Me-cyclopentane	4.1	N-octane	5.4		
Benzene	1.8	Ethyl-cyclohexane	2.0	Total	100.3

If a major part of the aromatic compounds present in the feed to the crackers could be separated up stream of the furnaces, it would offer several advantages: higher capacity, higher thermal efficiency and less fouling. The energy requirement of a thermal cracker is about 8.5 GJ/ton feed. The improved margin for the removal of 10% aromatic hydrocarbons from the feed to the naphtha cracker will be around € 20/ton of feed or € 48 million per year for a cracker with a feed capacity of 300 ton/hr, due to the lower operational costs, as was indicated by DSM. However, although separation of aromatic and aliphatic hydrocarbons after the furnace section is industrial practice, no suitable technology is currently available for the separation of aromatic compounds from the feed to cracker plants. Given this tremendous economic potential, the objective of this project is the development of a separation technology for the selective up stream recovery and purification of aromatic compounds benzene, toluene, ethylbenzene and xylenes (BTEX) from liquid ethylene cracker feeds. The project focuses on aromatics separation from feed streams that may contain up to 25% aromatics. For reasons of simplicity the toluene/heptane system was used as a model to represent the naphtha in most experiments.

For an economically feasible operation, the amount of aliphatic compounds in the aromatic product stream should be as low as possible. On the other hand, total removal of the aromatic compounds from the feed is not necessary, because aromatics are formed during the cracking process. Therefore, the recovery of the aromatic hydrocarbons is set to be at least 98% and the purity of the generated streams, one containing mainly aliphatic hydrocarbons and the other aromatic hydrocarbons, is also set to be at least 98%. If the aromatic hydrocarbons can be removed from the feed to the naphtha cracker, the energy efficiency of the cracker will be improved. Since not the complete cracker will be affected by the removal of the aromatic hydrocarbons, an energy saving of 5 – 10% is expected.

1.2 SELECTION OF SEPARATION PROCESSES

The separation of aromatic hydrocarbons (benzene, toluene, ethylbenzene and xylenes) from C_4 – C_{10} aliphatic hydrocarbon mixtures is challenging since these hydrocarbons have boiling points in a close range and several combinations form azeotropes. The separation of benzene and cyclohexane is one of the most important and most difficult processes in the chemical industry [2]. Since benzene and cyclohexane form close boiling point mixtures at the entire range of their compositions, the separation is difficult by means of a standard distillation process.

Since distillation is not a feasible option for the separation of aromatic hydrocarbons from C_4 – C_{10} aliphatics due to their boiling points in a close range and the formation of several azeotropes, separation processes based on differences in interaction or affinity must be used. Examples of such processes are extraction, extractive distillation, adsorption/desorption and membrane permeation.

The selection criteria are based on:

- Capacity
- Selectivity: >30
- Loss of solvent to raffinate: absent
- Recovery of aromatics: >98%
- Purity of the product streams: >98%
- Increase of investment costs with increased capacity

For each process option, the criterion with regard to capacity must be fixed. The capacity in an extraction process is determined by the distribution coefficient of the aromatics and the capacity of a membrane process is determined by the flux rate through the membrane. The benchmark for the selectivity (>30) is the selectivity obtained in the sulfolane extraction process, which is the most used process for separating aromatic and aliphatic hydrocarbons. The recovery of the aromatics needs not to be complete because of the formation of aromatics during the cracking process. Therefore, the value of 98% is an arbitrary value, just as the requirements of both product streams.

For processes like extraction and extractive distillation, the investment cost scale with the capacity to the power 0.6 – 0.65, while the adsorption/desorption and membrane processes are scaled up with a power of 0.85 – 0.95. The higher scale-up factor for adsorption/desorption and membrane processes is caused by the fact that the capacity of these processes is directly related to the amount of adsorbent or membrane area. Generally, it can be stated that adsorption and membrane processes are more suitable for small-scale processes than for large scale ones, unless the unit price of the adsorbent or membrane is very low.

1.3 POTENTIAL SEPARATION TECHNOLOGIES & THESIS OUTLINE

1.3.1 MEMBRANE PERMEATION

For membrane separation of aromatic and aliphatic hydrocarbons, a large number of literature articles deal with the development of polymeric membranes for the separation of benzene and cyclohexane or toluene and n-octane [3-26]. Multi-component separations are seldom mentioned. In recent years, pervaporation separation, and to a lesser extent also vapour permeation, have emerged as relatively simple alternatives to many water/organic and organic/water separation applications. Pervaporation and vapour permeation are especially attractive in azeotropic and close-boiling point separation applications, since these processes are not based on the relative volatilities of components, but on the difference in sorption and diffusion properties of the feed substances as well as the permselectivity of the membrane. If pervaporation or vapour permeation with high selectivity membranes produces permeate and retentate streams with a high purity, no additional separation processes are required. On the other hand, application of pervaporation or vapour permeation in organic/organic separations with organic membranes is still very limited because of their stability, a low selectivity and/or low flux rates. In a review article on pervaporation of benzene/cyclohexane mixtures with organic membranes, low selectivities, the majority in the range of 5 – 20, are reported [3]. Also, the flux rates are low, the majority of the normalized fluxes being in the vicinity of 1 – 10 kg.μm/m^2.hr. Unfortunately, the thickness of the selective layer of the membranes used is not given, so that the actual flux rates are unknown. In another publication, experimental benzene flux rates with polymeric membranes in the order of 1 – 1.5 kg/m^2.hr are reported [4]. Beside the low flux rate, polymeric membranes have limited thermal stability, especially in the presence of organic solvents. Therefore, the use of polymeric membranes for organic/organic separations is rare in industrial processes. For these reasons, polymeric membranes will not be considered for this separation.

In comparison to polymeric membranes, some zeolite membranes, like faujasite with a low Si/Al ratio, exhibit relatively high separation factors varying from 20 up to 260 for the separation of benzene/hexane and benzene/cyclohexane, depending on the temperature [5,6]. For organic/organic separations, zeolite membranes are to be preferred because of their robustness in organic solvents and their application at higher temperatures. Another advantage of using zeolite membranes is that these can be easily regenerated by calcination. Desorption in zeolite membranes is not difficult as in adsorption/desorption, because a partial pressure difference is the driving force in pervaporation and in vapour permeation. With pervaporation, the feed is in the fluid phase and the permeate is in the gas phase. In vapour permeation, both the feed and the permeate are in the gas phase. Desorption from zeolites of compounds in the gas phase by a partial pressure difference is a straightforward process. For these reasons, the economic feasibility of zeolite membranes for industrial scale separations of aromatic hydrocarbons is evaluated in Chapter 2.

1.3.2 ADSORPTION

A suitable adsorbent for the separation of aromatic and aliphatic hydrocarbons from a process stream such as naphtha, which contains 10 – 25 % aromatics, must adsorb the aromatic hydrocarbons. Most zeolites, because of the presence of the exchangeable cations, are polar adsorbents. Molecules such as water or ammonia (high dipole), CO_2, N_2 (quadrupolar) or aromatic hydrocarbons (π-layer interaction) are therefore adsorbed more strongly than non-polar species of comparable molecular weight [27]. Suitable zeolites for the adsorption of aromatic compounds have a low Si/Al ratio, for instance X and Y types [27]. However, since aromatic hydrocarbons are strongly adsorbed on zeolites, desorption is a difficult step. Desorption by pressure swing is difficult when the process streams are in the fluid phase and with thermal swing desorption the activity of the zeolite decreases with time. Steam stripping is not suitable because zeolites with a low Si/Al ratio quickly loose their stability in contact with water or steam. Suitable compounds for desorption by displacement are polar or polarisable compounds, which must have a larger interaction with the zeolite than the aromatic compounds, for instance alcohols, like methanol, ethanol, propanol or propylene glycol. A disadvantage is, of course, that a second separation step is required to remove the displacement liquid. An interesting alternative way of desorbing benzene from a NaX zeolite is described by Bellows et al. [28]. By hydrogenation of benzene to cyclohexane, desorption is facilitated, as the affinity of cyclohexane towards the zeolite is lower than the affinity of benzene towards the zeolite. After hydrogenation, the cyclohexane can then be displaced from the zeolite adsorbent using a fresh feed stream containing aromatics. The process can therefore be continuous, the cyclohexane desorption step of one feed cycle being the benzene adsorption of the next feed cycle.

With a feed containing a mixture of aromatic and aliphatic hydrocarbons, the aromatic hydrocarbons can be hydrogenated and be desorbed in a similar way. The disadvantage of this method is that the aromatic compounds are converted to cyclo-alkanes and that they are not available as feedstock for other compounds. However, due to the foreseen difficulties with desorption in comparison with zeolite membranes, the adsorption/desorption option was not pursued further.

1.3.3 EXTRACTION AND EXTRACTIVE DISTILLATION

The conventional processes for the separation of aromatic and aliphatic hydrocarbons are liquid extraction, suitable for the range of 20 – 65% aromatic content, extractive distillation, for the range of 65 – 90% aromatics, and azeotropic distillation for high aromatic content, >90% [2]. For the extraction of aromatic hydrocarbons, a solvent system must be designed. The solvents selected must preferably extract the aromatic hydrocarbons from the feed, since these are present in a relatively low concentration. For solvent selection, the following items are of importance in extraction processes:

- Group selectivity must be high
- Selectivity usually decreases with increasing temperature
- Selectivity can be increased by addition of a anti-solvent
- Selectivity decreases as more and more hydrocarbons are dissolved in solvent

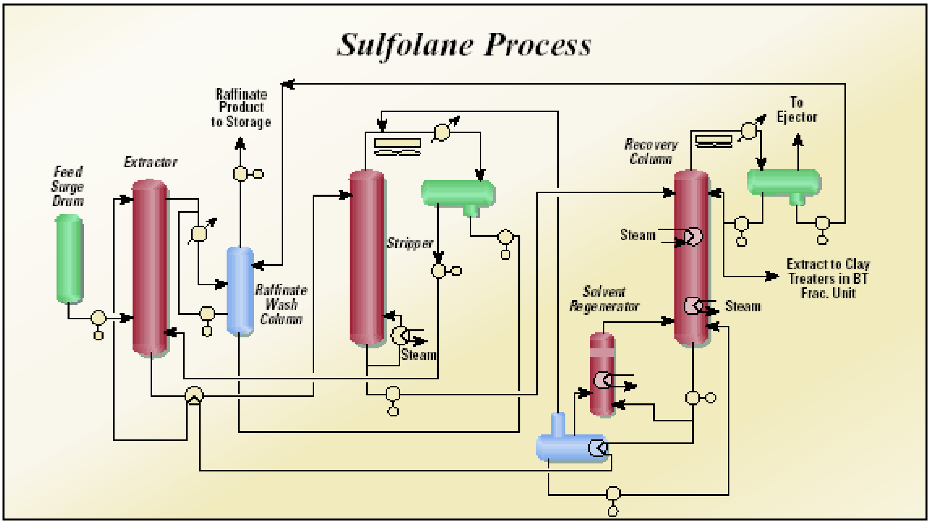

Figure 1.2. UOP Sulfolane process [29].

There are several commercial extraction processes available for the selective separation of aromatics from naphtha or gas condensates. Typical solvents used are polar components such as sulfolane [29-34] (UOP, Shell), N-methyl pyrrolidone (NMP) [33] (Lurgi), N-formyl morpholine (NFM) (Krupp Uhde, Snamprogetti), ethylene glycols [34-36] (UOP), propylene carbonate [37], furfural (Texaco) or DMSO (IFP). Overviews of the use of extraction and extractive distillation for the separation of aromatic hydrocarbons from aliphatic hydrocarbons can be found elsewhere [38-41]. The usual solvent-feed ratio is 1.5 – 4, which means that a large amount of solvent will be required for the feed to the ethylene crackers.

The raffinate stream from the extractor contains aliphatic hydrocarbons and a small amount of the solvent, which can be washed out by water. The aliphatic product stream can then be processed further. The extract contains aromatics and some light paraffins, which can be recovered and recycled to the extraction column as backwash. In commercial processes, solvent recovery can be carried out by:

- flashing or evaporation
- flashing, followed by stripping
- extractive stripping followed by distillation

The most used commercial extraction process is the one using sulfolane as a solvent, licensed by UOP (Figure 1.2) [29]. According to UOP, the extraction of aromatics from naphtha cracker feed is feasible with the Sulfolane or Carom processes. Normally, these processes are used for feed streams containing about 68% aromatics or more (reformed petroleum naphtha, pyrolysis gasoline or coke oven light oil). UOP has made a rough estimate for the sulfolane process for a naphtha feed stream of 300 t/hr, containing about 10 wt% aromatics. The investment costs for a plant with a feed of 300 MT/hr are:

	€ 10^6
Materials &Labour	51
Engineering	15
ISBL total:	66
OSBL:	20
Total:	86

The energy costs are estimated by UOP to be € 10/ton feed, which will amount to € 24 10^6/year. The variable capital costs (depreciation, 10%; ROI, 20% and other investment related costs, such as maintenance, 10%) are estimated to be 40% of the investment costs. The annual capital costs are € 34.4 10^6 and the total variable costs are then € 58.4 10^6/year. The improved margin for removing the aromatic hydrocarbons from the feed to the naphtha cracker is € 20/ton feed, which amounts to € 48 10^6/year, resulting in a annual loss of around € 10 10^6/year. This is confirmed by Weissermel and Arpe, who state that currently no feasible processes are available for the separation of aromatic and aliphatic hydrocarbons in the range below 20% aromatics in the feed mixture [2]. The main reasons being that these processes are highly complex, require high investments and exhibit a large energy consumption due to the unfavourable capacity and selectivity of the solvents used and the need for additional separation steps for solvent recovery and purification of both product streams.

Based on the previous information, it is obvious that no extraction process is in operation for removing aromatic compounds from streams containing relatively low concentration of these aromatic compounds anywhere. The only way to improve the economic feasibility of extraction technology at low aromatics content is the development of new solvent systems that exhibit a dramatically higher aromatic distribution coefficient and/or a higher aromatic/aliphatic selectivity than sulfolane. Literature information indicated that aqueous cyclodextrin solutions and ionic liquids could have the potential to fulfil these requirements. The separation of aromatic compounds from aliphatic hydrocarbons with aqueous solutions of cyclodextrins (CD) is an option, because cyclodextrins can incorporate several organic compounds and the separation of the aqueous solution of complexed cyclodextrins from the organic feed is simple. Cyclodextrins are not soluble in organic liquids, but cyclodextrin derivatives are highly soluble in water [42-45]. Therefore, aqueous cyclodextrin solutions could be used as extraction solvents for the separation of aromatic compounds from cracker feeds [46]. In Chapter 3, extraction of toluene and o-xylene from heptane with aqueous cyclodextrins is investigated.

Room temperature ionic liquids (RTIL) are liquids that are composed entirely of ions and in this sense alone resemble the ionic melts which may be produced by heating normal metallic salts such as sodium chloride to high temperature (e.g. NaCl is liquid above 800 °C). In fact, ionic liquids can now be produced which remain liquid at room temperature and below (even as low as -96 °C). Ionic liquids possess of a number of properties, which may be of importance in their application as extractive media in liquid/liquid extraction processes. They are liquid at room temperature and, in fact, they have an enormous liquid temperature range of 300 °C, which is larger than that of water (100 °C) and this offers the potential for considerable kinetic control of extractive processes. They are good solvents for a wide range of inorganic, organic and polymeric materials. The composition of ionic liquids may be adjusted enabling control of their acidity or basicity. Several ionic liquids are known which are neither air nor water sensitive or miscible with water, thus enabling the concept of liquid/liquid extraction from aqueous media.

Aromatic hydrocarbons are reported to have low activity coefficients at infinite dilution in several ionic liquids, while aliphatic hydrocarbons show high activity coefficients in the same ionic liquids [47-65]. This means that ionic liquids can indeed be used as extractants for aromatic hydrocarbons from aliphatic hydrocarbons. For the separation of aromatic hydrocarbons from a mixture of aromatic and aliphatic hydrocarbons, the use of aromatic cations and possibly aromatic anions will have a positive effect on the extraction of aromatic hydrocarbons from the mixture.

The constituents of ionic liquids (being ionic) are constrained by high coulombic forces and thus, exert practically no vapour pressure above the liquid surface. This property may allow the development of novel recovery schemes for certain organic species in relation to normal liquid/liquid extraction in which product recovery could be affected by distillation or pervaporation. The application of ionic liquids for extraction processes is promising because of their non-volatile nature [47]. This facilitates solvent recovery using techniques as simple as flash distillation or stripping.

The selection of ionic liquids for the extraction of aromatic hydrocarbons from aromatic/aliphatic mixtures is described in Chapter 4. A large number of ionic liquids with different cations and anions were tested. Three suitable ionic liquids were identified for the for a more detailed screening for the separation of aromatic and aliphatic hydrocarbons, notably 1,3-dimethylimidazolium methylsulfate, 1-ethyl-3-methylimidazolium ethylsulfate and 4-methyl-N-butylpyridinium tetrafluoroborate ([mebupy]BF_4), because they all showed a higher aromatic/aliphatic selectivity than sulfolane. Since the ionic liquid [mebupy]BF_4 showed both a higher toluene distribution coefficient and a higher toluene/heptane selectivity than sulfolane, this ionic liquid was selected for testing the extractive removal of toluene from a toluene/heptane mixture in a pilot scale RDC extraction column, as is described in Chapter 5. Since no thermodynamic data were available for the three selected ionic liquids, liquid-liquid-equilibrium data must be determined in order to evaluate the process performance. Experimental LLE data over a wide composition range were gathered and the phase compositions were correlated with the NRTL model in Chapter 6. Subsequently, the potential process performance of the investigated and some recently discovered ionic liquids was evaluated in Chapter 7 by developing a conceptual process model. The conclusions of this thesis and future outlook on potential technologies for aromatic/alkane separation at low aromatics concentrations are finally summarized in Chapter 8.

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2 ECONOMIC FEASIBILITY OF ZEOLITE MEMBRANES FOR INDUSTRIAL SCALE SEPARATIONS OF AROMATIC HYDROCARBONS

2.1 ABSTRACT

Naphtha cracker feedstocks contain 10 – 25 wt% aromatic hydrocarbons, which are not converted into the desired products ethylene and propylene. The conventional processes for the separation of aromatic and aliphatic hydrocarbons are extraction, extractive distillation and azeotropic distillation. These processes are highly complex and demand a high energy consumption. Therefore, alternative separation processes are of interest, such as pervaporation (PV) and vapour permeation (VP) with zeolite membranes.

For a feasible process, the purity of both the aromatic and aliphatic products must be 98 wt%. In order to obtain these purities with PV or VP, using a reasonably sized membrane area, the selectivity must be high, at least 40, and preferably above 80, and the flux rate (100 wt% benzene) has to be in the order of 8 $kg/m^2.hr$ (presently around 0.3 $kg/m^2.hr$). For a feed stream of 300 ton/hr, containing 10 wt% aromatics, a membrane area of more than 60,000 m^2 is required with these selectivities and flux rates.

The conclusion is that, with the current high price level of zeolite membrane modules, around € 2,000/m^2, the investments become uneconomic. Therefore, the membrane costs must be reduced, to about € 200/m^2.

2.2 INTRODUCTION

In this study, the economic feasibility is investigated of a pervaporation (PV) or vapour permeation (VP) process for the separation of aromatic hydrocarbons from naphtha cracker feed, which typically contain less than 25 wt% of aromatics. The separation of benzene and cyclohexane, which is considered one of the most important operations [1], is used as a model for the separation of aromatic and aliphatic hydrocarbons. Since mixtures of benzene and cyclohexane exhibit a very low relative volatility over their entire composition range, the separation is difficult by means of a conventional distillation process.

2.2.1 NAPHTHA CRACKER PROCESS

Naphtha crackers convert naphtha into ethylene, propylene and other hydrocarbons by thermal cracking. The aromatic compounds present in the cracker feed are not converted into olefins in the cracker furnaces, but remain as such in the process stream. The separation of aromatic hydrocarbons (benzene, toluene, ethylbenzene and xylenes) from C_4

– C_{10} aliphatic hydrocarbon mixtures is challenging since these hydrocarbons have boiling points in a close range and several combinations form azeotropes. The conventional processes for the separation of these aromatic and aliphatic hydrocarbons mixtures are liquid extraction, suitable for the range of 20 – 65 wt% aromatic content, extractive distillation for the range of 65 – 90 wt% aromatics, and azeotropic distillation for high aromatic content, >90 wt% [1].

In ethylene cracker plants, the industrial separation of aromatic compounds and C_5^+-aliphatic hydrocarbons from the cracker products is therefore carried out by extractive or azeotropic distillation, depending on the concentration of the aromatic compounds. Typical solvents used are polar components such as N-methyl pyrrolidone (NMP), ethylene glycols, N-formyl morpholine (NFM) or sulfolane.

Although separation of aromatic and aliphatic hydrocarbons after the furnace section is industrial practice, selective removal of aromatic compounds from the cracker feed has not yet been considered. Removing the major part of the aromatic compounds present in the feed to the crackers would offer several important advantages. The presence of aromatic compounds in the feed is undesirable, because they tend to foul the radiation sections (coking of the coils) and the Transfer Line Exchangers. Moreover, the presence of aromatic compounds in the feed to the cracker has a negative influence on the thermal efficiency. Further, they occupy a large part of the capacity of the furnaces and put an extra load on the separation section of the C_5^+-aliphatic compounds.

For an economically feasible operation, the amount of aliphatic compounds in the aromatic product stream should be as low as possible. An option is to obtain the pure aromatic hydrocarbons from the aromatic product stream. On the other hand, total removal of the aromatic compounds from the feed is not necessary, as aromatics are formed during the cracking process. Therefore, the purity of both the aromatic and aliphatic product streams is set to 98 wt%. To my knowledge, conventional processes are currently not applied for such low aromatic content feeds due to their high complexity, large energy consumption and because they require additional separation steps for the recovery of the solvents used and final purification of both product streams. Therefore, new technologies are explored that are considered promising for these low concentrations of aromatic hydrocarbons.

2.2.2 PERVAPORATION/VAPOUR PERMEATION

In recent years, pervaporation separation, and to a lesser extent also vapour permeation, have emerged as relatively simple alternatives to many water/organic and organic/water separation applications. Pervaporation and vapour permeation are especially attractive in azeotropic and close-boiling point separation applications, since these processes are not based on the relative volatilities of components, but on the difference in sorption and diffusion properties of the feed substances as well as the permselectivity of the membrane. If pervaporation or vapour permeation with high selectivity membranes produces permeate and retentate streams with a high purity, no additional separation processes are required. On the other hand, application of pervaporation or vapour permeation in organic/organic separations with organic membranes is still very limited because of their stability, low selectivity and/or low flux rates. In a review on pervaporation of benzene/cyclohexane mixtures with organic membranes, low selectivities, the majority in the range of 5 – 20, are reported [1]. Also, the flux rates are low, the majority of the normalized fluxes being in the vicinity of 1 – 10 kg.µm/m^2.hr. Unfortunately, the thickness of the selective layer of the membranes used is not given, so that the actual flux rates are unknown. In another publication, experimental benzene flux rates with polymeric membranes in the order of 1 – 1.5 kg/m^2.hr are reported [2].

In comparison to polymeric membranes, some zeolite membranes, like faujasite, exhibit relatively high separation factors varying from 20 up to 260 for the separation of benzene/hexane and benzene/cyclohexane, depending on the temperature [3,4]. For organic/organic separations, zeolite membranes are to be preferred because of their robustness in organic solvents and application at higher temperatures. Another advantage of using zeolite membranes is that these can be easily regenerated by calcination. In this chapter, recent findings on the technical and economic feasibility of zeolite membranes for the separation of benzene and cyclohexane are presented.

2.3 DESIGN CONSIDERATIONS

The feed stream to the cracker plant is 300 metric ton/hr with an aromatic BTEX content of 10 wt%. The requirements for the retentate are a purity of at least 98 wt% aliphatic hydrocarbons and for the permeate at least 98 wt% aromatic hydrocarbons. As the ethylene cracker feed has a 10 – 25 wt% aromatic content, the aromatic hydrocarbons should be the preferentially permeating components.

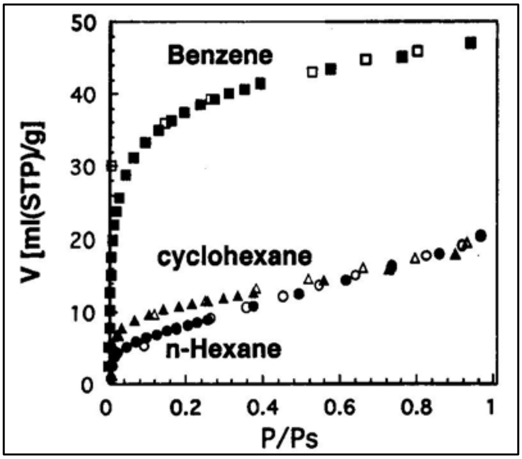

Figure 2.1. Sorption isotherms of benzene, cyclohexane and n-hexane at 50 °C on NaY zeolite. ■□ benzene, ▲△ cyclohexane, ●○ n-hexane. Filled symbols: adsorption; open symbols: desorption Reprinted from [4]

The separation of benzene and cyclohexane is used as a model for this separation. In Figure 2.1, the sorption isotherms of benzene, cyclohexane and hexane on zeolite NaY at 50 °C are shown. These isotherms illustrate clearly that aromatic hydrocarbons like benzene are preferentially adsorbed on zeolites with a low Si/Al ratio such as NaY. These zeolites are polar adsorbents due to the presence of exchangeable cations. The adsorbent characteristics of zeolites or ion-exchange resins are the most crucial factors for a separation process based on adsorption/desorption.

2.3.1 PERMEATE FLUX

The most important parameter is the permeate flux, as the membrane area is inversely proportional to the flux. Since the preferential adsorption of benzene on the surface is the most important separation step with zeolite membranes, the flux will not increase linearly with increasing benzene concentration, but reaches a maximum at maximum adsorption of benzene on the zeolite surface. Kita et al. [4] observed a sharp increase in benzene flux in the low benzene concentration region through a faujasite NaY zeolite membrane. Above 20 wt% benzene in the feed, the benzene flux is still increasing, but at a much slower rate, as is shown for a temperature of 150 °C in Figure 2.2.

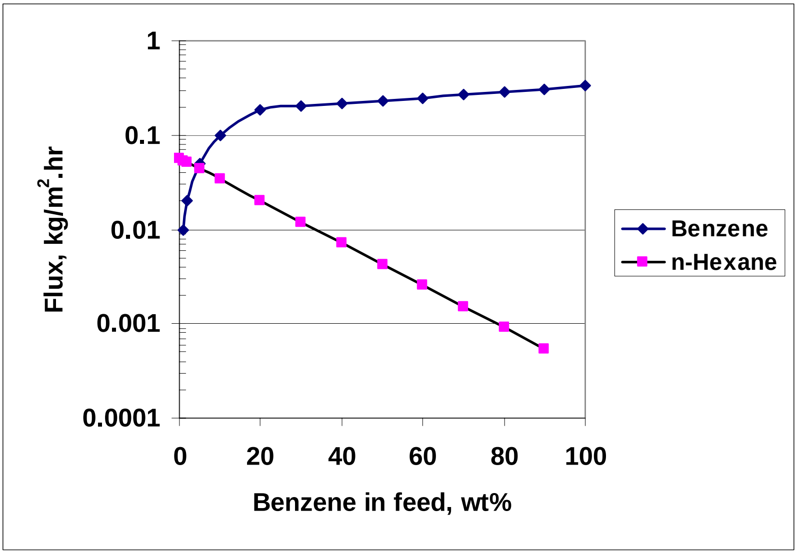

Figure 2.2. Effect of benzene feed concentration on benzene and n-hexane flux rates. NaY zeolite, vapour permeation at 150 °C. Adapted from [4].

At 20 wt% benzene in the feed, the total flux rate is around 0.19 $kg/m^2.hr$ and the flux rate increases to about 0.33 $kg/m^2.hr$ at 100 wt% benzene in the feed. However, the present thickness of the zeolite membrane layer is typically around 20 – 30 µm. It is anticipated that future developments will result in zeolite membranes with defect free active layers as thin as 1 – 2 µm, which would result in a 20 – 30 times higher flux rates when the flux is inversely proportional to the membrane thickness. In these calculations, the benzene flux pattern as shown in Figure 2.2 is increased by a factor of 25 and is used as input in the computer program. The flux increases linearly from 0 to 4.7 kg/m^2.hr at 20 wt% benzene and to 8.3 kg/m^2.hr at 100 wt% benzene in the feed at a temperature of 150 °C.

2.3.2 SELECTIVITY

According to the data from Kita [4], the selectivity for benzene/cyclohexane and for benzene/n-hexane increases with increasing benzene fraction in the feed. The benzene flux increased only slightly above 20 wt% benzene in the feed, but the hexane flux decreased with increasing benzene fraction in the feed over the whole range, see Figure 2.2. The obtained selectivities for the separation of benzene/n-hexane (50/50 wt%) vary from 46 (PV, 65 °C) via 260 (VP, 100 °C) to 44 (VP, 150 °C) and for benzene/cyclohexane (50/50 wt%) from 22 (PV, 75 °C) to 190 (VP, 150 °C). These selectivities are confirmed by Nikolakis et al. [3] who reported a selectivity of 160 for the separation of benzene/cyclohexane with faujasite zeolite membranes in the gas phase at a temperature of 100 °C with $P_{benzene}$= 5 kPa and $P_{cyclohexane}$= 5 kPa. Due to the lack of sufficient experimental data on the separation of benzene/cyclohexane mixtures, the selectivity in the calculations was kept constant at a value of 160 over the entire concentration range. It is expected that in a real process the average selectivity for a mixture of aromatic and aliphatic hydrocarbons will be significantly lower than 160. For other mixtures, like toluene/heptane the reported selectivity is 40 [3].

2.3.3 PROCESS

In principle, both pervaporation and vapour permeation can be used. The feed to the naphtha cracker has to be heated up to 900 – 1000 °C. Therefore, the feed to the membrane separation installation can be in the liquid or vapour phase. Since the major part of the feed consists of aliphatic hydrocarbons, which will be retained, the loss of energy is relatively low if the complete feed stream is raised in temperature. In the calculations, the feed has an initial temperature of 40 °C and is evaporated and heated up to 150 °C before entering the membrane unit. The temperature of the permeate is around 18 °C and temperature difference between feed and retentate is 6 °C. The permeate has a pressure of 100 mbar. The calculations were carried out by means of the computer program PVDesign 2.3 of the RWTH Aachen.

2.4 RESULTS AND DISCUSSION

With a benzene content of 10 wt% in the feed and a selectivity $S = (c_1^{perm}/c_2^{perm})/(c_1^{ret}/c_2^{ret}) = 160$, the required purity of the permeate cannot be obtained in one stage. Therefore, a membrane process with two stages is required in order to produce the desired purities for the retentate and permeate streams. In Figure 2.3, the process scheme is shown.

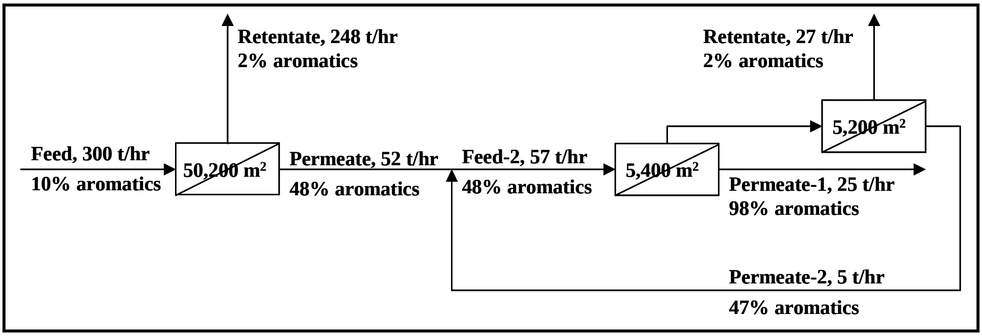

Figure 2.3. Pervaporation/vapour permeation of ethylene cracker feed, S=160

The first stage has a membrane area of about 50,200 m^2. The retentate stream is 248 t/hr, with 98 wt% aliphatic hydrocarbons, and the permeate stream is 52 t/hr, containing 48 wt% aromatic hydrocarbons. This permeate stream is then fed to a second stage of 10,600 m^2. The retentate stream from the second stage is 27 t/hr with 98 wt% aliphatic hydrocarbons. The permeate stream from the first part of the second stage (5,400 m^2) is 25 t/hr, containing 98 wt% aromatic hydrocarbons. The permeate from the second part of this stage (5,200 m^2) is 5 t/hr, containing 47 wt% aromatics, and is recycled to the feed side of the second stage. The total membrane area of the two stages is 60,800 m^2. The total recovery of the aromatic hydrocarbons is almost 82% and the recovery of the aliphatic hydrocarbons is about 99.8%. If the requirements for purity of both retentate and permeate are higher, e.g. > 99 wt%, then the required membrane area, with a selectivity of 160, will increase dramatically, to approximately 136,500 m^2, with three stages.

In these calculations, the selectivity of 160 for the separation of benzene and cyclohexane is used. However, the overall selectivity for a multi-component mixture of aromatic and aliphatic hydrocarbons will be significantly less than 160. Both Nikolakis [3] and Kita [4] report lower selectivities for other mixtures, in the order of 20 to 40, depending on the mixture and temperature. In Figure 2.4, the required membrane area at variable selectivities is shown for a feed stream of 300 t/hr with an aromatic hydrocarbon content of 10 wt%. From this figure, it is apparent that the minimal required selectivity is approximately 40. At selectivities lower than 40, significantly larger membrane areas are required in order to achieve the desired separation. Also, at selectivities of 60 and lower, more than two stages will be required. With a selectivity of 10, even five stages are necessary in order to achieve the required separation. With a selectivity of 80 or higher, the membrane area does not become significantly smaller.

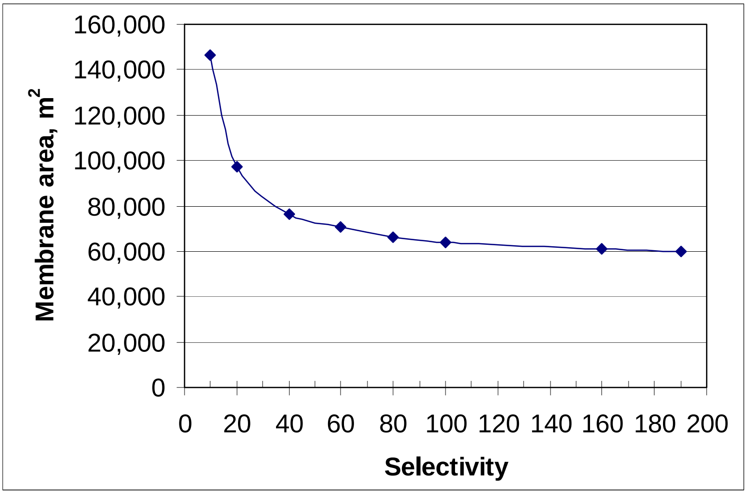

Figure 2.4. Effect of selectivity (benzene/cyclohexane) on membrane area. Feed 300 t/hr, 10 wt% benzene.

At the current price level of € 2,000 – 3,000/m^2 for zeolite membrane modules [5], the investment for the membrane modules alone will already amount between € 120 and 180 million. This indicates that the total investment costs for the complete installation with pumps, heat exchangers, condensers, etc. will be in the € 500 – 750 million range. The savings for the removal of aromatic hydrocarbons from the feed to the ethylene crackers are estimated to be € 20/ton feed or € 48 million per year. As a result, the pay back time of the initial investment alone will already be more than 10 years, while the actual pay back time will be much longer when also energy costs, membrane replacement etc. are taken into account.

This process is not optimised, since the investment costs are already too high for a feasible process. Therefore, any variable costs, such as heat requirements, membrane replacement, etc. were not calculated. Optimisation should only be carried out if the preliminary process design showed some economic feasibility.

2.5 CONCLUSIONS

Even for very optimistic conditions such as a high pure benzene flux of 8.3 kg/m^2.hr and an overall selectivity of 160 for the separation between the aromatics and aliphatics, still a relatively large membrane area is required for the separation of aromatic and aliphatic hydrocarbons from naphtha cracker feeds, both with a purity of 98 wt%, a recovery of 82% for the aromatic hydrocarbons and a recovery of 99.8% for the aliphatic hydrocarbons. Calculations indicated that the selectivity of the membranes for the aromatics should be at least 40, preferably around 80 to avoid large increases in the required membrane area or the use of more than two stages.

The application of a zeolite membrane installation will only become economically feasible if the membrane module cost price is reduced by a factor of 10, to € 200/m^2, and at least 25 times higher aromatic fluxes are obtained than currently reported [4]. Therefore, research regarding zeolite membranes should focus on ways to obtain significantly higher fluxes by reducing the zeolite layer thickness of the membrane, while maintaining selectivity and technologies to achieve considerable reductions in the manufacturing costs of zeolite membrane modules.

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3 EXTRACTION OF TOLUENE, O-XYLENE FROM HEPTANE AND BENZYL ALCOHOL FROM TOLUENE WITH AQUEOUS CYCLODEXTRINS

3.1 ABSTRACT

The separation of aromatic compounds (toluene and o-xylene) from heptane and of benzyl alcohol from toluene with aqueous solutions of cyclodextrins has been experimentally investigated, because cyclodextrins and its derivatives can selectively incorporate several organic compounds, whereas the separation of the aqueous solution of complexed cyclodextrins from the organic feed is simple. Cyclodextrins are not soluble in organic liquids, but cyclodextrin derivatives are highly soluble in water. Hydroxypropyl-β-cyclodextrins with different degrees of substitution and methylated β-cyclodextrin were selected for the extraction of toluene and o-xylene from heptane. Hydroxypropyl-β-cyclodextrin (two different substitution degrees) and hydroxypropyl-α-cyclodextrin were selected for the extraction of benzyl alcohol from toluene. The liquid-liquid distribution experiments were carried out at room temperature. Toluene and o-xylene form 1:1 complexes with different cyclodextrins and heptane can form 1:1 to 1:3 complexes. Benzyl alcohol forms 1:3 complexes with hydroxypropylated cyclodextrins. The models developed describe the experimental data reasonably well, considering the large deviations in the analyses.

Aqueous cyclodextrin solutions are not feasible for the separation of aromatic components from aliphatic hydrocarbons, due to low distribution ratios of toluene (0.05) and o-xylene (0.023) between the aqueous and organic phase. With high distribution ratios of benzyl alcohol, between 0.3 and 2.2 depending on the CD concentration (at a solvent-to feed ratio of 1) and a benzyl alcohol/toluene selectivity of at least 100, aqueous hydroxypropylated cyclodextrin solutions have sufficient potential for extracting benzyl alcohol from toluene.

3.2 INTRODUCTION

In this study, aqueous cyclodextrin (CD) solutions are explored for the recovery of specific organic compounds for two different industrial applications: aromatic compounds from the feed of a naphtha cracker and benzyl alcohol from the reaction mixture in the toluene oxidation process. Naphtha cracker feeds may contain a considerable amount of aromatic compounds, in the range of 10 – 25 wt%, that are not converted into olefins in the cracker furnaces, but remain as such in the process stream [1]. Moreover, the presence of aromatic compounds in the cracker feed occupies a large part of the capacity, causes a decrease in thermal efficiency and leads to fouling of the coils and the transfer line heat exchangers. Removal of these aromatic compounds from the cracker feed would, therefore, offer several advantages.

In the toluene oxidation process, separation of the products (benzyl alcohol, benzaldehyde and benzoic acid) from toluene is carried out by distillation. However, much higher selectivities towards benzyl alcohol can be achieved at low conversions (<5%) [2]. Due to the low product concentration, distillation would result in a very high energy consumption, since the toluene needs to be evaporated.

In both processes, the compounds that need to be separated are present in relatively low concentrations and differ in chemical structure from the other components in the mixture. This led us to the consideration that extraction with an immiscible (polar) solvent could provide interesting breakthroughs for both applications. Of all available extraction solvents, water is clearly the most abundant and environmentally benign. The main drawback is that the capacity of water for the solutes of interest (aromatics, benzyl alcohol) is far too low to be economically feasible [2]. Therefore, addition of a suitable extractant that will selectively and reversibly increase the solubility of the desired components is needed.

It is known that cyclodextrins form complexes with certain organic molecules. Cyclodextrins show negligible solubility in organic liquids and can be modified to achieve high solubilities in water [3-6]. Therefore, aqueous cyclodextrin solutions were selected as extraction solvents for the separation of aromatic compounds from cracker feeds and of toluene oxidation products from toluene [7]. Cyclodextrins are already used in separations, because of their ability to discriminate between isomers, for example xylenes [8], functional groups and enantiomers [9]. Furthermore, cyclodextrins are used in chromatography [9]. This can be either in the stationary phase, influencing the polarity and adding additional stability, or in the mobile phase in liquid chromatography, where it influences partitioning between the phases through complex formation.

Some research is reported on the use of cyclodextrins in liquid-liquid extraction [6,7,9]. Both γ and β-CD can be used in extracting polyaromatic hydrocarbons (PAH's) from soil or oil. α-CD is suitable for separating xylene isomers [3,9]. However, this research is scarce and no evaluation is made of industrial scale application, but it confirms the supposition that aqueous cyclodextrin solutions can be used in extraction.

The objectives of this research are to select suitable cyclodextrin derivatives for the two processes selected in order to determine the appropriate process conditions and to evaluate whether cyclodextrins are feasible for these purposes. The separation of benzyl alcohol is chosen as the toluene oxidation product to be separated from toluene, whereas toluene and o-xylene from heptane is used as a model system for the separation of aromatic compounds from a cracker feed. O-xylene is chosen, because its high complexation constant (300 M^{-1}) indicates maximum feasibility [10].

In order to achieve these goals, literature data will be collected for the initial selection of suitable cyclodextrins, after which the distribution coefficients of the compounds to be separated will be experimentally determined at phase equilibrium. From the ratio of distribution coefficients, the selectivity can be calculated. Finally, an evaluation will be carried out for the industrial feasibility of separations with aqueous cyclodextrins for the processes selected.

3.3 SELECTION OF CYCLODEXTRINS

A cyclodextrin is a cyclic, cone-shaped oligosaccharide consisting of six or more α-D-glucopyranose (α-D-glucose) units with a hydrophilic outer surface and a hydrophobic cavity. The most common cyclodextrins are the native or natural cyclodextrins: α-CD, β-CD and γ-CD, consisting of 6, 7 and 8 glucopyranose-units, respectively. Whether and to what extent a complex is formed, can be predicted on the basis of size, shape and polarity of the guest molecule and various interactions involving Van der Waals, dispersive forces, dipole-dipole interactions, electrostatic forces and hydrogen bonding [3,5]. The size of the guest determines whether it fits into the cavity; shape and polarity influence the possible stabilizing effects by interactions within the cavity or with side groups on the cavity rim [3]. To illustrate the effect of geometry: benzene and linear alkanes fit into the α-CD-cavity, toluene and ethylbenzene fit into β-CD and γ-CD accommodates xylenes [10-12].

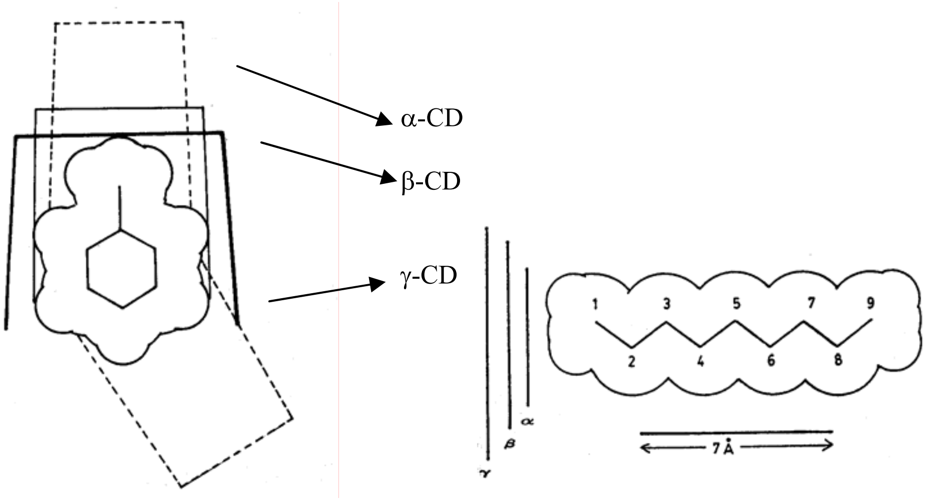

Figure 3.1. Toluene and alkane inclusion visualisation with cyclodextrins [10,12].

Figure 3.1 illustrates that toluene fits into the cavity of β-cyclodextrin very well [10]. The right hand figure in Figure 3.1 indicates that heptane (as well as other alkanes) is smaller than the β-CD and γ-CD cavity. α-CD is able to form complexes with both ends of the alkane, forming stable complexes with an increased stoichiometry [12].

The main disadvantage of native cyclodextrins is their low solubility in water (α-CD: 1.45 g/l, β-CD: 0.18 g/l, γ-CD: 2.3 g/l) [3]. In order to achieve high solvent capacity, the solubility of cyclodextrins needs to be as high as possible. This eliminates the use of native cyclodextrins, but a variety of modified cyclodextrins with increased solubility is available. Examples of highly soluble cyclodextrin derivates are sulfated, carboxymethylated, hydroxypropylated and methylated cyclodextrins. The latter two are most frequently used [5,13]. At certain degrees of substitution, the solubility of hydroxypropyl-β-cyclodextrins in water can be up to 75 wt% [13], of hydroxypropyl-α-cyclodextrins at least 33 wt% [14] and of sulfated β-cyclodextrins at least 35 wt% [15].

3.3.1 TOLUENE OR O-XYLENE/HEPTANE SEPARATION

The influence of the substituents on the complexation characteristics of toluene is not exactly known, although some suggestions are made in literature. It is discussed that alkyl-substituted cyclodextrins show higher complexation constants due to cavity extensions and additional stabilising hydrophobic interactions between the side groups and the guest [16]. However, these effects may be counteracted by the sterical hindrance by the presence of side groups close to the cavity entrance, causing the cavity opening to become narrower. An example is hydroxypropylated-β-CD: its solubility increases drastically as a function of the degree of substitution, but the binding capacities decrease [16].

The aqueous concentration of toluene is higher with the hydroxypropylated CD's (HP-CD's) than with α-CD and γ-CD and this effect is also observed for other aromatic compounds [11]. The occurrence of steric hindrance by the presence of the methyl side groups is not observed [17]. Similar effects are also reported for methylated β-CD and for the complexation of xylenes with methylated α-CD, while complexation with other α-CD's is negligible [18].

Therefore, a HP-β-CD with a degree of substitution of 0.8 was experimentally evaluated for the separation of toluene and o-xylene from toluene/heptane or o-xylene/heptane mixtures. Because of the presumable stabilising influence of methyl substituents, m-β-CD with a substitution degree of 1.7 was also selected. Although sulfated β-CD also seemed to be a suitable candidate, initial experiments with s-β-CD indicated that the presence of s-β-CD had a negligible effect on the distribution coefficient of toluene. This in combination with the fact that sulfated β-CD is insoluble in ethanol, and that thus no GC analysis of the aqueous phase is possible, led to the decision to discard further investigation of s-β-CD.

3.3.2 BENZYL ALCOHOL/TOLUENE SEPARATION

For the benzyl alcohol/toluene mixture, the inclusion model from Figure 3.1 can probably be applied to both compounds since there is no large difference in geometry between both molecules. In general, the hydroxyl group of a guest in a CD cavity is not part of the complex, but stays in contact with the surrounding water to form hydrogen bonds. Since these interactions are already present when the guest is in solution, this will not facilitate selective complexation [19]. Aromatic hydroxyl groups, like in benzyl alcohol, however, form an exception. They will penetrate deep into the cavity and form hydrogen bonds with the hydroxyl groups located on the cavity rim [20,21]. It is thus possible that benzyl alcohol forms more stable complexes with β-CD than toluene. Although the size of the cavity of a α-cyclodextrin does not enable inclusion complexation of toluene, it is reported that a toluene-size molecule with a hydroxyl group has a significantly higher complexation constant that toluene itself [5,20,21]. Therefore, a HP-α-CD with an average molar substitution of 0.6 and two HP-β-CD's with different degrees of substitution (0.6 and 1.0) were experimentally evaluated for the separation of benzyl alcohol from mixtures of benzyl alcohol and toluene.

3.4 COMPLEX FORMATION AND EXTRACTION

The exact nature of the driving force of complexation of cyclodextrins with guest molecules is not known. It is a combination of CD-ring strain release upon complexation, geometrical compatibility, Van der Waals, electrostatic and hydrophobic interactions and in the case of some guests, hydrogen bonding between the cyclodextrin and the guest [3,5]. The effect of water substitution by a guest of appropriate size, shape and polarity is, however, always present [5]. Upon complexation, the hydrophobic guest enters the hydrophobic cavity from a polar water environment. This also contributes to the energy decrease of the system [3,5]. Complexation is always exothermic and decomplexation thus occurs at elevated temperatures. The change in entropy can be either positive or negative, depending on the driving forces dominating complexation.

The phase and reaction equilibria of the CD extraction process are schematically shown in Figure 3.2. Compound G denotes the component to be selectively extracted from component F. In order for a complexation with the cyclodextrin to occur, the compounds G and/or F have to dissolve in the aqueous phase. Due to very low solubilities, the concentrations of water, cyclodextrins and complexes in the organic phase can be neglected. A β-cyclodextrin cavity can accommodate more than one small molecule like methanol or ethanol, thereby increasing complexation stoichiometry. Larger molecules can form complexes with multiple cyclodextrins, where the side groups are accommodated in the cavity [3]. However, these considerations do not apply for the compounds involved in this project (toluene, o-xylene, heptane and benzyl alcohol). It has been suggested in literature that in these cases also 1:2 and 1:3 stoichiometry are possible [22], but others suggests this to be highly unlikely [10].

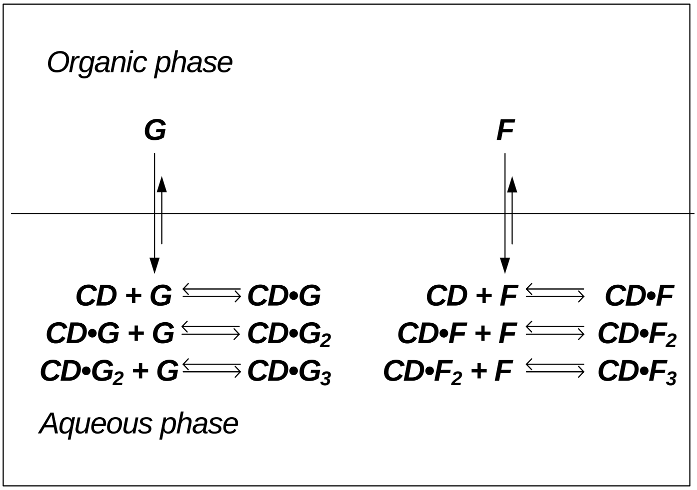

Figure 3.2. Visualization of the extraction process of G from a mixture of G and F. CD-G: primary complex; CD-G_2: secondary complex; CD-G_3 tertiary complex.

A 1:1 complexation formation between cyclodextrin and guest in the aqueous phase is given by the following equilibrium reaction:

$$\mathrm{CD} + \mathrm{G} \leftrightarrow \mathrm{CD} \bullet \mathrm{G} \tag{3.1}$$

Analogous equilibrium reactions and equations are valid for the complexation of component F.

At equilibrium, the association or complexation constant (assuming activity coefficients of 1) can be expressed in the following way:

$$\mathrm{K}_{\mathrm{G},1:1} = \frac{[\mathrm{CD} \bullet \mathrm{G}]^{\mathrm{aq}}}{[\mathrm{CD}]^{\mathrm{aq}}_{\mathrm{free}} \cdot [\mathrm{G}]^{\mathrm{aq}}_{\mathrm{free}}} \tag{3.2}$$

If the concentration of the guest molecule is higher than that of the cyclodextrin, then also a 1:2 and a 1:3 complex can be formed, provided that the guest molecule is small enough compared to the cavity of the cyclodextrin:

$$\mathrm{CD} \bullet \mathrm{G} + \mathrm{G} \leftrightarrow \mathrm{CD} \bullet \mathrm{G}_2 \tag{3.3a}$$

$$K_{G,1:2} = \frac{\left[CD \bullet G_2\right]^{aq}}{\left[CD \bullet G\right]^{aq} \cdot \left[G\right]^{aq}_{free}} = \frac{\left[CD \bullet G_2\right]^{aq}}{K_{G,1:1} \cdot \left[CD\right]^{aq}_{free} \cdot \left(\left[G\right]^{aq}_{free}\right)^2} \tag{3.3b}$$

$$CD \bullet G_2 + G \leftrightarrow CD \bullet G_3 \tag{3.4a}$$

$$K_{G,1:3} = \frac{\left[CD \bullet G_3\right]^{aq}}{\left[CD \bullet G_2\right]^{aq} \cdot \left[G\right]^{aq}_{free}} = \frac{\left[CD \bullet G_3\right]^{aq}}{K_{G,1:1} . K_{G,1:2} \cdot \left[CD\right]^{aq}_{free} \cdot \left(\left[G\right]^{aq}_{free}\right)^3} \tag{3.4b}$$

The following mass balances will apply:

$$\begin{aligned}\left[CD\right]^{aq}_{tot} = {} & \left[CD\right]^{aq}_{free} + \left[CD \bullet G\right]^{aq} + \left[CD \bullet G_2\right]^{aq} + \left[CD \bullet G_3\right]^{aq} \\ & + \left[CD \bullet F\right]^{aq} + \left[CD \bullet F_2\right]^{aq} + \left[CD \bullet F_3\right]^{aq}\end{aligned} \tag{3.5a}$$

$$\left[G\right]^{aq}_{tot} = \left[G\right]^{aq}_{free} + \left[CD \bullet G\right]^{aq} + 2\left[CD \bullet G_2\right]^{aq} + 3\left[CD \bullet G_3\right]^{aq} \tag{3.5b}$$

$$\left[G\right]^{org}_{tot} = \left[G\right]^{org}_{0} - \left[G\right]^{aq}_{tot} \tag{3.5c}$$

$$\left[F\right]^{aq}_{tot} = \left[F\right]^{aq}_{free} + \left[CD \bullet F\right]^{aq} + 2\left[CD \bullet F_2\right]^{aq} + 3\left[CD \bullet F_3\right]^{aq} \tag{3.5d}$$

$$\left[F\right]^{org}_{tot} = \left[F\right]^{org}_{0} - \left[F\right]^{aq}_{tot} \tag{3.5e}$$

The distribution coefficients of components G and F are defined by the ratio of the mole fractions in the extract (CD) phase and in the raffinate (organic) phase, according to:

$$D_G = \frac{\left[G\right]^{aq}_{tot}}{\left[G\right]^{org}_{tot}} = \frac{\left[G\right]^{aq}_{free} + \left[CD \bullet G\right]^{aq} + 2\left[CD \bullet G_2\right]^{aq} + 3\left[CD \bullet G_3\right]^{aq}}{\left[G\right]^{org}_{tot}} \tag{3.6a}$$

and

$$D_F = \frac{\left[F\right]^{aq}_{tot}}{\left[F\right]^{org}_{tot}} = \frac{\left[F\right]^{aq}_{free} + \left[CD \bullet F\right]^{aq} + 2\left[CD \bullet F_2\right]^{aq} + 3\left[CD \bullet F_3\right]^{aq}}{\left[F\right]^{org}_{tot}} \tag{3.6b}$$

If only a 1:1 complex is formed, the concentrations [CD•G$_2$], [CD•G$_3$] etc. are, of course, 0. The selectivity, $S_{G/F}$ is defined as the ratio of the distribution coefficients of G and F:

$$S_{G,F} = \frac{D_G}{D_F} \tag{3.7}$$

An overview of reported complexation constants of the studied solutes with α-, β- and γ-CD is given in Table 3.1. It can be concluded that complexation constants with β-CD for o-xylene, toluene, heptane and benzyl alcohol are larger than those with the other cyclodextrins. This means that with β-CD the complex concentrations are higher than with the other CD's. Considering the solubilities of o-xylene (0.0003 M), toluene (0.0014 M), heptane (0.0005 M) and benzyl alcohol (0.425 M), and the complexation constants of β-CD, a separation of o-xylene from heptane, of toluene from heptane and of benzyl alcohol from toluene is, in principle, possible. However, the reported complexation constants with β-CD for benzyl alcohol (215 M^{-1}, 50 M^{-1} and 22 M^{-1}) are not consistent with each other.

Table 3.1: Complexation constants of o-xylene, toluene, heptane and benzyl alcohol with native cyclodextrins.

Cyclodextrin	o-Xylene	Toluene	Heptane	Benzyl alcohol		
	K_1 (M^{-1}) [10]	K_1 (M^{-1}) [10]	K_1 (M^{-1}) [12]	K_1 (M^{-1}) [23]	K_1 (M^{-1}) [19]	K_1 (M^{-1}) [24]
α-CD	22	33	37	22	22	-
β-CD	300	140	69	215	50	22
γ-CD	34	20	30			

3.5 METHODS AND MATERIALS

3.5.1 CHEMICALS

The cyclodextrins hydroxypropyl-α-CD (molar substitution, M.S. = 0.6, purity 99 wt%), hydroxypropyl-β-CD (M.S. = 0.6, purity 99 wt %), hydroxypropyl-β-CD (M.S. = 0.8, purity 99 wt %), hydroxypropyl-β-CD (M.S. = 1.0, purity 99 wt%), sodium salt of sulfated-β-CD, (M.S. ~2.2, purity 98 wt%), randomly methylated-β-CD (M.S. = 1.7, purity 98 wt %) were obtained from Sigma-Aldrich.

n-Heptane (purity > 99 wt%), toluene (purity 99.5 wt%), o-xylene (purity 99 wt%), benzyl alcohol (purity 99.5 wt%), ethylbenzene (purity > 99 wt%), dibenzofuran (purity 98 wt%) and ethanol (purity 99.8 wt%) were purchased from Merck.

3.5.2 LIQUID – LIQUID DISTRIBUTION EXPERIMENTS

Extraction experiments were conducted in 100 ml glass jacketed vessels closed with a glass cap. The jackets were connected to a water bath maintaining a constant temperature in the vessels. All experiments were carried out with a constant temperature of 25 °C. The vessels were equipped with a magnetic stirrer (400 rpm). Comparing results at different stirring times showed that at 25 °C equilibrium was established after about four hours.

The vessel was filled with approximately 25 ml of demineralised water containing a certain amount of cyclodextrin, ranging from 0 to a maximum of 45 wt%, and with approximately 25 ml of organic solution (phase ratio = 1). This organic solution contained approximately 12.5 wt% toluene (0.95 M) or 12.5 wt% o-xylene (0.83 M) in heptane or

1,5 wt% benzyl alcohol (0.15 M) in toluene. Experiments were carried out with HP-β-CD (0.8) and m-β-CD (1.7) for the toluene – heptane distribution experiments, with HP-β-CD (0.8) for the o-xylene-heptane distribution experiments and with HP-α-CD (0.6), HP-β-CD (0.6) and HP-β-CD (1.0) for the benzyl alcohol – toluene distribution experiments.

Samples were taken with a syringe from the organic phase and the aqueous phase after phase separation was complete. The sample from the organic phase was taken through the top opening with a pipette; the sample from the aqueous phase was taken via a sample port at the bottom. To determine the concentrations in both phases, both samples were analysed with a gas chromatograph. The aqueous phase was first diluted with ethanol (approximately ten times), because too much water in the sample would extinguish the flame of the GC detector.

3.5.3 ANALYTICAL TECHNIQUE

Samples were analysed with a Varian CP-3800 Gas chromatograph with an Alltech capillary column with ECTM-wax (length: 30 m, diameter: 0.32 mm, film thickness: 0.25 μm) and FID detector. Quantification of the components was carried out with the help of an internal standard. Dibenzofuran was used for samples containing benzyl alcohol and toluene; ethylbenzene was used in samples containing toluene or o-xylene and heptane (± 1 wt% in water-ethanol samples, ± 2.5 wt% in organic samples). The deviation of the analyses varied from about 4 to 25% and these are shown as error bars of the experimental points in the figures. These deviations are sufficient for our screening purposes.

3.6 RESULTS AND DISCUSSION

3.6.1 PURE TOLUENE AND PURE BENZYL ALCOHOL – HP-β-CD (0.6) SYSTEMS

In Figure 3.3, the results of distribution experiments of pure toluene and pure benzyl alcohol with an aqueous phase containing varying concentrations of HP-β-CD (0.6) are given. The lowest line represents the complexation of toluene with HP-β-CD (0.6) with a 1:1 stoichiometry. The accompanying complexation constant has a value of 780 M^{-1}. Based on the toluene-cyclodextrin inclusion model from Figure 3.1, it can be predicted that one toluene molecule in a β-CD cavity leaves no room for one or two other molecules.

It is clearly seen that a 1:1 complexation with benzyl alcohol does not represent the experimental data. Therefore, also the models for 1:2 and 1:3 stoichiometries are presented. A possible explanation for the deviation of the 1:1 complexation is the presence of an OH-group in the benzyl alcohol molecule, which can form hydrogen bonds with the cyclodextrin. Since toluene has no such groups, a similar complexation with the cyclodextrin is not possible.

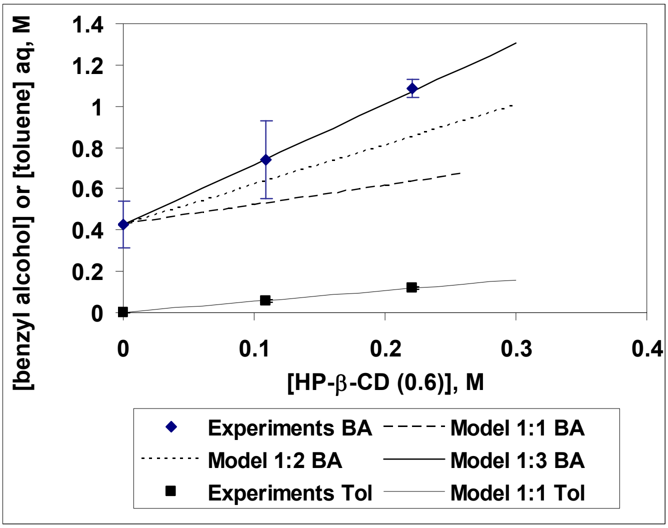

Figure 3.3: Total aqueous phase concentration of toluene (Tol) and benzyl alcohol (BA) as a function of HP-β-CD (0.6) concentration. Model: complexation of pure toluene or pure benzyl alcohol.

From Figure 3.3, it is clear that the experimental data of benzyl alcohol with HP-β-CD (0.6) can best be fitted by a 1:3 complexation. This can also be clarified by the fact that in the presence of 0.22 M of cyclodextrin, a total aqueous phase concentration of 1.07 M of benzyl alcohol was measured. Assuming a constant free benzyl alcohol concentration of 0.43 M, which is the maximum solubility of benzyl alcohol in water at 25 °C, this indicated that 0.64 M benzyl alcohol must be present in complexed form, which is three times as much as the cyclodextrin concentration. The 1:2 and 1:3 complexation is described as: $[BA]_{tot}^{aq} = 2 * [CD]^{aq} + [BA]_0^{aq}$ and $[BA]_{tot}^{aq} = 3 * [CD]^{aq} + [BA]_0^{aq}$, respectively. There were not enough data points in order to calculate the complexation constants.

3.6.2 TOLUENE / O-XYLENE – HEPTANE – CYCLODEXTRIN SYSTEM

Liquid-liquid equilibrium data were collected for mixtures of 12.5 wt% (initial) toluene in heptane and for mixtures of 12.5 wt% (initial) o-xylene in heptane at 25 °C with the cyclodextrins HP-β-CD (0.8) and m-β-CD (1.7). The methylated-β-CD was selected because a higher distribution coefficient for toluene was expected.

In Figure 3.4, it is shown that the distribution coefficients of both toluene and o-xylene with m-β-CD and HP-β-CD increase linearly with increasing CD concentration. Apparently, there is some threshold value in the CD concentration, in the range of 0.025 – 0.07 M, required in order to complex the aromatic compounds in a mixture. In Figure 3.5, it can be seen that the distribution coefficient of heptane increases sharply at cyclodextrin concentrations around 0.2 M. This is especially evident for HP-β-CD in the presence of both toluene and o-xylene, but it is less obvious for m-β-CD. Since n-heptane is a small molecule and is present in excess, it can also form 1:2 and 1:3 complexes with cyclodextrins. The lines in Figure 3.5 represent the models of the 1:1 to 1:3 complexation of heptane in the cyclodextrins. In the model, it is assumed that the 1:2 and 1:3 complexations are occurring consecutively and not simultaneously. This means that a 1:2 complex can only be formed when the concentration of the 1:1 complex has reached a certain value and that the 1:3 complex can be formed when the concentration of the 1:2 complex is high enough. In Table 3.2, indications of the order of magnitude of the complexation constants with different complexation models are given for the system toluene or o-xylene and heptane.

Table 3.2. Overview of results from model 1:1, 1:2 and 1:3 stoichiometry for the system toluene or o-xylene and heptane.

Cyclodextrin	o-Xylene	Toluene	Heptane		
	$K_{1:1}$ (M^{-1})	$K_{1:1}$ (M^{-1})	$K_{1:1}$ (M^{-1})	$K_{1:2}$ (M^{-1})	$K_{1:3}$ (M^{-1})
HP-β-CD (0.8)		145	40	2400	5000
HP-β-CD (0.8)	320		250	4500	8000
m-β-CD (1.7)		220	400	1700	

It can be seen from Figures 3.4 and 3.5 that higher distribution ratios are occurring for both toluene and heptane in the case of m-β-CD (1.7) compared to HP-β-CD (0.8). It has been suggested in literature that pyrene forms more stable complexes with methylated γ-CD than with native γ-CD, because of the stabilizing interaction of the guest with the hydrophobic side groups of the cyclodextrin [17]. The substituent groups are also supposed to make the hydrophobic cavity of the CD large enough to include an aromatic molecule completely. This effect is also suggested to explain the higher complexation constants observed of HP-CD's compared to native cyclodextrins with aromatic molecules. The number of possible hydrophobic interaction sites of m-β-CD (1.7) is, however, twice as high as HP-β-CD (0.8). The hydrophobic interactions could be a reason for the higher distribution coefficients for both toluene and heptane; both compounds interact with the methyl side groups.

From Figure 3.5, it can be seen that the distribution coefficient of heptane in the o-xylene/heptane mixture is also higher than in toluene/heptane mixtures. This can be attributed to the fact that o-xylene occupies less of the available cyclodextrin cavities. Since heptane is present in excess, it makes preferentially use of the presence of more available cyclodextrin cavities.

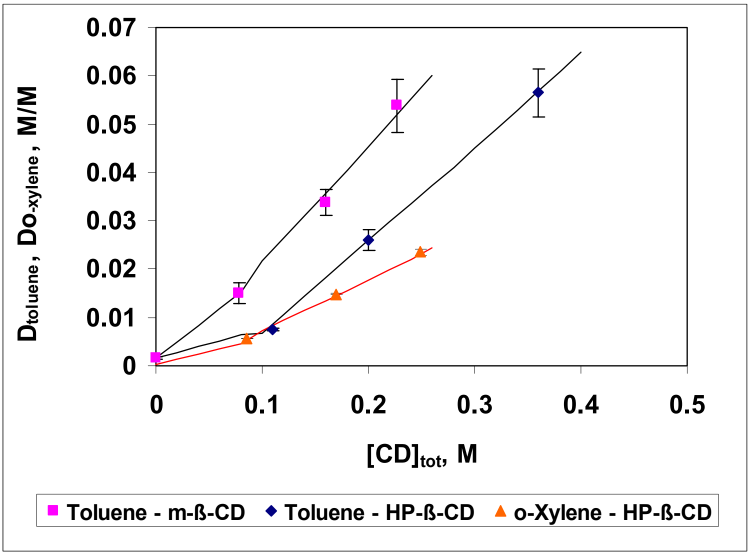

Figure 3.4. Distribution coefficients of 12.5 wt% (initial) toluene or o-xylene in heptane, T = 25 °C. The lines represent the1:1 models for the distribution coefficients.

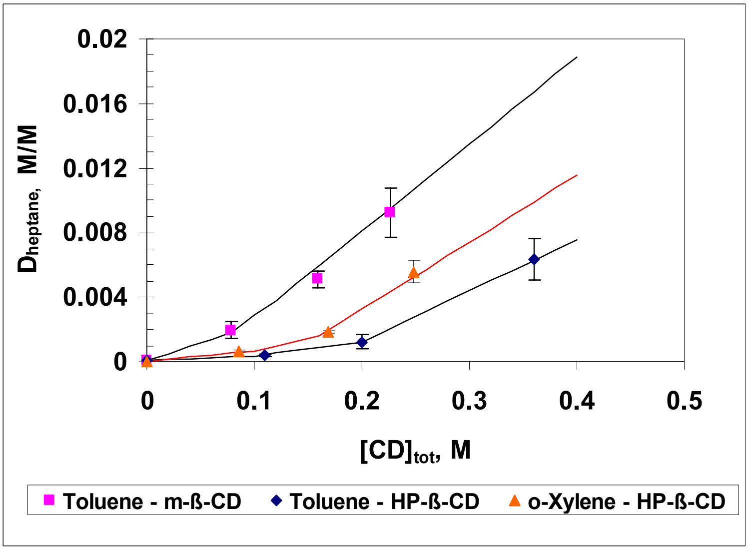

Figure 3.5. Distribution coefficients of heptane, T = 25 °C. The lines represent the 1:2 (toluene – m-β-CD), 1:3 (o-xylene – HP-β-CD) and 1:3 (toluene – HP-β-CD) models for the distribution coefficients of heptane.

This is shown in Figure 3.6, where the amount of cyclodextrin involved in complexation is depicted, calculated from the difference in total concentration in the aqueous phase and the solubility of the compound in pure water. The amount of cyclodextrins involved in complexation increases linearly with increasing CD concentration with HP-β-CD, but with m-β-CD it increases only linearly for the experimental points given, from [CD] = 0.075 – 0.225 M. The cause of the jump in the amount of cyclodextrin involved in the complexation in the case of m-β-CD is not known.

In Figure 3.7, the selectivity of toluene and o-xylene over heptane with several cyclodextrins is shown. The toluene/heptane selectivity in water is 19.4 and the toluene/heptane selectivity with HP-β-CD is around 20 for [CD] < 0.2 M. Addition of HP-β-CD hardly changes the toluene/heptane selectivity with HP-β-CD (0.8), since both form 1:1 complexes with the cyclodextrin below a CD concentration of about 0.2 M. At higher cyclodextrin concentrations, the distribution coefficient of heptane increases more than that of toluene (see Figures 3.4 and 3.5), due to the fact that n-heptane also forms 1:2 to 1:3 complexes with cyclodextrins. With m-β-CD, the toluene/heptane selectivity is lower compared to that in water, probably caused by the jump in complexed CD as seen in Figure 3.6. The average toluene/heptane selectivity with m-β-CD is around 6.7.

The o-xylene/heptane selectivity with HP-β-CD in water is 10 and decreases slightly with addition of CD in the aqueous phase, because o-xylene forms a 1:1 complex with HP-β-CD and heptane can form 1:1 and 1:2 complexes.

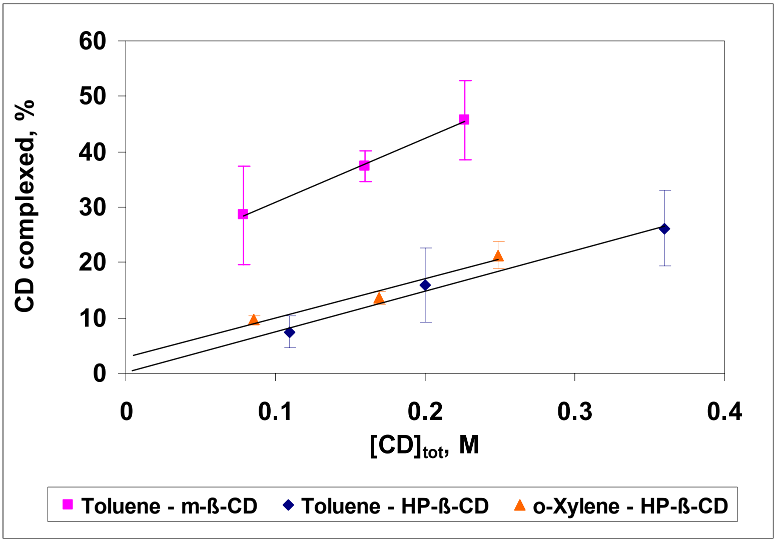

Figure 3.6. Percentage of total CD complexed in extraction assuming 1:1 complex stoichiometry of the aromatic compound and constant free aqueous phase concentrations of toluene and heptane. The lines represent the model fits.

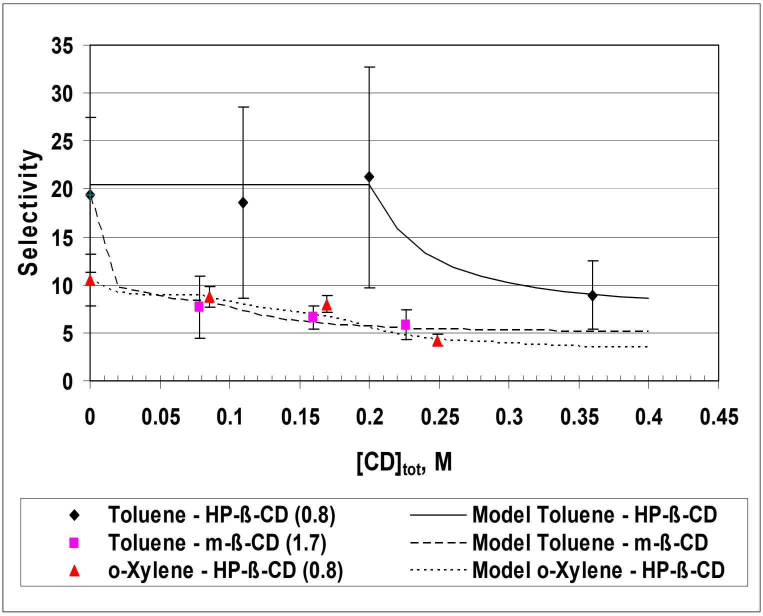

Figure 3.7. Selectivity of toluene or o-xylene/heptane. The lines represent the models for the selectivity.

3.6.3 BENZYL ALCOHOL – TOLUENE – CYCLODEXTRIN SYSTEM

In the following figures, results are presented for the distribution experiments with benzyl alcohol – toluene and HP-β-CD (0.6), HP-β-CD (1.0) and HP-α-CD (0.6) solutions. In these figures, the combination of three different models is also presented. The solubility of benzyl alcohol in water is 0.425 M.

Table 3.3. Overview of results from model 1:1, 1:2 and 1:3 stoichiometry for the system benzyl alcohol and toluene.

Cyclodextrin	Benzyl alcohol			Toluene
	$K_{1:1}$ (M^{-1})	$K_{1:2}$ (M^{-1})	$K_{1:3}$ (M^{-1})	$K_{1:1}$ (M^{-1})
HP-α-CD (0.6)	4			200
HP-β-CD (0.6)	14	5	5	780
HP-β-CD (1.0)	11	3	3	500

In Table 3.3, the complexation constants of the system with benzyl alcohol and toluene with different CD derivatives are given. The results for benzyl alcohol with HP-β-CD (0.6) and HP-β-CD (1.0) can be explained by the 1:3 complexation model, as was shown with the pure component with HP-β-CD (0.6). The toluene distribution coefficients with all cyclodextrins at a concentration below around 0.18 M follow the 1:1 model found for pure toluene.

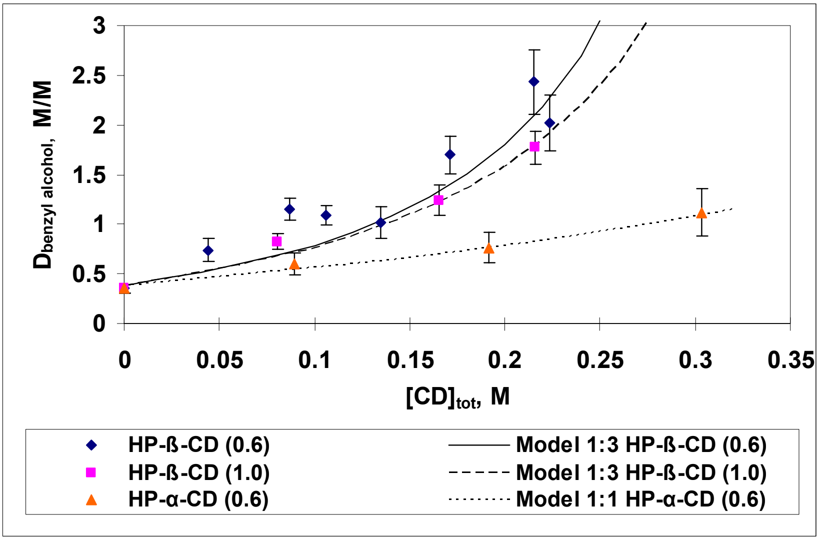

Figure 3.8. Distribution coefficient of benzyl alcohol of 1.5 wt% (initial) benzyl alcohol in toluene and an aqueous phase with varying concentrations of HP-β-CD (0.6), HP-β-CD (1.0) and HP-α-CD (0.6).

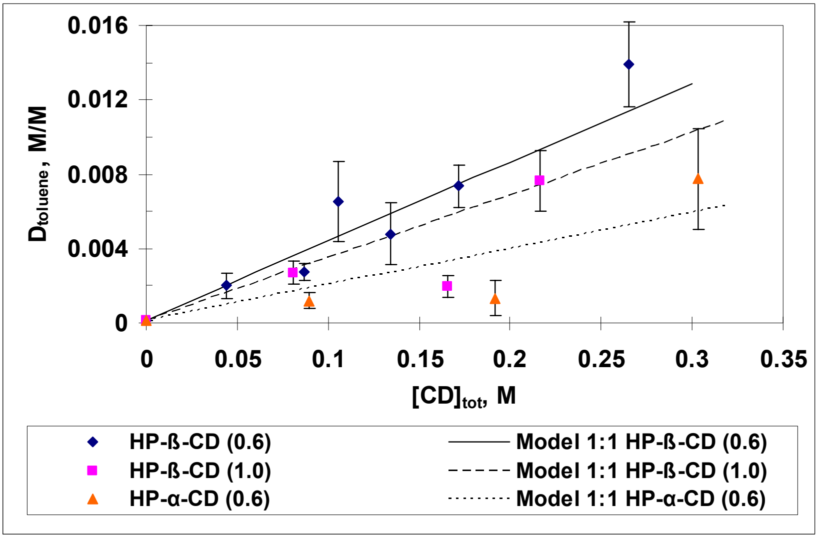

Figure 3.9. Distribution coefficient of toluene of 1.5 wt% (initial) benzyl alcohol in toluene and an aqueous phase with varying concentrations of HP-β-CD (0.6), HP-β-CD (1.0) and HP-α-CD (0.6).

3.6.4 COMPARISON OF THE DIFFERENT CYCLODEXTRINS

It can be seen in Figures 3.8 and 3.9 that distribution coefficients of both toluene and benzyl alcohol are lower for the HP-α-CD than for the HP-β-CD's. It is very probable that this is caused by the smaller cavity of HP-α-CD in comparison with HP-β-CD, the differences between HP-β-CD (0.6) and HP-β-CD (1.0) are less distinct. The distribution coefficient of benzyl alcohol with HP-β-CD (1.0) seems to be somewhat less than with HP-β-CD (0.6). This can be explained on the basis of interaction of the OH-groups of benzyl alcohol with the OH-group on the cyclodextrin cavity rim. HP-β-CD (1.0) has a higher substitution degree than HP-β-CD (0.6) and there are less OH-groups available for this stabilising effect, which could result in a slightly lower value for the complexation constant and thus in a slight difference in distribution coefficient of benzyl alcohol. It is also possible that the OH-groups of the hydroxypropyl side groups interact with the OH-group of benzyl alcohol to provide a stabilizing effect, but these interactions will be obstructed by steric limitations.

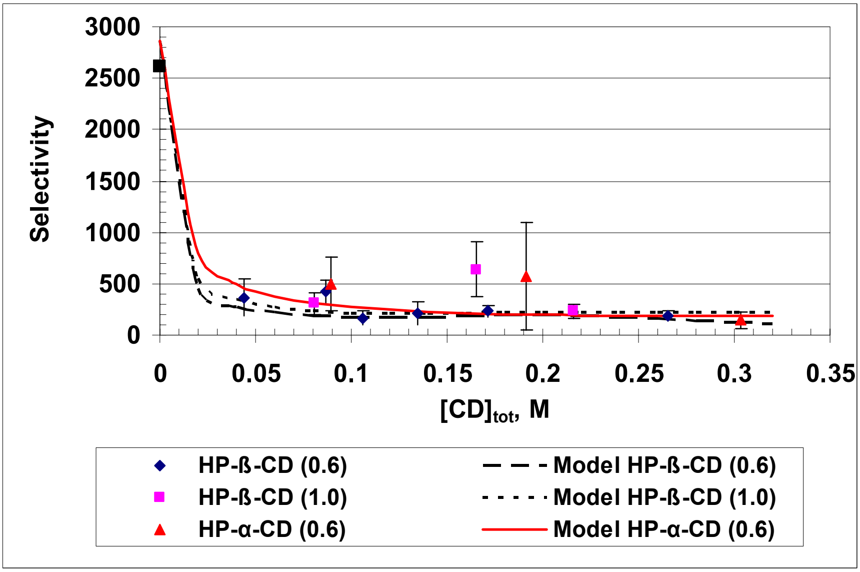

Figure 3.10. Benzyl alcohol/toluene selectivity.

The difference in toluene distribution coefficients between both HP-β-CD's is more obvious. This cannot be explained by the stabilising effect of OH-groups on the cavity rim. HP-β-CD (1.0) has more substituents and can, therefore, cause more sterical hindrance, which could lower the complexation constant for toluene compared to HP-β-CD (0.6). The size of the HP-β-CD cavity is 1.2 Å larger than that of HP-α-CD and the molecular diameter of toluene is similar to the size of the HP-β-CD. Therefore, the inclusion ability of

HP-β-CD for toluene and benzyl alcohol was larger than that of HP-α-CD because of the smaller cavity. If this causes the difference in toluene distribution coefficient, this could also contribute to the difference in benzyl alcohol distribution coefficient.

From Figure 3.10, it is clear that the benzyl alcohol/toluene selectivity decreases dramatically with the addition of cyclodextrins compared to a pure aqueous solution ($S = 2612$). Benzyl alcohol is much more soluble in water than toluene. The distribution coefficients of both compounds, however, increase with increasing CD concentration. The toluene distribution coefficients with HP-β-CD (0.6) increases more than with the other CD's and, therefore, the benzyl alcohol/toluene selectivity decreases at CD concentrations of about 0.09 M and higher. The selectivity for CD concentration of 0.10 to 0.22 M is in the range of 160.

The benzyl alcohol/toluene selectivities with the other cyclodextrins are much higher, in the range of 300 – 650.

3.6.5 EVALUATION OF INDUSTRIAL SUITABILITY

For the separation of toluene from heptane, a toluene distribution ratio of about 0.026 can be achieved with HP-β-CD (0.8) at a CD concentration of 0.2 M with a toluene/heptane selectivity of 21. With m-β-CD (1.7) at a CD concentration of about 0.22 M, the toluene distribution coefficient is 0.05 and the toluene/heptane selectivity is 6. The solvent to feed ratios for these separations are $S/F = 1.5 * (S/F)_{min} = 1.5 * (1/0.026) = 58$ and $S/F = 1.5 * (1/0.05) = 30$, respectively. These are such an unrealistic high ratios that separation of toluene from toluene/heptane is, therefore, not feasible. The o-xylene distribution coefficient for the o-xylene/heptane separation is lower than that of toluene ($D = 0.0235$ at [HP-β-CD (0.8)] = 0.25 M). This means that this separation is even less feasible than the toluene/heptane separation.

For the separation of benzyl alcohol from toluene, a distribution ratio of roughly 2 is possible with HP-β-CD (1.0) (± 0.22 M) and with HP-β-CD (0.6) (0.2 M). A decrease in temperature or the presence of other compounds in the aqueous phase (like glycerol [15]) is a possibility to further increase the distribution coefficient. The minimum solvent to feed ratio for this separation is in the order of 0.75. With a distribution ratio of about 2 (at a solvent-to-feed ratio of 1) and a benzyl alcohol/toluene selectivity of at least 100, aqueous solutions of hydroxypropylated cyclodextrins have sufficient potential to be used for the recovery of benzyl alcohol.

3.7 CONCLUSIONS

Aqueous phase concentrations of the organic compounds toluene, o-xylene, benzyl alcohol and n-heptane can be increased by the addition of cyclodextrins, due to complexation.

Toluene and o-xylene form 1:1 complexes with the CD derivatives tested with complexation constants in the range of 145 to 780 M^{-1}. Benzyl alcohol forms a 1:1 complex with HP-α-CD (0.6), but it forms a 1:3 complex with HP-ß-CD (0.6) and with HP-ß-CD (1.0). n-Heptane forms, due to its small size, 1:1 to 1:3 complexes with several cyclodextrins.

The models developed describe the experimental data reasonably well, considering the large deviations in the analyses.

Aqueous solutions of cyclodextrin derivatives are not suitable for the extraction of toluene or o-xylene from n-heptane and, in general, not suitable for the extraction of aromatic compounds from aliphatic hydrocarbons, due to the low aromatic distribution coefficients (D = 0.05 for toluene at [m-ß-CD (1.7)] = 0.22 mole/L and D = 0.023 for o-xylene at [HP-β-CD (0.8)] = 0.25 mole/L) and a low aromatic/aliphatic selectivity (S = 6 for toluene/heptane with m-ß-CD (1.7)).

Aqueous hydroxypropyl-β-cyclodextrin solutions have sufficient potential to be used for extracting benzyl alcohol from toluene, since a high distribution coefficient (D > 2) and a high selectivity (S >100) are achieved.

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4 SELECTION OF IONIC LIQUIDS FOR THE EXTRACTION OF AROMATIC HYDROCARBONS FROM AROMATIC/ALIPHATIC MIXTURES

4.1 ABSTRACT

The separation of aromatic hydrocarbons (benzene, toluene, ethylbenzene and xylenes) from C_4 – C_{10} aliphatic hydrocarbon mixtures is challenging since these hydrocarbons have boiling points in a close range and several combinations form azeotropes. In this chapter, we investigated the separation of toluene from heptane by extraction with ionic liquids.

Several ionic liquids are suitable for extraction of toluene from toluene/heptane mixtures. The toluene/heptane selectivities at 40 °C and 75 °C with several ionic liquids, [mebupy]BF_4, [mebupy]CH_3SO_4, [bmim]BF_4 (40 °C) and [emim] tosylate (75 °C), are a factor of 1.5 – 2.5 higher compared to those obtained with sulfolane ($S_{tol/hept}$ = 30.9, D_{tol} = 0.31 at 40 °C), which is industrially the most used solvent for the extraction of aromatic hydrocarbons from a mixed aromatic/aliphatic hydrocarbon stream. Of these four ionic liquids, [mebupy]BF_4 appeared to be the most suitable, because of a combination of a high toluene distribution coefficient (D_{tol} = 0.44) and a high toluene/heptane selectivity ($S_{tol/hept}$ = 53). Therefore, with [mebupy]BF_4 also extraction experiments with other aromatic/aliphatic combinations (benzene/n-hexane, ethylbenzene/n-octane and m-xylene/n-octane) were carried out. The aromatic/aliphatic selectivities were all in the same range, from which it can be concluded that the toluene/heptane mixture is a representative model system for the aromatic/aliphatic separation.

4.2 INTRODUCTION

The separation of aromatic hydrocarbons (benzene, toluene, ethylbenzene and xylenes) from C_4 – C_{10} aliphatic hydrocarbon mixtures is challenging since these hydrocarbons have boiling points in a close range and several combinations form azeotropes. The conventional processes for the separation of these aromatic and aliphatic hydrocarbon mixtures are liquid extraction, suitable for the range of 20 – 65 wt% aromatic content, extractive distillation for the range of 65 – 90 wt% aromatics and azeotropic distillation for high aromatic content, >90 wt% [1]. Typical solvents used are polar components such as sulfolane [2-6], N-methyl pyrrolidone (NMP) [5], N-formyl morpholine (NFM), ethylene glycols [6-8], propylene carbonate [9]. This implicates additional distillation steps to separate the extraction solvent from both the extract and raffinate phases, and to purify the solvent, with consequently, additional investments and energy consumption. Overviews of the use of extraction and extractive distillation for the separation of aromatic hydrocarbons from aliphatic hydrocarbons can be found elsewhere [10-13].

According to Weissermel and Arpe, no feasible processes are available for the separation of aromatic and aliphatic hydrocarbons in the range below 20% aromatics in the feed mixture [1]. We are focussing on the separation of aromatic hydrocarbons from the feed stream of naphtha crackers, which may contain up to 25% aromatics. Preliminary calculations, based on information from UOP, showed that extraction with conventional solvents is not an option since additional separation steps are required to purify the raffinate, extract and solvent streams, which would induce high investment and energy costs. The costs of regeneration of sulfolane are high, since the sulfolane, which has a boiling point of 287.3 °C, is in the current process taken overhead from the regenerator and returned to the bottom of the aromatics stripper as a vapour [14]. The application of ionic liquids for extraction processes is promising because of their non-volatile nature [15]. This facilitates solvent recovery using techniques as simple as flash distillation or stripping.

Table 4.1. Overview of measured distribution coefficients and selectivities for aromatic/aliphatic separations. Data from literature.

Solvent	Separation	T, °C	Mole % arom.	D_{arom}	$S_{arom/alk}$	Remarks	Ref.
Sulfolane	Toluene/heptane	40	5.9	0.31	30.9	This work	
[emim]I_3	Toluene/heptane	45	7.5	0.84	48.6	Very corrosive	17
[bmim]I_3	Toluene/heptane	35	17.0	2.3	30.1	Very corrosive	17
[omim]Cl	Benzene/heptane	25	26.6	0.58	6.1*	Extraction	21
	Benzene/heptane	25	-	0.50	10.7	Act. Coeff.	22
	Benzene/heptane	40	-	0.63	11.3	Act. Coeff.	29
	Toluene/heptane	35	-	0.38	8.0	Act. Coeff.	22
	Toluene/heptane	40	-	0.43	7.7	Act. Coeff	29
[mmim]Tf_2N	Toluene/heptane	40	-	0.49	29.8	Act. Coeff.	19
[emim]Tf_2N	Benzene/cyclohexane	24.5	27.8	n.a.	17.7	Extraction	18
	Benzene/cyclohexane	30	-	0.84	13.2	Act. Coeff.	18
	Toluene/heptane	40	-	0.55	22.2	Act. Coeff.	19
	Toluene/heptane	40	-	0.58	22.1	Act. Coeff.	27
	Toluene/heptane	40	-	0.56	16.5	Act. Coeff.	29
[bmim]Tf_2N	Toluene/heptane	40	-	0.81	16.7	Act. Coeff.	19
[emmim]Tf_2N	Toluene/heptane	40	-	0.61	22.7	Act. Coeff.	27
[bmim]PF_6	Benzene/cyclohexane	22	-	0.66	3.1	Solubility	24
	Toluene/heptane	68	-	0.43	9.7	Solubility	25
	Toluene/heptane	40	-	0.34	21.3	Act. Coeff.	29
	Toluene/heptane	60	-	0.30	18.3	Act. Coeff.	29
[hmim]PF_6	Benzene/heptane	25	4.1	0.70	8.2*	Extraction	23
	Benzene/heptane	25	-	0.97	29.7	Act. Coeff.	20
[hmim]BF_4	Benzene/heptane	25	12.8	0.81	8.4	Extraction	23
[mebupy]BF_4	Toluene/heptane	40	-	0.38	32.8	Act. Coeff.	26
[mmim]$(CH_3)_2PO_4$	Toluene/octane	40	-	0.14	48.0	Act. Coeff.	28
[mmim]CH_3SO_4	Toluene/heptane	40	-	0.06	16.4	Act. Coeff.	28
[emim]$C_2H_5SO_4$	Toluene/heptane	40	-	0.19	43.0	Act. Coeff.	19

*selectivity calculated from the data given.

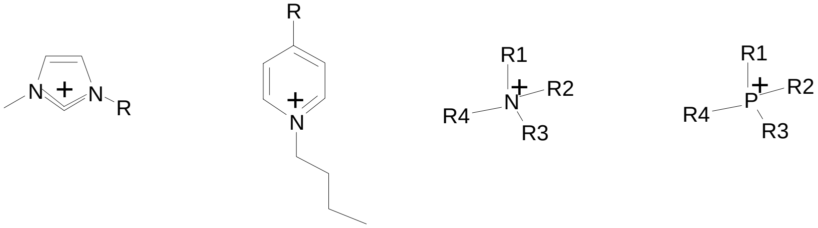


Figure 4.1. Structure of 1-R-3-methylimidazolium, 4-R-N-butylpyridinium, quaternary ammonium and quaternary phosphonium cations.

Aromatic hydrocarbons are reported to have low activity coefficients at infinite dilution in several ionic liquids, while aliphatic hydrocarbons show high activity coefficients in the same ionic liquids [15-32]. In Table 4.1, aromatic distribution coefficients and aromatic/aliphatic selectivities for toluene/heptane and some other aromatic/aliphatic systems, determined by either extraction [17-19,21,23], solubility [24,25] or by activity coefficients at infinite dilution [18-20,22,26-29] are shown. This suggests that these ionic liquids can be used as extractants for the separation of aromatic hydrocarbons from aliphatic hydrocarbons. Extraction of aromatics from mixed aromatic/aliphatic streams with ionic liquids is expected to require less process steps and less energy consumption than extraction with conventional solvents because ionic liquids have a negligible vapour pressure.

Ionic liquids are organic salts that are liquid at low temperatures (<100 °C) and consist of large organic cations based on methylimidazolium [Rmim], N-butylpyridinium [R-N-bupy], quaternary ammonium or phosphonium ions (Figure 4.1) and others, and anions such as hexafluorophosphate, tetrafluoroborate, alkylsulfates, alkylsulfonates, chloride, bromide, nitrate, sulfate, aluminium chloride, triflate ($CF_3SO_3^-$), bis(trifyl)imide ($(CF_3SO_2)_2N^- = Tf_2N$), etc. [33]. The R group of the cation is variable (e.g. methyl, ethyl, butyl, etc.). The variability of the anion and R groups in the imidazolium, pyridinium, ammonium or phosphonium cations may be used to adjust the properties of the ionic liquids. Ionic liquids have a wide liquid range (~300 °C), which allows a better kinetic control on reactions. They are non-flammable, have a high thermal stability and a high ionic conductivity. These properties permit their use in many fields. They are used as reaction media to substitute VOC's, as homogeneous catalysts and as extractive media in liquid/liquid extraction processes [15,16]. However, the use of ionic liquids also has some disadvantages: the physical properties are not always known, their viscosity is usually higher than common solvents and their toxicity is unknown. In order for a successful application of ionic liquids in industrial processes, these aspects must be taken into consideration.

The use of ionic liquids in separations is presently mostly in the extraction of metal ions with [bmim]PF_6, [hmim]PF_6 and other PF_6^--based IL's [34-37], alcohols using [Rmim]PF_6 (R = butyl, pentyl, heptyl and octyl) and [emim]Tf_2N [38-40], separation of alcohols and alkanes or alkenes with [omim]Cl, [hmim]BF_4 or [hmim]PF_6 [41,42], desulphurisation of oils with [emim]$AlCl_4$, [bmim]$AlCl_4$, [bmim]BF_4, [bmim]PF_6, trimethylamine hydrochloride/$AlCl_3$, [emim] ethylsulfate and [bmim] octylsulfate [43-46], ethers from ethanol with [omim]Cl and [bmim] trifluoromethanesulfonate [47,48]. It is also possible to separate compounds from each other by selective transport by using supported liquid membranes based on ionic liquids, such as [bmim]PF_6 [49-51]. Environmental pollutants, such as aromatic and polycyclic aromatic hydrocarbons, can be extracted from aqueous solutions with ionic liquids [bmim]PF_6 and [omim]PF_6 [52]. There are only a few publications concerning extraction of aromatic hydrocarbons from mixtures of aromatic and aliphatic hydrocarbons, notably with [emim]I_3, [bmim]I_3, [emim]$(CF_3SO_2)_2N$, [omim]Cl and trimethylamine chloride/$AlCl_3$, [hmim]BF_4 and [hmim]PF_6 [17,18,21,23].

It is remarkable that most of the ionic liquids used for extraction of the compounds mentioned are PF_6^- -containing imidazolium based ionic liquids. The reason is that these ionic liquids are very versatile and easy to prepare, although HF formation is likely [53].

The requirements of a suitable ionic liquid for the separation of aromatic and aliphatic hydrocarbons are:

- High solubility of aromatic hydrocarbons in the IL
- No or low solubility of aliphatic hydrocarbons in the IL
- High separation factor and a high distribution coefficient
- Simple recovery of the IL from both the extract and the raffinate phase
- Fast mass transport from the feed phase to the IL phase

A higher selectivity means a purer product and less extraction of aliphatics and a higher distribution coefficient requires a lower solvent to feed ratio.

4.3 SELECTION OF SUITABLE IONIC LIQUIDS

Brennecke and Maginn [33] reported in 2001 that until that date hardly any chemical engineer was involved in the design and development of ionic liquids for practical applications. Considering the low number of relevant publications on extractions and other separations, this is still true today. Beside the publications about extraction of aromatic and aliphatic hydrocarbons, other publications concerning this separation are patents, mainly dealing with extraction of dibenzothiophene from dodecane with trimethylamine hydrochloride/Al_2Cl_7 or trimethylamine hydrochloride/$AlCl_3$ and absorption of single components in these ionic liquids [30] or extractive distillation of close boiling compounds and azeotropic mixtures with for instance [omim]BF_4, [emim]BF_4, [emim]PF_6 etc. [31].

Although the separation of aromatic and aliphatic hydrocarbons is claimed in the patent by Arlt et al., no examples of this separation are given [31].

The extraction of toluene from mixtures of toluene and heptane is used as a model for the aromatic/aliphatic separation. The mixture of 10 (v/v)% toluene in heptane is taken as a reference for the selection of ionic liquids for the aromatic/aliphatic separation at two temperatures (40 and 75 °C). Based on initial screening results, three ionic liquids are chosen for more detailed equilibrium tests. Extraction experiments with other aromatic/aliphatic hydrocarbons will be performed with the most suitable ionic liquid from these selection tests. The solvent sulfolane is used as a benchmark for this separation ($S_{tol/hept} = 30.9$, $D_{tol} = 0.31$ at 40 °C), because it is one of the most common solvents for extraction of aromatic hydrocarbons from mixtures of aromatic and aliphatic hydrocarbons used in industry. Therefore, suitable ionic liquids for this separation must show $S_{tol/hept} \geq 30$ and/or $D_{tol} \geq 0.3$ at 40 °C. From Table 4.1, only the following ionic liquids have a sufficiently high aromatic/aliphatic selectivity ($S_{tol/hept}$>30): [emim]I_3, [bmim]I_3, [emim]$C_2H_5SO_4$, [mmim]$(CH_3)_2PO_4$ and [mebupy]BF_4.

Selvan et al. describe the separation of toluene and heptane using [emim]I_3 and [bmim]I_3 at temperatures of 45 °C and 35 °C, respectively (Figure 4.2) [17].

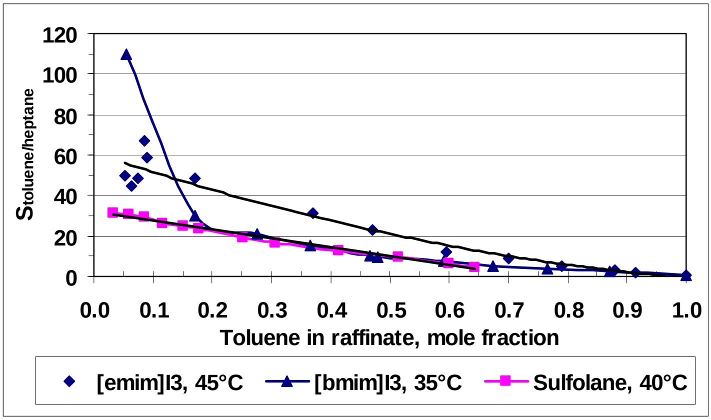


Figure 4.2. Selectivity of toluene/heptane; IL data from [17], sulfolane data from own experiments

These ionic liquids are in principle suitable for the extraction of aromatic hydrocarbons from a mixed aromatic/aliphatic feed stream, since they show both a high selectivity and a high distribution coefficient at low toluene concentrations, although [bmim]I_3 showed a comparable selectivity as sulfolane at toluene concentrations above 17%. As the data at low concentrations of toluene are quite scattered ([emim]I_3) or consist of only one point ([bmim]I_3), it was necessary to carry out experiments in the low toluene concentration range to determine whether these ionic liquids are indeed suitable for the separation of aromatic and aliphatic hydrocarbons.

However, we soon stopped experimenting with these ionic liquids, since they appeared extremely corrosive. Our stainless steel stirrers were corroded after only a few extraction experiments. Selvan et al. did not report any corrosion, but they used a Teflon paddle stirrer. Therefore, it is not surprising that we could not find any other references regarding these ionic liquids and we decided not to follow up on these two ionic liquids as extractants.

The other suitable ionic liquids from Table 4.1 with a high toluene/heptane selectivity with a reasonable toluene distribution coefficient are [emim]$C_2H_5SO_4$, [mmim]$(CH_3)_2PO_4$ and [mebupy]BF_4. Since some of the ionic liquids from Table 4.1 were either not suitable due to corrosion ([emim]I_3 and [bmim]I_3) or showed a too low aromatic/aliphatic selectivity, other ionic liquids must be selected for the separation of toluene from toluene/heptane mixtures. However, information in literature on specific properties of ionic liquids, such as miscibility with aromatic and/or aliphatic hydrocarbons, activity coefficients at infinite dilution or selectivities, is scarce and sometimes misleading, such as the values of the benzene/heptane selectivity with [hmim]PF_6, obtained with extraction (8.2) and calculated from the activity coefficients at infinite dilution (29.7), as can be seen in Table 4.1. Therefore, screening of suitable ionic liquids cannot be entirely based on literature data. Hence, the selection of suitable ionic liquids for the separation of aromatic and aliphatic hydrocarbons is partly speculative. Brennecke and Maginn [33] reported that halide containing IL's are certainly corrosive and Swatloski et al. [53] reported that HF formation is possible when using [bmim]PF_6. Therefore, ionic liquids with PF_6^- as anion were excluded.

The following imidazolium containing ionic liquids were selected: [Hmim] hydrogensulfate (H=hydrogen), [mmim] methylsulfate (If reference [28] already would have been published when we made this selection, we would probably not have chosen this IL, but our measured toluene/heptane selectivity, 69.0, is quite different from the selectivity calculated by activity coefficients at infinite dilution, 16.4.), [mmim] dimethylphosphate, [emim] hydrogensulfate, [emim] methylsulfonate, [emim] ethylsulfate, [emim] diethylphosphate, [emim] tosylate, [emim] tetrafluoroborate, [bmim] tetrafluoroborate, [bmim] methylsulfate and [omim] tetrafluoroborate (Reference [23] was not yet published at the time when the selection was made. Otherwise, we would not have chosen this IL.) The length of the alkyl chain on the imidazolium cation was varied from none (hydrogen) to octyl. A shorter R-group is favourable for a high aromatic/aliphatic selectivity, but results in a decrease in the distribution coefficient [19]. This observation of a higher selectivity with shorter R-groups is in accordance with the findings of Hanke et al. [54]. The existence of π-electrons in orbitals above and below an aromatic ring results in a much stronger electrostatic field around an aromatic molecule compared to a saturated aliphatic molecule. Alkyl substitution on the aromatic ring may effectively disturb the molecular interaction in preferred orientation.

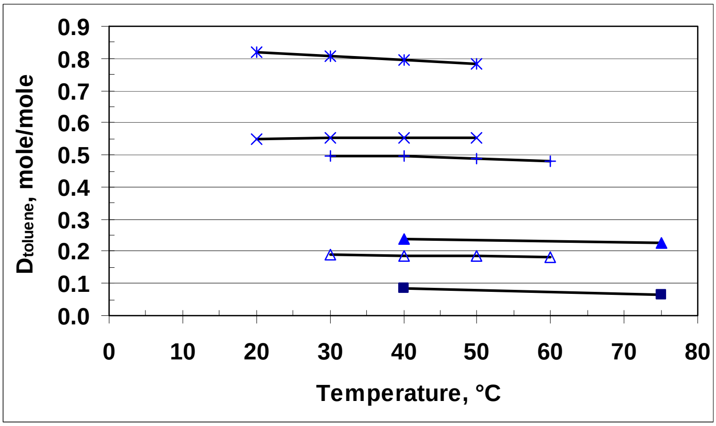


Figure 4.3 Distribution coefficients of toluene using several ionic liquids.
Data from[19], estimated from activity coefficients at infinite dilution: △ *[emim]$C_2H_5OSO_3$,*
+[mmim]$(CF_3SO_2)_2N$, x*[emim]$(CF_3SO_2)_2N$,* ∗*[bmim]$(CF_3SO_2)_2N$.*
Own LLE data at 5% toluene: ■*[mmim]CH_3OSO_3,* ▲ *[emim]$C_2H_5OSO_3$.*

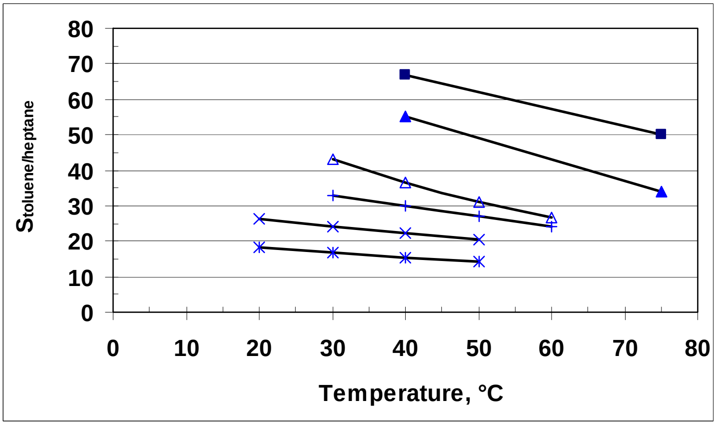


Figure 4.4. Selectivities of toluene/heptane using several ionic liquids.
Data from [19], estimated from activity coefficients at infinite dilution: △*[emim]$C_2H_5OSO_3$,*
+[mmim]$(CF_3SO_2)_2N$, x*[emim]$(CF_3SO_2)_2N$,* ∗*[bmim]$(CF_3SO_2)_2N$.*
Own LLE data at 5% toluene: ■*[mmim]CH_3OSO_3,* ▲ *[emim]$C_2H_5OSO_3$.*

Krummen et al. [19] have measured activity coefficients at infinite dilution (γ_i^∞) for several solutes in the ionic liquids [mmim]Tf_2N, [emim]Tf_2N, [bmim]Tf_2N and [emim] ethylsulfate. From these data, distribution coefficients ($k_i^\infty = 1/\gamma_i^\infty$) and selectivities ($S_{ij}^\infty = \gamma_i^\infty/\gamma_j^\infty$) of these solutes can be estimated. The ionic liquid [emim] ethylsulfate showed the highest selectivity (S = 36.4 at 313.15 K) for toluene/n-heptane, which is higher than the selectivity with sulfolane (S = 31). In Figure 4.3, the distribution coefficients of toluene and in Figure 4.4, the toluene/heptane selectivities with these ionic liquids at different temperatures are shown. The same trend is seen for other aromatic/aliphatic hydrocarbons tested: benzene/cyclohexane and benzene/hexane. If the same trend is occurring as with the $[Tf_2N]^-$-containing IL's, a higher selectivity and a lower capacity is expected using [mmim] methylsulfate or [mmim] dimethylphosphate than with [emim] ethylsulfate or [emim] diethylphosphate, because both the R-group of the cation and the alkyl chain in the anion is shorter. Also with the IL's [emim]BF_4, [bmim]BF_4 and [omim]BF_4 a decreasing selectivity and an increasing distribution coefficient is expected in this order.

Next to the imidazolium containing ionic liquids, butylpyridinium IL's were tested, because we expected a higher interaction between the aromatic ring of the hydrocarbons and the pyridinium ring of the IL. The pyridinium containing ionic liquids tested were [bupy] methylsulfate, [mebupy] methylsulfate and [mebupy] tetrafluoroborate [26]. Also, an isoquinolinium IL, ethylisoquinolinium ethylsulfate, was chosen, because of the conjugated aromatic rings of this compound, which could result in a high aromatic selectivity [55]. Beside imidazolium, pyridinium and isoquinolinium containing ionic liquids, one quaternary ammonium IL, methyl-tributylammonium methylsulfate, and a quaternary phosphonium IL, tetrabutylphosphonium bis[oxalato(2-)]borate, were chosen.

4.4 EXPERIMENTAL SECTION

4.4.1 CHEMICALS

The ionic liquids 1,3-dimethylimidazolium methylsulfate ([mmim]CH_3SO_4) (98%), 1,3-dimethylimidazolium dimethylphoshate ([mmim]$(CH_3)_2PO_4$) (>98%), 1-butyl-3-methylimidazolium methylsulfate ([bmim]CH_3SO_4) (98%) and 1-ethyl-3-methylimidazolium tosylate ([emim]$C_7H_7SO_3$) (98%) were purchased from Solvent Innovation. Sulfolane (>98%), diethylsulfate (>99%) and the ionic liquids 1-ethyl-3-methylimidazolium tetrafluoroborate ([emim]BF_4) (>97%), 1-octyl-3-methylimidazolium tetrafluoroborate ([omim]BF_4) (>97%) and 4-methyl-N-butylpyridinium tetrafluoroborate ([mebupy]BF_4) (>97%) were purchased from Fluka. Toluene (p.a., 99.9%), n-heptane (p.a., >99%), benzene (p.a., 99.7%), ethylbenzene (>99%), m-xylene (>99%), n-octane (>99%), n-hexane (p.a., 99%), n-pentane (>99%), 1-butanol (p.a., >99%), 1-methylimidazole (for synthesis, >99%) and the ionic liquids 1-butyl-3-methylimidazolium tetrafluoroborate ([bmim]BF_4), N-butylpyridinium methylsulfate ([bupy]CH_3SO_4), 3-methyl-N-butylpyridinium methylsulfate ([mebupy]CH_3SO_4) and tetrabutylphosphonium bis[oxalato(2-)]borate ($[(C_4H_9)_4P]C_4BO_8$) (purity: for synthesis) were purchased from Merck. The ionic liquids 1-methylimidazolium hydrogensulfate ([Hmim]HSO_4), 1-ethyl-3-methylimidazolium hydrogensulfate ([emim]HSO_4), 1-ethyl-3-methyl-imidazolium methylsulfonate ([emim]CH_3SO_3), 1-ethyl-3-methylimidazolium diethylphosphate ([emim]$(C_2H_5)_2PO_4$) and methyl-tributylammonium methylsulfate ([CH_3-N-$(C_4H_9)_3$]CH_3SO_4 or MTBS) (purity >95%) were obtained from BASF. Acetone (p.a., >99.5%) was purchased from Acros and acetone-d_6, (99.5 atom% D) was purchased from Aldrich.

4.4.2 PREPARATION OF [EMIM] ETHYLSULFATE AND ETHYL-ISOQUINOLINIUM ETHYLSULFATE

The ionic liquid 1-ethyl-3-methylimidazolium ethylsulfate was prepared from 1-methylimidazole (Merck-Schuchardt, >99%) and diethylsulfate (Fluka, >99%) according to the procedure described by Holbrey et al. [56]. Diethyl sulfate (116 mL) was added drop-wise to a mixture of 1-methylimidazole (70 mL) in toluene (400 mL), cooled in an ice-bath under argon. After addition of the diethylsulfate, the reaction mixture was stirred at room temperature for five hours. Formation of two phases occurred: the toluene solution and a denser ionic liquid phase. The upper, organic phase was decanted and the lower, ionic liquid phase, was three times washed with toluene (total amount of toluene: 200 mL), dried at 75 °C under reduced pressure (0 bar) in a rotary evaporator and finally in a vacuum exsiccator to remove any residual organic solvents.

Samples of this ionic liquid were dissolved in acetone-d_6 and analysed by ^1H NMR (Varian 300 MHz).

The ionic liquid 1-ethyl-isoquinolinium ethylsulfate ([C_9H_7N-C_2H_5]$C_2H_5SO_4$) was prepared from isoquinoline (Fluka, >97%) and diethylsulfate according to the procedure described by Willems and Nys, but with toluene as the solvent instead of benzene [57].

4.4.3 EXPERIMENTAL PROCEDURE

Before each experiment, the ionic liquids were dried at 75 °C under reduced pressure in a rotary evaporator (Büchi Rotavapor R-200), because all ionic liquids are very hygroscopic and the presence of water can change their properties. Liquid-liquid extraction experiments were carried out in jacketed vessels with a volume of approximately 70 mL. The top of the vessel was closed using a PVC cover, through which a stirrer shaft passed. Two stainless steel propellers were used with an electronic stirrer (Heidolph RZR 2051 control). The vessels were jacketed to circulate water from a water bath (Julabo F32-MW) in order to maintain the temperature inside the vessels at either 40 or 75 °C ± 0.1 °C.

For each experiment, 20 mL of the ionic liquid and 10 mL of a toluene/n-heptane mixture were placed into the vessel. The temperature and the ratio of toluene in n-heptane were varied. We established that equilibrium was reached within 5 minutes. This was done for one IL by taking samples after 5, 10, 15, 30, 65 and 120 minutes and analysing them. In order to avoid this procedure for the other ternary mixtures, the extraction experiments were continued for 20 minutes. After stirring, the two phases were allowed to settle for about one hour.

4.4.4 ANALYSIS

Samples (approximately 0.5 mL) were taken from both phases. 1-Butanol (0.5 mL) was added to each sample to avoid phase splitting and to maintain a homogeneous mixture, and n-hexane was added to samples as an internal standard for the GC analysis, 0.2 mL to the raffinate phase and 0.1 mL to the extract phase samples. For the analysis of n-hexane from the experiments with mixtures of benzene+n-hexane, acetone was used as solvent instead of 1-butanol and n-pentane was used as the internal standard.

The concentrations of toluene and n-heptane in the samples were analysed by a Varian CP-3800 gas chromatograph with an Alltech Econo-Cap EC-Wax column (30 m x 0.32 mm x 0.25 μm) and with a Varian 8200 AutoSampler. Because the ionic liquid has no vapour pressure, it cannot be analysed by GC. The IL was collected in a pre-column in order not to disrupt the analysis. The GC program parameters for the analyses are:

Column oven	35 °C (1 min) → 115 °C (40 °C/min); benzene/hexane (1.2 min)→ 70 °C
Carrier gas	hydrogen; column flow 3 mL/min
Injector	250 °C; split ratio 1:100 raffinate and 1:25 extract phase
Detector	FID; 250 °C

In a ternary mixture, one has to analyse only two components and the third one, the IL, can then be determined by subtracting the sum of the measured molar fractions of the aromatic and the aliphatic hydrocarbons from a value of 1.

Measurements were carried out in duplicate in order to increase the accuracy in the measurements. Each sample was injected in triple. The deviation in the calibration curves with a maximum of 1% and a possible contamination of the gas chromatograph can cause a variance in the mole fractions (estimated on 1%). The averages of the two measurements were used in our results. As a consequence, the errors in the determination of the distribution coefficients and the selectivities are normally around 2 and 5%, respectively. However, when the heptane concentrations in the extract phase are very small with an error of 0.001 mole fraction, especially with [mmim]CH_3SO_4, the error in the selectivity can be as high as 10%, as is shown in Figure 4.13.

4.5 RESULTS AND DISCUSSION

4.5.1 SCREENING EXPERIMENTS WITH TOLUENE/HEPTANE MIXTURES AT 40 AND 75 °C

Liquid-liquid equilibrium data were collected for mixtures of 5, 10 and 15 v/v% toluene in heptane at 40 and 75 °C with the selected ionic liquids. The distribution coefficient, D_i, is directly calculated from the ratio of the mole fractions in the extract and raffinate phases at equilibrium. The distribution coefficients of toluene and heptane are defined by the ratio of the mole fractions of the solute in the extract (IL) phase and in the raffinate (organic) phase, according to:

$$D_{tol} = C^{IL}_{tol}/C^{org}_{tol} \quad \text{and} \quad D_{hept} = C^{IL}_{hept}/C^{org}_{hept} \qquad (4.1)$$

The selectivity, $S_{tol/hept}$, of toluene/heptane is defined as the ratio of the distribution coefficients of toluene and heptane:

$$S_{tol/hept} = D_{tol}/D_{hept} = (C^{IL}_{tol}/C^{org}_{tol})/(C^{IL}_{hept}/C^{org}_{hept}) \qquad (4.2)$$

The results of the experiments with 5, 10 and 15(v/v)% toluene in the feed at 40 °C are shown in Figures 4.5, 4.6 and 4.7 and the results at 75 °C in Figures 4.8, 4.9 and 4.10. In these figures, the toluene/heptane selectivity is shown as function of the distribution coefficient of toluene. Some of the ionic liquids used are not liquid at 40 °C and were tested at 75 °C only: [emim] tosylate (m.p.~ 48 °C), [1-ethyl-isoquinolinium] ethylsulfate (m.p.~88 °C), [tetrabutylphosphonium] bis[oxalato(2-)]borate] (m.p. 43 °C), and [methyl-tributylammonium] methylsulfate (m.p. 62 °C).

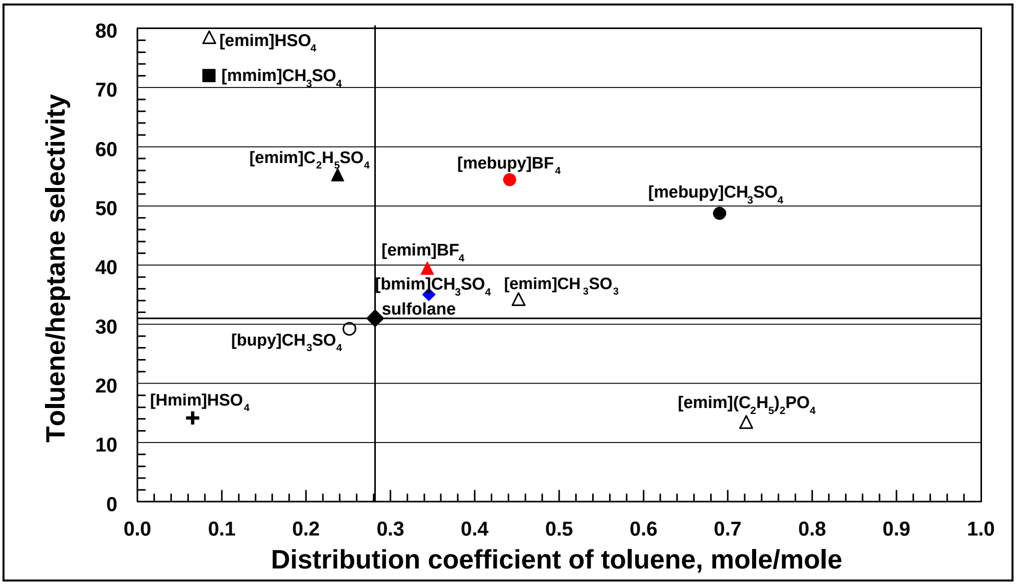


Figure 4.5. Toluene/heptane separation with ionic liquids, 5(v/v)% toluene, T = 40 °C

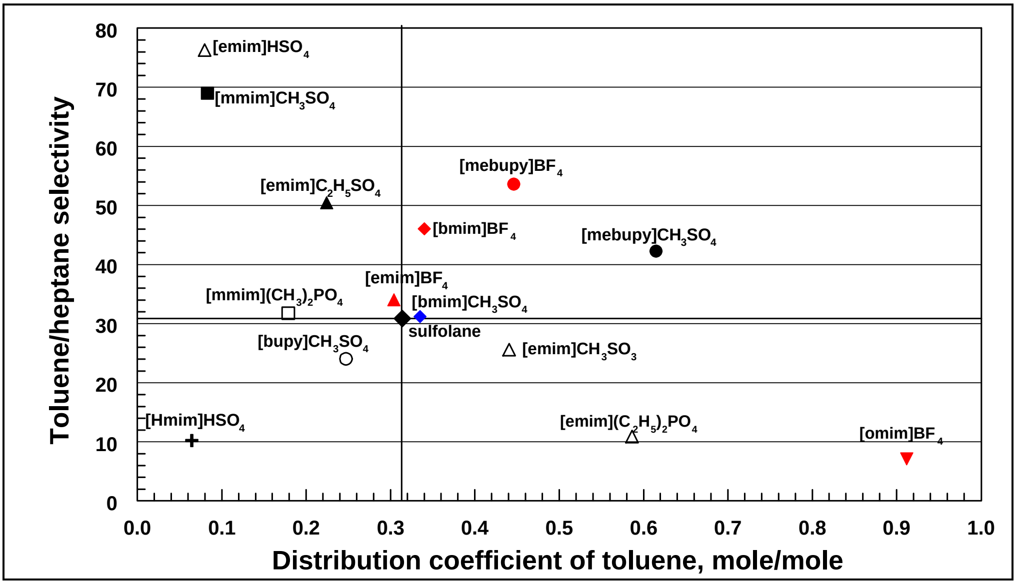


Figure 4.6. Toluene/heptane separation with ionic liquids, 10 (v/v)% toluene, T = 40 °C.

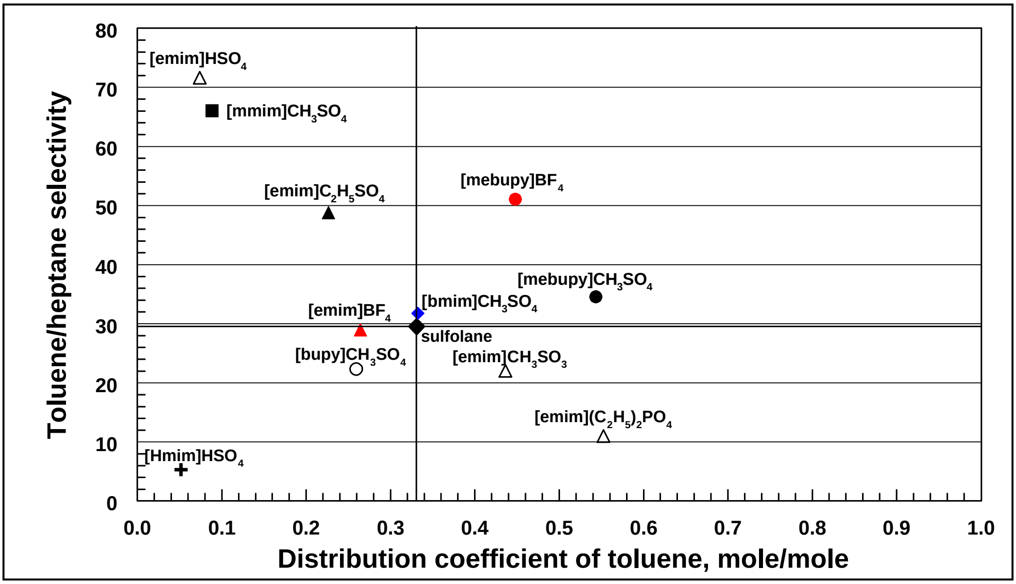


Figure 4.7. Toluene/heptane separation with ionic liquids, 15(v/v)% toluene, T = 40 °C

Comparing the results at 40 °C with the different toluene contents of the mixture, it is apparent that the ionic liquids [mebupy]BF$_4$, [mebupy]CH$_3$SO$_4$, [bmim]BF$_4$ and [bmim]CH$_3$SO$_4$ show both a higher toluene distribution coefficient and a higher toluene/heptane selectivity than sulfolane. The toluene distribution coefficients and the toluene/heptane selectivities with [mebupy]BF_4 and [bmim]CH_3SO_4 remain at about the same level. With the ionic liquid [mebupy]CH_3SO_4 both the toluene distribution coefficient and the toluene/heptane selectivity decease with increasing initial toluene concentration. At 5 (v/v)% toluene in the initial mixture, also [emim]BF_4 and [emim]CH_3SO_3 have a higher toluene distribution coefficient and a higher toluene/heptane selectivity than sulfolane, but not at higher toluene concentrations. With [emim]BF_4, the heptane distribution coefficient remains at about the same level, while the toluene distribution coefficient decreases with increasing toluene content, resulting in a lower toluene/heptane selectivity. With [emim]CH_3SO_3, the heptane distribution coefficient increases with increasing toluene content and the toluene distribution coefficient decreases only slightly with increasing toluene content in the feed. This causes the decrease in selectivity for [emim]CH_3SO_3 at higher toluene concentrations. With 10 (v/v)% toluene in the feed mixture, also [bmim]BF_4 showed a higher toluene distribution coefficient and an higher toluene/heptane selectivity than sulfolane.

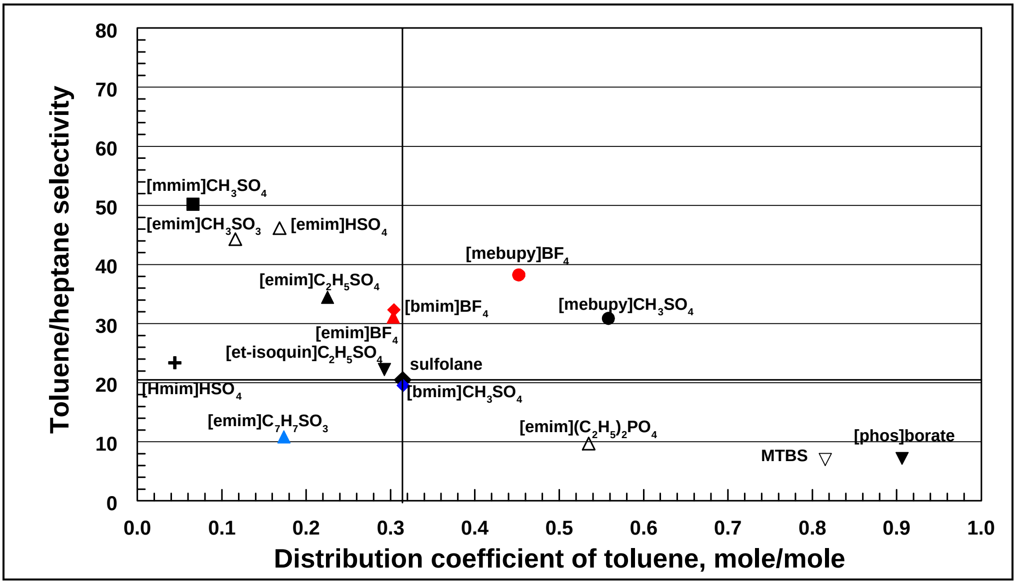


Figure 4.8. Toluene/heptane separation with ionic liquids, 5(v/v)% toluene, T = 75 °C

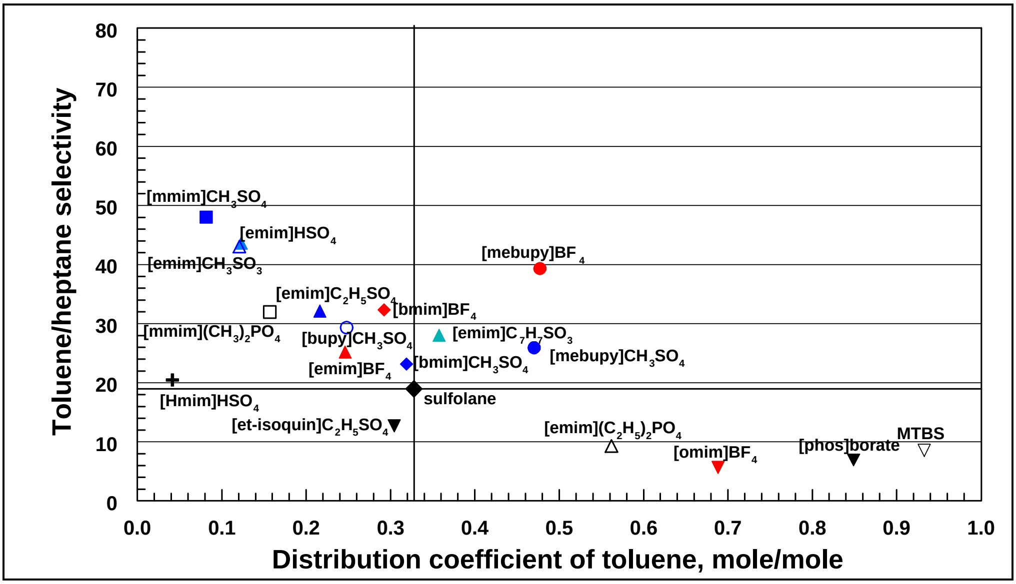


Figure 4.9. Toluene/heptane separation with ionic liquids, 10(v/v)% toluene, T = 75 °C

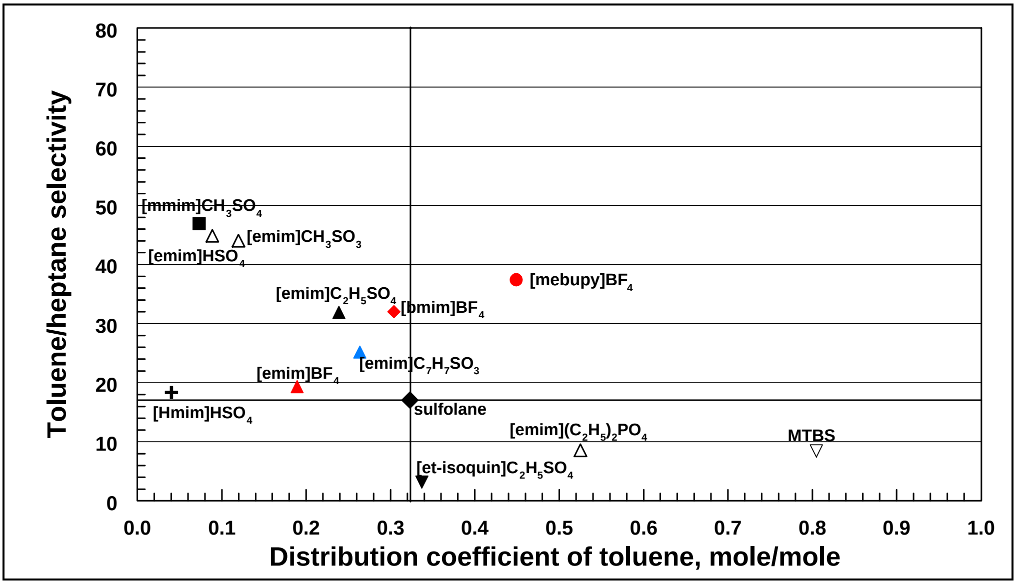


Figure 4.10. Toluene/heptane separation with ionic liquids, 15(v/v)% toluene, T = 75 °C

Only at 10(v/v)% toluene in the initial mixture, the ionic liquid [emim] tosylate shows both a higher toluene distribution coefficient and a higher toluene/heptane selectivity than sulfolane.

At 75 °C, the distribution coefficients of toluene with most of the ionic liquids tested remain at about the same level or are slightly lower compared to those at 40 °C. The interaction of the ionic liquid with the aromatic toluene is mainly π-ionic nature, which is not very dependent on temperature [54]. However, the toluene distribution coefficients with [emim]CH_3SO_3 decrease dramatically with temperature: from 0.44 to 0.12. This is seen at all toluene concentrations tested. Surprisingly, the selectivity with [emim]CH_3SO_3 increases with temperature, from 25.6 to 43.1. Hanke et al [54] reported differences in interaction of benzene and the ionic liquids [mmim]Cl and [mmim]PF_6, indicating that the nature of the anion does have an effect on the interaction. The interaction of the methylsulfonate groups with toluene is apparently less at higher temperatures. For [mebupy]CH_3SO_4 and also for the three BF_4^- containing imidazolium ionic liquids, the toluene distribution coefficients decrease about 15 – 25% with increasing temperature. As the distribution coefficients of heptane increase with temperature in most cases, the toluene/heptane selectivities with the ionic liquids tested will decrease with temperature.

Comparing the results at 40 °C with the different toluene contents of the mixture, it is apparent that the ionic liquids [mebupy]BF_4, [bmim]BF_4 and [mebupy]CH_3SO_4 show both a higher toluene distribution coefficient and a higher toluene/heptane selectivity than sulfolane. Also at 75 °C, the ionic liquids [mebupy]BF_4 and [mebupy]CH_3SO_4, as well as [emim] tosylate at an initial toluene concentration of 10 (v/v)% show both a higher toluene distribution coefficient and a higher toluene/heptane selectivity than sulfolane.

4.5.2 EFFECT OF ALKYL CHAIN LENGTH

Comparison of the experiments with ionic liquids [emim] ethylsulfate and [mmim] methylsulfate and with [emim] diethylphosphate and [mmim] dimethylphosphate at 10 (v/v)% toluene (Figures 4.6 and 4.9) lead to the conclusion that a shorter alkyl chain on the imidazolium ion is favourable for higher aromatic/aliphatic selectivities, but results to lower distribution coefficients, as expected from the data of Krummen et al. [19] (Figures 4.3 and 4.4). The same observation holds for [emim]BF_4 and [omim]BF_4. However, if the results of [emim]BF_4 and [bmim]BF_4 are compared, the unexpected conclusion is that a butyl chain on the imidazolium ion with BF_4^- as anion gives both a higher distribution coefficient of toluene and a higher toluene/heptane selectivity.

Apparently, the absence of a alkyl chain on the imidazolium group leads to a lower selectivity as can be seen by comparing the results of [Hmim]HSO_4 and [emim]HSO_4 at 10(v/v)% toluene (Figures 4.6 and 4.9) (40 °C: $S_{tol/hept} = 10.2$ and $S_{tol/hept} = 76.3$; 75 °C: $S_{tol/hept} = 20.5$ and $S_{tol/hept} = 43.6$ respectively). The same observation can be made for the butylpyridinium ion at 40 °C, as the methyl group has a favourable effect on both the distribution coefficient of toluene and the toluene/heptane selectivity, as can be seen by comparing [bupy] methylsulfate ($D_{tol} = 0.25$, $S_{tol/hept} = 24.0$) and [mebupy] methylsulfate ($D_{tol} = 0.61$, $S_{tol/hept} = 42.3$). However, at 75 °C, the toluene distribution coefficient with [mebupy]CH_3SO_4 is higher than with [bupy]CH_3SO_4 (0.47 and 0.25), but the toluene/heptane selectivity is slightly lower (25.9 and 29.3).

A shorter alkyl group on the imidazolium cation of the ionic liquids generally results in a more aromatic character of the ionic liquid and, hence, to a higher toluene distribution coefficient and to a higher toluene/heptane selectivity.

4.5.3 EFFECT OF THE CATION

Ionic liquids containing the methyl-N-butylpyridinium cation have a more aromatic character than the imidazolium based ionic liquids and this results not only in a high toluene/heptane selectivity, but also in a high distribution coefficient of toluene. The toluene distribution coefficients at 10(v/v)% toluene in the initial mixture of the ionic liquids [mebupy]BF_4 and [mebupy]CH_3SO_4 at 40 °C are 0.44 and 0.61, and the toluene/heptane selectivities 53 and 42, respectively (Figure 4.6). Also at 75 °C, both the toluene distribution coefficients (0.48 and 0.47) and the selectivities (39 and 26) with these two ionic liquids are higher than those with sulfolane (Figure 4.9).

The quaternary phosphonium and ammonium ionic liquids show a low toluene/heptane selectivity (7 and 9, respectively) and relatively high toluene distribution coefficients (0.85 and 0.93). Also, the isoquinolinium ionic liquid shows a low toluene/heptane selectivity of 13. The experiments with this ionic liquid were carried out at 90 °C, because its melting point was about 88 °C. Although a higher selectivity would be expected, due to the conjugated aromatic core of the isoquinolinium cation [55], the toluene distribution coefficient with the isoquinolinium containing IL is 0.30, slightly lower than that with sulfolane (0.33) at 75 °C.

With an aromatic cation, such as pyridinium, both the toluene distribution coefficient and the toluene/heptane selectivity are higher than with other IL's.

4.5.4 EFFECT OF THE ANION

The nature of the anion has also an important effect. Hanke et al. [54] reported that the solute–solvent interaction of benzene with the chloride ion of the ionic liquid [mmim]Cl is much stronger than that with the [mmim] cation and that this interaction is dominated by the electrostatic terms. Also, a difference in interaction with benzene was found between [mmim]Cl and [mmim]PF_6.

With the anion HSO_4^-, the toluene distribution coefficient is very low, around 0.07 at 40 °C with 10% toluene, for both [Hmim]HSO_4 and [emim]HSO_4. At 75 °C, the distribution coefficients are 0.041 and 0.123, respectively. The distribution coefficients of both toluene and heptane with [emim] containing ionic liquids increase in the following order at 40 °C: $HSO_4^- < C_2H_5SO_4^- < BF_4^- < CH_3SO_3^- < (C_2H_5)_2PO_4^-$. Since the solubility of heptane increases more in this series than that of toluene, the toluene/heptane selectivity decreases in this order. At 75 °C, the order in the distribution coefficient with the [emim] containing ionic liquids is: $HSO_4^- \approx CH_3SO_3^- < C_2H_5SO_4^- < BF_4^- < C_7H_7SO_3^- < (C_2H_5)_2PO_4^-$. The toluene/heptane selectivity at 75 °C decreases in the following order: HSO_4^- ≈ $CH_3SO_3^-$> $C_2H_5SO_4^-$>$C_7H_7SO_3^-$>BF_4^->$(C_2H_5)_2PO_4^-$.

With tetrafluoroborate as anion at 40 °C, both the toluene distribution coefficients (with 10(v/v)% toluene in the initial mixture: 0.30 for [emim]BF_4, 0.38 for [bmim]BF_4 and 0.44 for [mebupy]BF_4) and the toluene/heptane selectivities are high (34, 49 and 53 respectively). At 75 °C, also relatively high distribution coefficients (0.25, 0.29 and 0.48) and selectivities are observed (25, 32 and 39 respectively). The same effect of high selectivities with BF_4^- containing compounds is reported for olefin/paraffin separations with silver salts. With $AgBF_4$, much higher separation factors are achieved than with other Ag-salts, such as ClO_4^-, $CF_3SO_3^-$, $CF_3CO_2^-$, NO_3^- [58,59]. Although the toluene distribution coefficient for [omim]BF_4 is also high: 0.91 at 40 °C and 0.69 at 75 °C, the toluene/heptane selectivity is, however, low: 7.1 and 5.7, due to the long alkyl chain on the imidazolium group. The only [emim] containing ionic liquid with both a higher toluene distribution coefficient and a higher toluene/heptane selectivity than with sulfolane is [emim] tosylate, but only with 10% toluene, probably caused by the aromatic character of the anion (toluene sulfonate), since all other ionic liquids with $[emim]^+$ as cation show lower toluene distribution coefficients than with sulfolane.

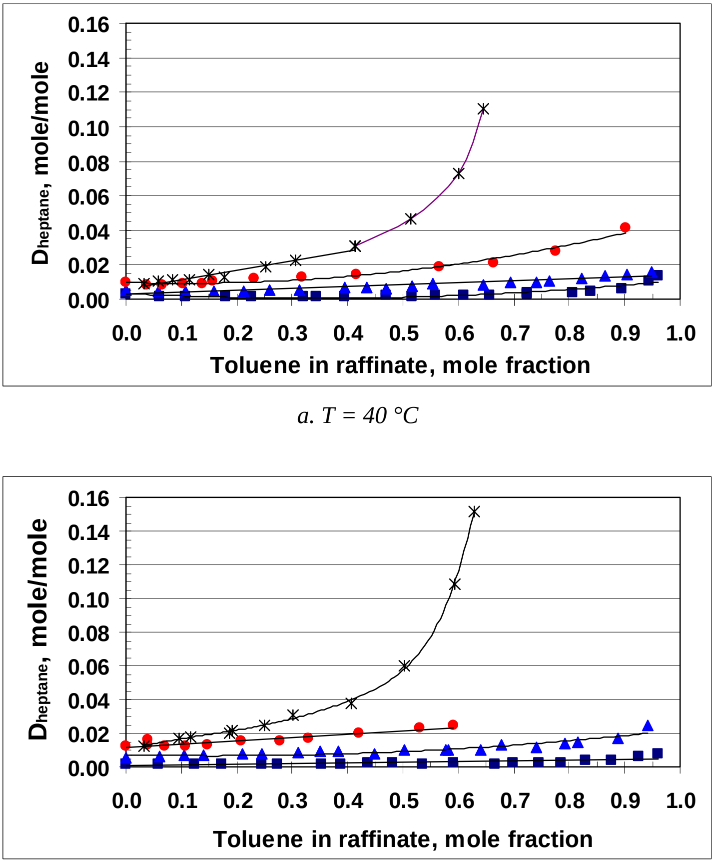
IL's with HSO_4^--anions show a low toluene distribution coefficient and IL's with a BF_4^--anion usually show a relatively high toluene distribution coefficient.

4.5.5 FINAL SELECTION

Based on the initial screening results, further tests were carried out with the IL [mmim] methylsulfate, because it shows the highest toluene/heptane selectivity of all the ionic liquids tested. The ionic liquid [emim] ethylsulfate was selected in order to compare the results of this ionic liquid with [mmim] methylsulfate. Since the ionic liquid [mebupy]BF_4 shows at both temperatures a higher toluene distribution coefficient and a higher toluene/heptane selectivity than sulfolane, this ionic liquid was also selected. With these three ionic liquids, more detailed equilibrium experiments for the full concentration range of 0 – 100% toluene in heptane at 40 and 75 °C were carried out.

4.5.6 DETAILED SCREENING EXPERIMENTS OF [MMIM] METHYLSULFATE, [EMIM] ETHYLSULFATE AND [MEBUPY] TETRAFLUOROBORATE FOR VARIOUS TOLUENE/HEPTANE MIXTURES

From Figures 4.11a and b, it can be seen that the distribution coefficient of heptane with [mmim] methylsulfate is very low: from 0.0014 – 0.014 (40 °C) and from 0.0014 – 0.0075 (75 °C). Also with [emim] ethylsulfate, the heptane distribution coefficient is low at both temperatures: ranging from 0.0043 – 0.0160 (40 °C) and from 0.0057 – 0.025 (75 °C). The heptane distribution coefficient with [mebupy] BF_4 is slightly higher: from 0.0083 – 0.044 at 40 °C and from 0.0120 – 0.024 at 75 °C. The heptane distribution coefficient with sulfolane increases more with increasing toluene content than with the ionic liquids at both temperatures, from 0.0091 to 0.111 at 40 °C and from 0.0126 to 0.152 at 75 °C.

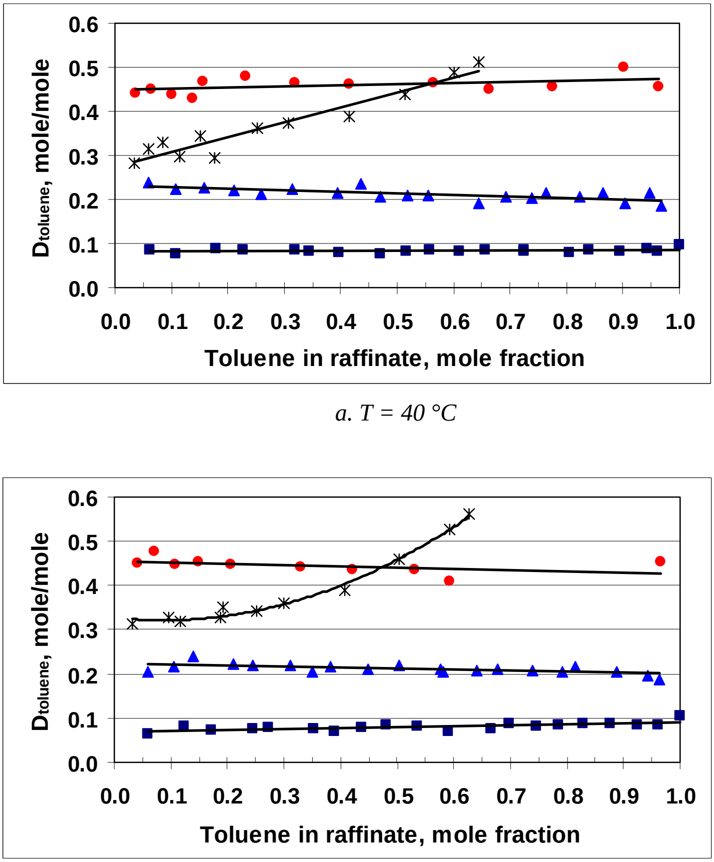


a. T = 40 °C

b. T = 75 °C

Figure 4.11. Distribution coefficients for heptane, ■[mmim]methylsulfate, ▲ [emim]ethylsulfate, ●[mebupy]BF$_4$, ∗ sulfolane

From Figures 4.12a and b, it can be seen that the distribution coefficient of toluene, using [emim] ethylsulfate as extractant, remains slightly above 0.2 over the entire concentration range for both 40 and 75 °C. The distribution coefficient of toluene with [mmim] methylsulfate is about 0.08 over the entire concentration range, also for both temperatures. It is lower than with [emim] ethylsulfate, due to the shorter alkyl chain in the imidazolium cation, as expected from the data of Krummen et al. [19]. The distribution coefficient of toluene with [mebupy]BF$_4$ is about 0.46 over the entire concentration range at 40 °C and about 0.43 at 75 °C. The distribution coefficient of toluene with sulfolane decreased from 0.51 at 64 mole% toluene to 0.28 at 3 mole% toluene at 40 °C and from 0.56 at 63 mole% toluene to 0.32 at 3 mole% toluene at 75 °C.

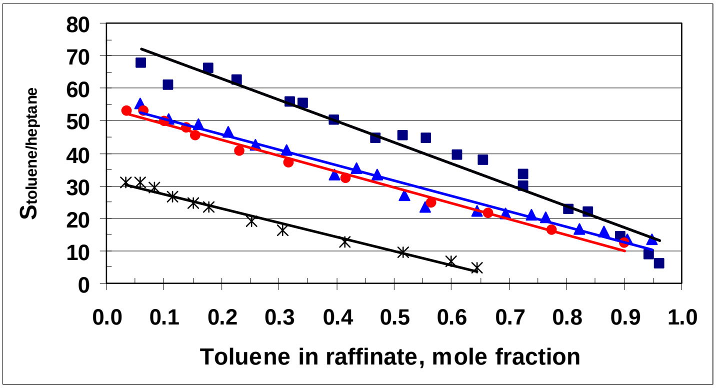


a. T = 40 °C

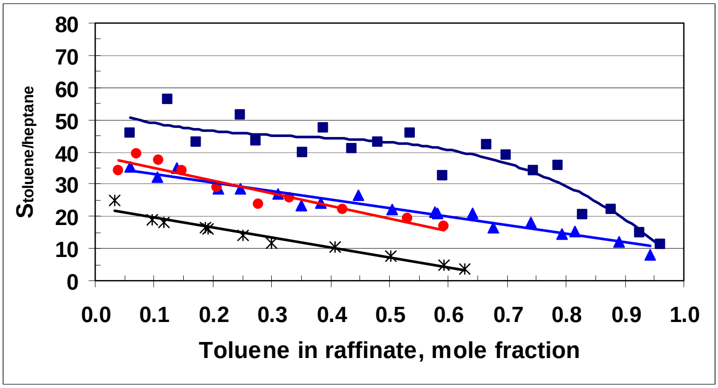
b. T = 75 °C

Figure 4.12. Distribution coefficients for toluene, ■[mmim]methylsulfate, ▲ [emim]ethylsulfate, ●[mebupy]BF_4, ∗ sulfolane

With [emim] ethylsulfate, the toluene/heptane selectivity at 40 °C increases from 13.4 to 55.3 with decreasing toluene content in the raffinate, from 95 to 6 mole% (Figure 4.13a). The toluene/heptane selectivity at 75 °C increases from 8 (95 mole% toluene in the raffinate) to 35 (6 mole% toluene in the raffinate) (Figure 4.13b). The selectivity at 75 °C is lower than at 40 °C, mainly due to higher concentrations of heptane in the extract (IL phase), resulting in higher distribution coefficients of heptane (0.0043 at 40 °C and 0.0057 at 75 °C with 6 mole% toluene), while the distribution coefficient of toluene remains about constant: 0.21 at 40 °C and 0.22 at 75 °C. The higher distribution coefficient of heptane at a higher temperature is in accordance with the findings of Krummen et al. [19]. From his data, distribution coefficients of heptane with [emim] ethylsulfate can be estimated: 0.0051 at 40 °C and 0.0069 at 60 °C. With [mmim] methylsulfate, which has both a shorter alkyl chain on the imidazolium ring and a shorter alkyl group in the anion, the selectivity is considerably higher than using [emim] ethylsulfate, which is according to our expectations. The selectivities obtained with this IL range from 6 (96 mole% toluene in the raffinate) to 67.8 (6 mole% toluene in the raffinate) at 40 °C and from 11.4 to 55 at 75 °C (Figure 4.13a and b).



a. T = 40 °C



b. T = 75 °C

*Figure 4.13. Toluene/heptane selectivities, ■[mmim]methylsulfate, ▲ [emim]ethylsulfate, ●[mebupy]BF$_4$, * sulfolane*

The data with [mmim] methylsulfate are quite scattered, because the analysis of heptane in the extract phase proved to be very difficult as the concentrations were extremely low: between 0.03 and 0.14 mole% at both temperatures. For high toluene concentrations, the selectivity with [mmim]methylsulfate at 75 °C increases at decreasing toluene content in the feed, but it levels off at concentrations of 65 mole% and lower. This is caused by the distribution coefficient of heptane, which increases only slightly from 0.0014 to 0.0018 from 6 mole% to 65 mole% toluene in the raffinate and increases from 0.0018 to 0.0075 for 65 mole% to 96 mole% toluene in the raffinate. The distribution coefficients of toluene remained at about the same level of 0.08 over the entire concentration range. With [mebupy]BF_4, the toluene/heptane selectivity increases from 12 to 53 (90 mole% to 4 mole% toluene in the raffinate) at 40 °C and from 17 to 39 (59 to 4 mole% toluene in the raffinate) at 75 °C.

Both the distribution coefficients of toluene and the toluene/heptane selectivities with [mmim] methylsulfate, [emim] ethylsulfate and with [mebupy]BF_4 in our extraction experiments are higher than the values estimated by respectively Kato [28], Krummen [19] and Heintz [26] from activity coefficients at infinite dilution. The distribution coefficients of toluene with [mmim] methylsulfate at 40 °C are 0.085 (exp. at 5% toluene in the feed) and 0.06 (act. coeff.), with [emim] ethylsulfate 0.214 and 0.187, and with [mebupy]BF_4 0.46 and 0.33, respectively. We measured a toluene/heptane selectivity at 40 °C of 69.0 at 5 v/v% toluene in the feed with [mmim] methylsulfate, compared to 16.4 from the data of Kato and Gmehling [28] and a selectivity of 55.3 at 5 v/v% toluene in the feed with [emim] ethylsulfate, compared to 36.4 from the data of Krummen et al. With [mebupy]BF_4, the experimental and estimated toluene/heptane selectivities at 40 °C are 53.1 and 32.8. The differences in these values are probably due to the different methods used to obtain the data, because Kato, Krummen and Heintz used VLE measurements to obtain activity coefficients at infinite dilution and estimated the capacity and selectivity from the activity coefficients. We have used LLE experiments and calculated the distribution coefficients and selectivities directly from the concentrations of the components in the extract and raffinate phases with formulas (4.1) and (4.2). Differences in distribution coefficient and selectivity, determined by different methods and authors, can also be seen from the data in Table 4.1, notably with the ionic liquids [omim]Cl, [emim]Tf_2N and [hmim]PF_6.

The distribution coefficients obtained with [mmim] methylsulfate and [emim] ethylsulfate are lower than with sulfolane. However, with [mebupy]BF_4, the distribution coefficient is higher than for sulfolane for concentrations less than 60 mole% toluene at 40 °C and less than 40 mole% at 75 °C, as can be seen in Figures 4.12a and b. The toluene/heptane selectivities with these IL's are a factor of 2 – 3 higher than those with sulfolane. The toluene/heptane selectivity with sulfolane as extractant increases from 4.6 (64 mole% toluene in the raffinate) to 31 (3 mole% toluene in the raffinate) at 40 °C and from 3.7 (63 mole% toluene) to 19 (10 mole% toluene) at 75 °C, as can be seen in Figure 4.13 a and b. A higher distribution coefficient requires a lower solvent to feed ratio and a higher selectivity means a purer product and less extraction of aliphatics.

4.5.7 TESTS WITH OTHER AROMATIC/ALIPHATIC MIXTURES

With [mebupy]BF_4, which showed of all ionic liquids tested the best combination of a high toluene distribution coefficient and a high toluene/heptane selectivity, further extraction tests with benzene/n-hexane, ethylbenzene/n-octane and m-xylene/n-octane were carried out at 40 and 75 °C (60 °C for benzene/n-hexane, because of the low boiling point of hexane, 69 °C) with initial aromatic compound concentrations in the aliphatic compound of 5, 10, 15, 30, 45 and 60 v/v%. The results are shown in Figures 4.14a and b (distribution coefficients of the alkanes at two temperatures), Figures 4.15a and b (distribution coefficients of the aromatics at both temperatures) and Figures 4.16a and b (aromatic/aliphatic selectivities at both temperatures). In Table 4.2, the distribution coefficients and the selectivities from literature data [2,3,26], estimated from activity coefficients at infinite dilution, and our experimental data at an initial aromatic concentration of 5v/v%, and literature data with sulfolane at 25 °C are compared for the same combinations. The activity coefficients are determined at 40 and 70 °C and our experiments were carried out at 40 and 75 °C, except the benzene/hexane experiments, which were carried out at 40 and 60 °C, because of the low boiling point of hexane, 69 °C.

Comparing the distribution coefficients for the aliphatic hydrocarbons, it can be concluded that the distribution coefficients estimated from the activity coefficients at infinite dilution are in most cases higher than our experimental data. The differences can be up to 40%. On the other hand, the estimated distribution coefficients for the aromatic compounds are in all cases much lower than our experimental data. Therefore, it is not surprising that the experimental selectivities are then also much higher than the estimated ones from activity coefficients.

From Table 4.2 and Figures 4.14a and b, it is apparent that the distribution coefficients for the aliphatic hydrocarbons decrease with increasing tail length. The distribution coefficients for n-octane with either ethylbenzene or m-xylene are at the same level, as can be expected. The distribution coefficients for the aliphatic hydrocarbons increase linearly with increasing aromatic concentration in the raffinate phase up to a concentration of about 65 mole% (Figure 4.14a, 40 °C). Above an aromatic concentration in the raffinate of around 65 mole%, the heptane distribution coefficient increase is steeper. The same trend can be seen with the heptane distribution coefficient with the ionic liquids [mmim] methylsulfate and [emim] ethylsulfate (Figures 4.11a and b). The heptane distribution coefficient with sulfolane increases linearly with increasing toluene concentration in the raffinate up to 40 mole%. After 40 mole% the increase is steeper. At higher temperatures, the distribution coefficients for the aliphatic hydrocarbons are higher, both the estimated ones as our experimental ones.

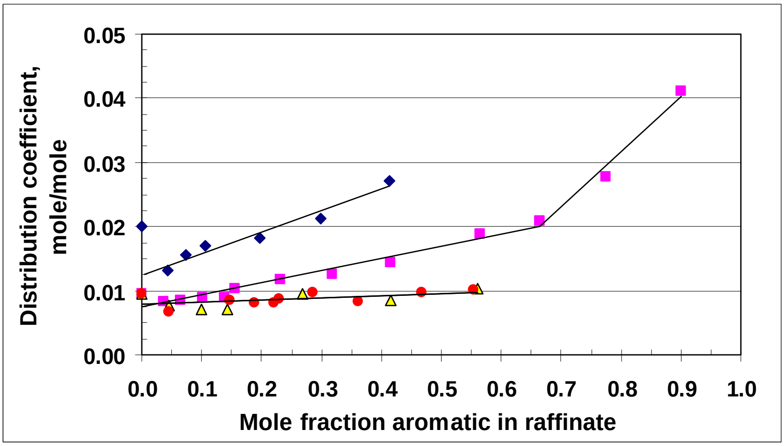
From Table 4.2, it is also clear that the estimated distribution coefficients from activity coefficients for the aromatic compounds hardly change with temperature. In our experiments, the distribution coefficients at higher temperatures are generally lower, with the exception of the distribution coefficient of toluene.

Table 4.2. Distribution coefficients and selectivities with [mebupy]BF_4 and sulfolane (*T = 60 °C)

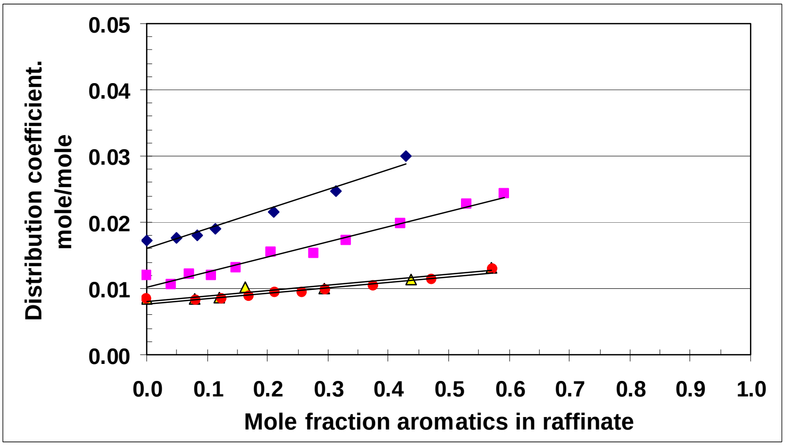
	T = 40 °C		T = 70 °C	T = 75 °C	T = 25 °C
	Data from [26]	Exp. 5% arom.	Data from [26]	Exp. 5% arom.	Sulfolane data [2,3]
Hexane	0.0165	0.0132	0.0183*	0.0177*	0.0162
Heptane	0.0116	0.0083	0.0137	0.0107	0.0143
Octane	0.0077	0.0078	0.0096	0.0084	0.0084
Benzene	0.61	1.37	0.61*	1.26*	0.82
Toluene	0.38	0.44	0.37	0.46	0.41
Ethylbenzene	0.21	0.50	0.21	0.44	n.a.
m-Xylene	0.22	0.36	0.22	0.32	0.29
$S_{benz/hex}$	37	104	33*	71*	33
$S_{tol/hept}$	33	53	27	43	29
$S_{eb/oct}$	27	65	22	52	n.a.
$S_{mx/oct}$	29	46	23	39	35

It can be seen from Table 4.2 that the estimated distribution coefficients for the aromatic compounds decrease with increasing alkyl chain length on the benzene ring. In Figures 4.15a and b, the same general trend can be seen for decreasing distribution coefficients of the aromatic compounds. Also, hardly any differences in distribution coefficients can be detected for ethylbenzene and m-xylene, at least at aromatic concentrations in the raffinate phase above around 25 mole%. At lower concentrations of the aromatic compound in the raffinate, the distribution coefficients of ethylbenzene and m-xylene are increasing and approaching or even surpassing that of toluene.

The measured aromatic/aliphatic selectivities are for all the combinations investigated much higher, up to a factor of almost 3, than the estimated ones from activity coefficients at infinite dilution. Since the distribution coefficients for the aliphatic hydrocarbons decrease and those for the aromatic compounds increase at decreasing aromatic concentration in the raffinate, it follows that the aromatic/aliphatic selectivities increase at lower aromatic content in the raffinate.

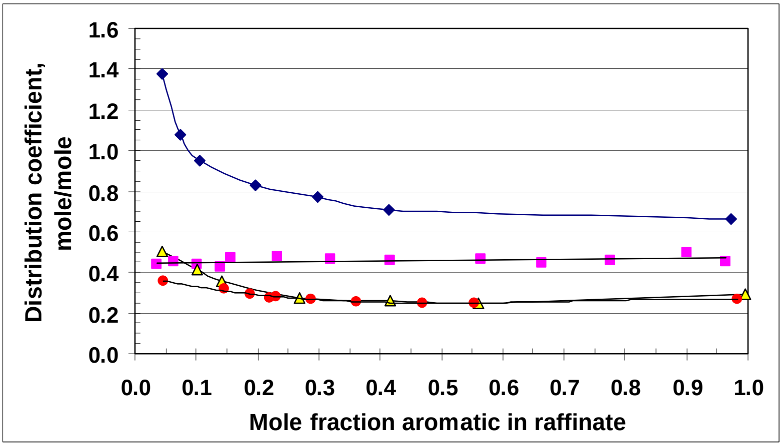


a. T = 40 °C

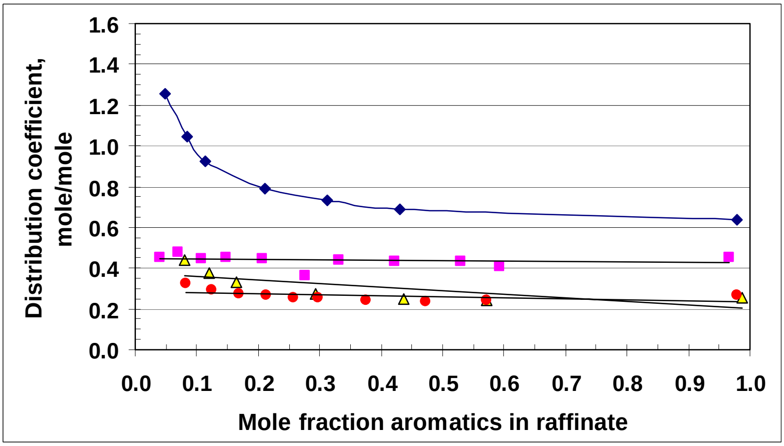


b. T = 75 °C

Figure 4.14. Distribution coefficients for aliphatic hydrocarbons with [mebupy]BF$_4$.
◆Benzene/hexane), ■Toluene/heptane, △Ethylbenzene/octane, ●M-Xylene/octane



a. T = 40 °C

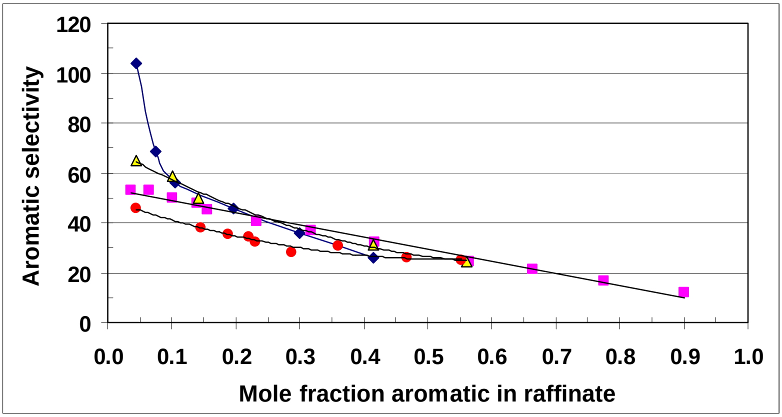


b. T = 75 °C

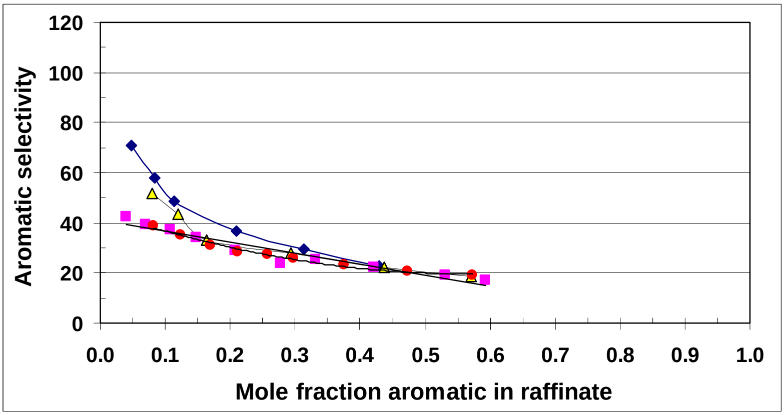
Figure 4.15. Distribution coefficients for aromatic hydrocarbons with [mebupy]BF$_4$
◆Benzene/hexane, ■Toluene/heptane, △Ethylbenzene/octane, ●M-Xylene/octane

Since the distribution coefficients for the aliphatic hydrocarbons decrease and those for the aromatic compounds increase at decreasing aromatic concentration in the raffinate, it follows that the aromatic/aliphatic selectivities increase at lower aromatic content in the raffinate. As the distribution coefficients of both the n-alkanes and alkylbenzenes decrease with increasing alkyl chain in a similar way, it follows that also the aromatic/aliphatic selectivities are quite similar, except at low aromatic concentrations, as can be seen in Figures 4.16a and b. The interaction between the ionic liquid [mebupy]BF$_4$ and the alkylbenzenes is most probably of a ionic-π nature. Therefore, this interaction is not much affected by the temperature, as can be seen from Figures 4.15a and b. This ionic interaction explains also the higher distribution coefficients for benzene, which is the most aromatic compound of the alkylbenzenes tested.

The selectivities with sulfolane for the same combinations of aromatic/aliphatic compounds are also in the same range of each other ($S_{benz/hex} = 33$, $S_{tol/hept} = 29$, $S_{m\text{-}x/oct} = 35$) [2,3], but much lower than those with the ionic liquid (Table 4.2).



a. T = 40 °C



b. T = 75 °C

Figure 4.16b. Aromatic/aliphatic selectivities with [mebupy]BF$_4$

◆*Benzene/hexane,* ■*Toluene/heptane,* △*Ethylbenzene/octane,* ●*M-Xylene/octane*

4.5.8 REGENERATION OF THE IONIC LIQUIDS

Evaporating the organic compounds from the extract in a rotary evaporator at 75 °C could easily regenerate the ionic liquids used. The results of the equilibrium experiments were obtained with regenerated ionic liquids. Visible inspection of the NMR spectra of both the original ionic liquid and the regenerated product showed no differences between the two samples. Furthermore, several ionic liquids ([mmim]CH_3SO_4, [emim]$C_2H_5SO_4$ and [mebupy]BF_4) were continuously heated in an oven at 150 °C during 7.5 weeks and no degradation of the ionic liquid could be detected. This confirms the assumption that the regeneration and recycling of the ionic liquids are indeed simple.

The presence of the ionic liquid [mebupy]BF_4 in the raffinate phase is very low, in the order of 0.3 mole% at 40 and 75 °C. The average concentration of the ionic liquid [emim] ethylsulfate in the raffinate phase, which also contains some toluene, is low: 0.9 mole% at 40 °C and 2.5 mole% at 75 °C. Removal of these ionic liquids from the raffinate phase is possible by using water, since these ionic liquids are water-soluble.

4.6 CONCLUSIONS

Ionic liquids are suitable for the separation of aromatic hydrocarbons from mixtures of aromatic and aliphatic hydrocarbons. The ionic liquids [bmim]BF_4, [mebupy]BF_4, [mebupy]CH_3SO_4, tested at 40 °C, and also [emim]$C_7H_7SO_3$, tested at 75 °C, are the most suitable ones for extraction of toluene from toluene/heptane mixtures. Both the equilibrium distribution coefficients of toluene and the toluene/heptane selectivities are higher with these ionic liquids than with sulfolane. The IL [mebupy]BF_4 showed the best combination of both a high toluene distribution coefficient and a high toluene/heptane selectivity.

The distribution coefficients of the aliphatic hydrocarbons decrease with increasing length of the compound and just as the distribution coefficients of the aromatic compounds decrease with an increasing alkyl chain on the benzene ring.

The aromatic/aliphatic selectivities (benzene/hexane, toluene/heptane, ethylbenzene/octane and m-xylene/octane) using [mebupy]BF_4 increase with decreasing concentration of the aromatic compound in the raffinate phase. The aromatic/aliphatic selectivities are all in the same range of each other. Therefore, the selection of toluene/heptane as a model for aromatic/aliphatic separations is a valid one.

Calculation of selectivities from activity coefficients at infinite dilution cannot be used as reliable data for an actual extraction, since they can differ up to a factor of four from each other. Therefore, more physical properties of ionic liquids must be determined in order to evaluate their suitability for industrial applications.

The toxicity data of ionic liquids are a pre-requisite for application of ionic liquids in industrial processes.

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5 EVALUATION OF CONTACTOR PERFORMANCE FOR EXTRACTION WITH IONIC LIQUIDS

5.1 ABSTRACT

The application of ionic liquids for separation processes is promising because of their non-volatile nature. This facilitates solvent recovery using techniques as simple as flash distillation or stripping. Promising equilibrium results with 4-methyl-N-butyl-pyridinium tetrafluoroborate ([mebupy]BF_4) initiated the present study on the scale-up of aromatics extraction in a pilot scale RDC column. The performances of sulfolane and [mebupy]BF_4 as the solvent were compared for the extractive removal of 10 wt% toluene from an n-heptane feed. For sulfolane, an S/F ratio of 4 and for [mebupy]BF_4 an S/F ratio of 2 was used. Both solvents were evaluated as the dispersed phase with the toluene/heptane feed as the continuous phase. Additionally, the effect of reversing the phases was also studied for the ionic liquid. The best performance was obtained with [mebupy]BF_4 as the dispersed phase at 40 °C and at the highest rotation speed used with the extraction experiments (643 rpm) in the pilot RDC column. At a flux of 10 m^3/m^2.hr, excellent hydrodynamic behaviour was observed and about three equilibrium stages were contained in the 1.80 m high active section of the column.

5.2 INTRODUCTION

The separation of aromatic hydrocarbons (benzene, toluene, ethylbenzene and xylenes) from C_4 – C_{10} aliphatic hydrocarbon mixtures is challenging since these hydrocarbons have boiling points in a close range and several combinations form azeotropes. Typical solvents for these processes are polar components such as sulfolane, N-methyl pyrrolidone (NMP), N-formyl morpholine (NFM) or ethylene glycols. Extraction of aromatics with ionic liquids is expected to require less process steps and less energy consumption than extraction with conventional solvents because ionic liquids have a negligible vapour pressure. Therefore, recovery of the ionic liquids can easily be achieved by flash distillation or stripping. Ionic liquids are organic salts that are liquid at low temperatures (<100 °C) and consist of cations based on methylimidazolium, N-butylpyridinium, quaternary ammonium or phosphonium ions and others, and anions such as PF_6^-, BF_4^-, alkylsulfates, alkylsulfonates, Cl^-, Br^-, NO_3^-, HSO_4^-, aluminium chloride, triflate ($CF_3SO_3^-$), bis(trifyl)imide ($(CF_3SO_2)_2N^-$), etc. In our previous research, the ionic liquid 4-methyl-N-butylpiridinium tetrafluoroborate ([mebupy]BF_4) was selected for further testing in our extraction pilot plant, because of both a higher toluene distribution coefficient

(0.44) and a higher toluene/heptane selectivity (53) at 10 wt% toluene at 40 °C compared to the commonly used solvent sulfolane: D_{tol}=0.31 and $S_{tol/hept}$=31. The extraction of toluene from mixtures of toluene and n-heptane is used as a model system for the aromatic/aliphatic separation.

In this study, the extraction with the ionic liquid [mebupy]BF_4 is compared to the benchmark extraction with sulfolane. As can be seen in table 5.1, the main difference between [mebupy]BF_4 and sulfolane is its considerable higher viscosity, which may hamper the extraction efficiency. Until this date, no pilot plant scale experiments with extraction with ionic liquids have been carried out. A rotating disk contactor (RDC) is used for the extraction experiments. The RDC was chosen because it is the most commonly used extractor in petrochemical processing. In the extraction process, hydrodynamics (drop size, hold-up and operational window) and mass transfer efficiency determine the column performance [1]. In this study, the hydrodynamics and mass transfer characteristics of the RDC for the extraction with [mebupy]BF_4 are compared with sulfolane. The investigated parameters concern the applied temperature, solvent to feed ratio, total flux, and the rotating speed of the RDC [2,3]. In these experiments, two configurations will be tested for the ionic liquid: one where the solvent stream is the continuous phase and the other where the solvent stream is the dispersed phase. The results of these experiments will show what the best configuration is.

Table 5.1. Physical properties of the chemicals used for the extraction experiments, NA = not available [4]

	Toluene	N-heptane	Sulfolane	[mebupy]BF_4
Molar mass (g/mol)	92.14	100.20	120.17	237.05
Melting point (°C)	-93	-90.6	27.4–27.8	NA
Boiling point (°C)	110.6	98.4	285	NA
Density (kg/m^3 at 20 °C)	867	684	1261	1184
Kin. viscosity (10^{-4} m^2/s at 20 °C)	0.681	0.598	8.17 (30 °C)	246.90
Dyn. Viscosity (10^{-3} Pa.s at 20 °C)	0.590	0.409	10.3 (30 °C)	293.33

5.3 EXPERIMENTAL SECTION

5.3.1 EXPERIMENTAL SETUP

In Figure 5.1, the process scheme of the pilot plant in shown. From storage tank T-1 and T-2, respectively the sulfolane or ionic liquid and the heptane/toluene phase are transported into the RDC. In the column countercurrent extraction occurs. The heavy phase, which is the solvent phase, will be transported to the top of the column and the lighter phase to the bottom of the column. The extract is collected in storage tank T-3 and the raffinate phase in storage tank T-4.

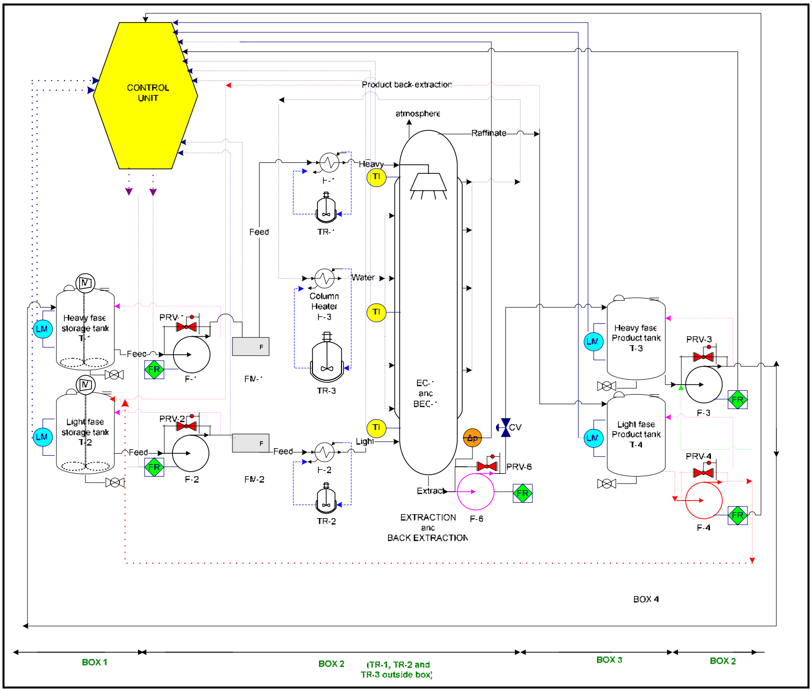

Figure 5.1. Process scheme of the pilot plant, T=storage tank, EC=extraction column, P=pump, TI=temperature indicator, LM=level meter, CV=control valve, PC=power (heat) control, H=heat exchanger, TR=thermo regulator, PVR=pressure relief valve.

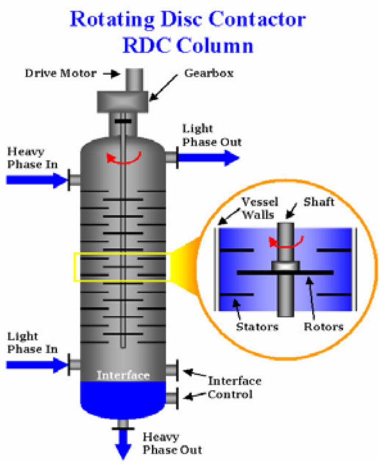

Figure 5.2. Schematic representation of a rotating disc column [5].

The pilot RDC extraction column is schematically shown in Figure 5.2. The column consisted of five jacketed glass segments of each 360 mm in length and an inside diameter 60 mm, with each eight stirred compartments. Settlers of 240 mm (bottom) and 210 mm (top) with an internal diameter of 90 mm enclosed the stirred segments. The internals of the stirred segments consist of alternating discs and doughnuts. The outside diameter of the doughnuts is 60 mm, the inner 22 mm and the thickness is 1.5 mm. The discs have a diameter of 40 mm and a thickness of 1.5 mm. The distance between two doughnuts is 32 mm, just as the distance between two discs. The internals are made of stainless steel.

The concentration profiles of toluene and heptane in both phases along the column were determined by taking samples at different column heights through sample ports. The sample ports consisted of two metal tubes and inside one of the two tubes a Teflon tube was placed. The solvent was fed to the top of the column and the extract phase was collected from the bottom settler. The heptane/toluene phase was fed from the bottom and the raffinate phase was collected from the top settler.

The solvents were regenerated in the extraction column at 80 ^{o}C by bubbling nitrogen through the column for 16 to 22 hours. Total removal of heptane was possible, but total removal of toluene was not: 0.78 mole% was left in the sulfolane and 0.88 mole% in [mebupy]BF_4. The regenerated solvents were used in the extraction experiments. In Figure 5.3, the removal rates of heptane and toluene form both sulfolane and the ionic liquid [mebupy]BF_4 are shown.

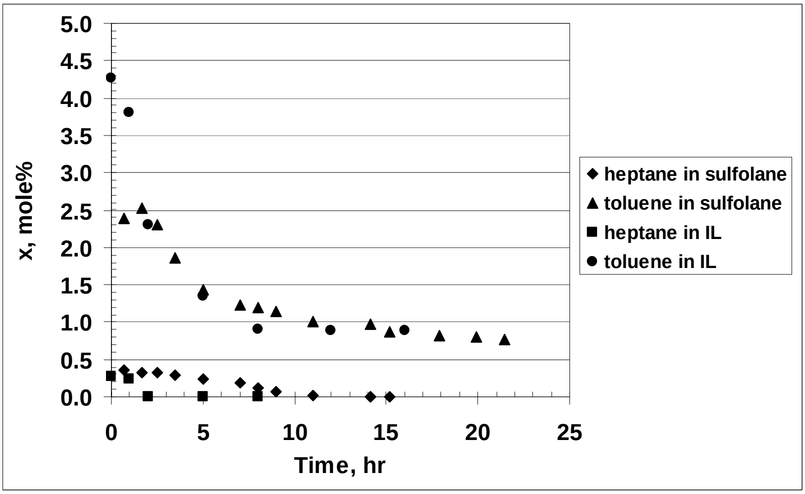

Figure 5.3. Regeneration of sulfolane and [mebupy]BF_4 in the extraction column, T = 80 °C.

5.3.2 HYDRODYNAMICS OF LIQUID-LIQUID EXTRACTION EQUIPMENT

In describing an extraction column, the hydraulic characteristics, being hold-up, drop size and operational window, are key parameters in order to determine column capacity and, therefore, the required column diameter in order to provide the desired throughput [1].

5.3.2.1 Drop size

The mean drop size normally reported is the Sauter mean diameter, or volume-surface mean diameter, defined by:

$$d_{32} = \frac{\Sigma n_i d_i^3}{\Sigma n_i d_i^2} \tag{5.1}$$

This equation was further extended and improved, but equation 5.1 will be used for calculating the mean drop sizes and using these data to explain the operational windows and column capacities [1].

5.3.2.2 Dispersed phase hold-up

When the dispersed phase flows into the extraction column, the droplets initially formed, whether or not uniform in size, undergo repeated coalescence and breakage until a final equilibrium size distribution is reached which generally remains constant, provided that the physical properties are not changed by solute mass transfer.

As the dispersed phase flow rate is increased, while that of the continuous phase is maintained constant, it is found that for most extractor types the fractional volumetric hold-up of dispersed phase increases approximately linearly with flow rate up to a transition value of 0.10 to 0.12. After this, the hold-up increases with U_d to the power 2 – 3. U_d is the superficial velocity of the dispersed phase and can be calculated by dividing the flow of the dispersed phase by the cross sectional area of the column (F_d/A_{cross}). The region of rapidly increasing hold-up persists up to an upper transition point, when the second interface forms at the dispersed phase inlet. Further increase in dispersed phase flow is rejected from the column and the column is said to flood.

The hold-up, which can be determined by taking samples at different heights in the column while the column is running in a stationary state, is found to have an optimum of around 0.50 at zero continuous phase flow and decreases with a decrease in flow ratio (F_d/F_c) and the flood-point also decreases correspondingly. The hold-up will be experimentally determined by measuring the total volume (V_c+V_d) and the volume of the dispersed phase (V_d) after settling has been completed:

$$\varphi = \frac{V_d}{V_d + V_c} \tag{5.2}$$

When the hold-up at different flows for the dispersed phase and continuous phase are determined, the velocity of the dispersed phase can be determined as well.

The concept of ‘slip’ or relative velocity of the dispersed phase droplets has been proven to be useful in relating hold-up to the phase flow rates. The slip velocity is defined as difference in 'true' velocities of the continuous and dispersed phases:

$$v_s = \frac{U_d}{\varepsilon\varphi} + \frac{U_c}{\varepsilon(1-\varphi)} \tag{5.3}$$

where φ is the fractional volumetric hold-up of the dispersed phase, and ε is the fractional volume of the internals in the column. The most common alternative for directly correlating the hold-up or slip velocity, has been to define a characteristic velocity (v_K) by:

$$v_S = v_K(1-\varphi)^n \tag{5.4}$$

For expressing U_d in terms of v_K eqn. 5.4 was used and eqn. 5.3 becomes eqn. 5.5.

$$U_d + U_c\frac{\varphi}{(1-\varphi)} = \varepsilon v_K \varphi(1-\varphi)^n \tag{5.5}$$

In this equation, v_K can be replaced by v_N, which is the characteristic drop velocity for rotor speed N, defined as the mean droplet velocity in the extractor when U_c=0 and $U_d \to 0$. The value for v_N can be obtained by plotting the left-hand side of eqn. 5.5 against $\varphi(1-\varphi)^n$, giving a line with slope εv_N through the origin.

The capacity of the RDC is determined by the velocity of the droplets and the amount of dispersed phase present per unit of volume, which is expressed as the hold-up. When the flux is increased, by increasing both flows, the hold-up will increase because the solute mass transfer per droplet cannot increase (unless the droplet becomes larger). Both phases will hinder each other more when the flows are increased and, therefore, the velocity of the droplets will decrease. The decrease of the droplet velocity together with the increasing hold-up results in a capacity increase of the column. At a certain point, the solute mass transfer cannot be increased anymore and a maximum is reached. A larger solute mass transfer will induce flooding and, therefore, this hold-up is indicated as the flooding hold-up [1].

5.3.2.3 Flooding point and operating regime

A continuous increase in the flow rate of dispersed (or continuous) phase finally results in flooding of the extractor, which is manifested by the appearance of a second interface at the opposite end to the main interface. This condition corresponds to the maximum in the value of the hold-up, or alternatively, to a maximum in the values of the flows beyond which the hold-up remains constant. This condition can be found by maximising U_c and U_d in eqn. 5.4 for n = 1, as follows:

$$\frac{dU_d}{d\varphi} = 0 : U_c = \varepsilon v_N (1-2\varphi_f)(1-\varphi_f)^2 \tag{5.6}$$

$$\frac{dU_c}{d\varphi} = 0 : U_d = 2\varepsilon\, v_N \varphi_f^{\,2} (1-\varphi_f) \tag{5.7}$$

where φ_f is the limiting value of φ at flood point and it is obtained by solving eqns. 5.6 and 5.7 for φ_f and putting $U_r = U_d/U_c$, thus

$$\varphi_f = \frac{\left(U_r^{\,2} + 8U_r\right)^{1/2} - 3U_r}{4(1-U_r)} \tag{5.8}$$

Flooding point data for a given extractor (other than packed or spray) can be represented by calculating the value of φ_f for each run from eqn. 5.8 and plotting U_d against $\varphi_f^2(1- \varphi_f)$, then a straight line through the origin of slope $2\varepsilon v_N$ should be obtained. The value of v_N in eqns. 5.6 and 5.7 should be the same as that in eqn. 5.8, so that flood-point values can be obtained from hold-up data and visa versa. The hold-up and flood point data are correlated to the column variables and physical parameters, within ±15 % as follows:

$$\frac{\overline{v_N}\mu_c}{\gamma} = 0.012 \left(\frac{\Delta\rho}{\rho_c}\right)^{0.90} \left(\frac{g}{d_r N^2}\right)^{1.0} \left(\frac{d_s}{d_r}\right)^{2.3} \left(\frac{h_c}{d_r}\right)^{0.90} \left(\frac{d_r}{d_c}\right)^{2.7} \tag{5.9}$$

In this equation, γ is the interfacial tension, μ_c the viscosity of the continuous phase, ρ_c the density of the continuous phase, g the acceleration due to gravity, d_r the rotor diameter, N the rotations per second, d_s the inner diameter of the stator ring, h_c the height of the compartment (i.e. stage) and d_c the column diameter. Eqn. 5.9 in conjunction with eqns. 5.5 and 5.7 can be used with reasonable confidence for the prediction of hold-up and flood point. However, it should be noted that measurements of the hold-up profile along the column show that the local hold-up increases from the base to a maximum at a point midway up the column and subsequently decreases.

For the practical operation of an RDC, it is not desirable to work near the flooding point. An operating hold-up of 75% of the flooding hold-up is recommended [2].

5.3.2.4 Droplet coalescence

For successful operation of liquid extraction equipment, it is of vital importance that effectively complete coalescence of dispersed phase droplets are obtained at liquid-liquid interface at one end or the other of a column, or within individual settlers in a mixer-settler cascade [2]. There are several forms of coalescence that have to be taken into account in liquid extraction equipment:

1. Single drop coalescence at interfaces. Coalescence takes place by means of two mechanisms: droplet-droplet interaction as the interface is approached and droplet-interface coalescence at the interface itself.
2. Inter-droplet coalescence
3. Coalescence in settlers

5.3.2.5 Mass transfer

The prediction of mass transfer performance requires the knowledge of the interfacial area and of the interphase mass transfer coefficients. The effective interfacial area of contact for mass transfer is given by:

$$a = \frac{6\,\varphi}{d_{32}} \tag{5.10}$$

where φ is the hold-up and d_{32} the Sauter average mean drop diameter. The total molar flux of transfer (in mol/m^3.s) can be expressed by the concentration difference of the two phases, Δc, the mass transfer coefficient, k, and the interfacial area:

$$J = k \cdot \Delta c \cdot a \tag{5.11}$$

From eqn. 5.11 it is clear that total amount of mass transferred is high when the interfacial area is large (small drop sizes and large hold-ups), when the concentration difference between the two phases is large and when the mass transfer coefficient is high [3].

5.3.2.6 Hydrodynamics and Operational Region

For determination of the operational regions, the total flux is varied while keeping the flow ratio constant. When performing these experiments, the system has to be operated in steady state and the phases must be in equilibrium. The flux (m^3/m^2.hr) is defined as the volume that passes through the cross-section of the column in a time period of one hour:

$$J_{total} = \frac{F_{m,d}/\rho_d + F_{m,c}/\rho_c}{A_{cross}} \tag{5.12}$$

In order to find the flooding point, the rotor speed is increased at constant flux. When the rotor speed increases, the dispersed phase droplets become smaller and the droplets are slowed down and, consequently, the hold-up increases, until the d_{32} becomes too small or the hold-up becomes too large and flooding or phase inversion occurs.

Figure 5.4. Pilot plant extraction column.

Flooding of the extractor is manifested by the appearance of a second interface at the opposite end to the main interface.

Phase inversion is a phenomenon caused by a change in mixing conditions such that the dispersed and continuous phases interchange. Until the maximum rotor speed at which flooding occurs for a certain flux, the dispersed phase hold-up and drop size can be determined at each rotor speed. The drop sizes in the column were determined by taking digital photos of the column contents. By comparing the drop diameter with the known size of the column internals, the drop diameter could be calculated. For this comparison, the characteristic length of the doughnut thickness was taken as a point of reference. The drop size was determined as the Sauter mean diameter. For determination of the hold-up, 250 ml samples were taken through the different sample ports and collected in a separation funnel. The two liquids in the separation funnel settled and the volumes of the two phases were determined. This procedure is repeated for different fluxes. In Figure 5.4, two compartments of the column are partly shown. Below the first segment is the bottom settler located. At the right side of the column, the sample ports and taps are visible.

5.3.2.7 Number of Equilibrium Stages

The number of equilibrium stages (N_S) was determined graphically with an equilibrium line and an operating line in an extraction diagram and the results were confirmed by means of the well known Kremser equation:

$$N_S = \frac{\ln\left[\left(\frac{X_F - Y_S/m}{X_R - Y_S/m}\right)\left(1 - \frac{1}{E}\right) + \frac{1}{E}\right]}{\ln E} \tag{5.13}$$

where X_F is the weight faction of toluene in the feed, X_R the weight fraction of toluene in the raffinate, Y_S the weight fraction of toluene in the solvent, m the toluene distribution coefficient and E the extraction factor (E = m∗S/F).

5.4 RESULTS AND DISCUSSION

5.4.1 DROP SIZE

In Figures 5.5 and 5.6, examples of photos taken for drop size determination are shown. Figure 5.4 shows the column contents when the organic phase is the continuous phase and the ionic liquid the dispersed phase and Figure 5.6 shows the reversed configuration.

Figure 5.5.Photo of column contents when the organic phase is continuous and the ionic liquid phase dispersed, T = 75 °C, F = 10.8 m^3/m^2.hr and N = 643 rpm.

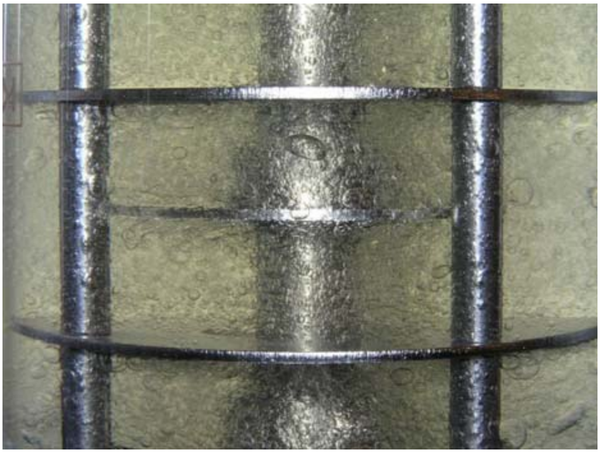

Figure 5.6. Photo of column contents when the ionic liquid phase is continuous and the organic phase dispersed, T = 40 °C, F = 5.6 m^3/m^2.hr and N = 305 rpm.

The difference between the contents of the column in the two configurations is distinct. When the ionic liquid is the continuous phase (Figure 5.6), the droplets are dispersed over the total segment. On the contrary, when the organic phase is the continuous phase, there seem to be regions underneath the doughnuts, where there is hardly any dispersed phase. Also the drops seem to be more uniform in the configuration where the ionic liquid is the continuous phase.

The difference in Sauter mean drop size between the two configurations can be seen in Figure 5.7. Drop sizes in the configuration with the ionic liquid as the continuous phase are twice as small as drop sizes in the configuration where the organic phase is continuous. This difference is caused by a difference in physical properties of the dispersed and continuous phase and difference in coalescence

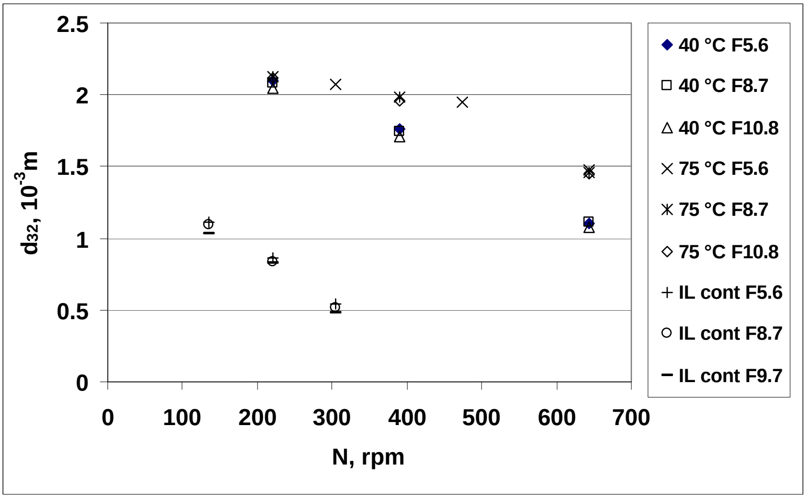

Figure 5.7. Sauter mean drop size in an RDC column for different fluxes in m^3/m^2.hr, temperatures and configurations with [mebupy]BF_4 as solvent.

The Sauter mean drop sizes for sulfolane were not determined. The only remark that can be made is that the drop sizes of sulfolane were larger than those of [mebupy] BF_4 (estimated between 1.50 and 2.50 mm). The variance in the Sauter mean drop size between two measurements was 5% and, therefore, the estimated error in the measurement is set on 5% as well. The drop size is dependent on the physical properties of the continuous and dispersed phase. In an RDC, the dispersed phase trapped by a disc impeller was discharged into the stage space as dispersed drops due to a centrifugal force of the rotating disc. Therefore, it is expected that drop size is greatly influenced by rotor speed and the flow rate of the dispersed phase [6]. In fact, in the case of a low rotation speed, dispersed phase trapped widely by the disc moved about unsteadily together with rotation of the impeller. This indicates that there is a minimum energy input required.

5.4.2 HOLD-UP

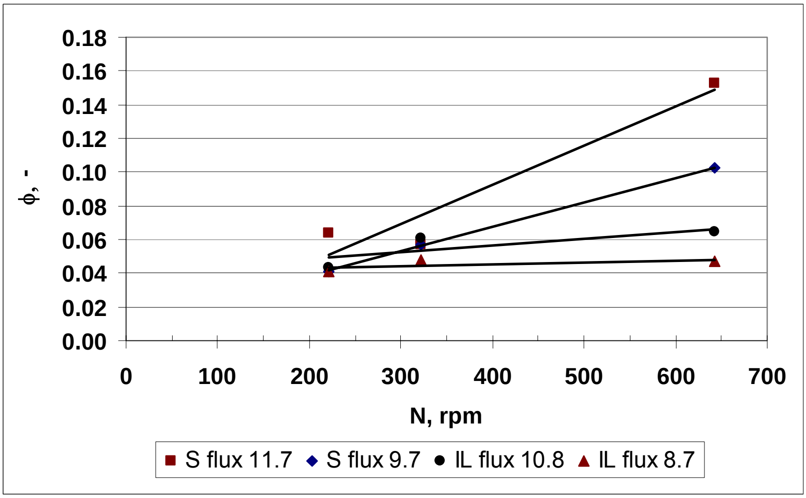

Figure 5.8. Hold-up for sulfolane and [mebupy]BF$_4$, 10% toluene, T = 40 °C, heptane continuous (flux in m^3/m^2.hr).

A typical result of the experimental hold-up fraction for constant flow rates of both phases is shown in Figure 5.8. An increasing flux and an increasing rotor speed both give more interaction. This results in a lower velocity of the droplets, thereby increasing the hold-up. A higher rotor speed means smaller droplets and, hence, a decrease in velocity, resulting in a higher hold-up. The difference between sulfolane and the ionic liquid can be explained by the differences in viscosity. The sulfolane droplets could more easily be broken up than the ionic liquid droplets at higher rotor speed, thereby increasing the hold-up.

5.4.3 OPERATIONAL REGIONS

The performances of sulfolane and [mebupy]BF$_4$ as the solvent and the dispersed phase were compared for the extractive removal of 10 wt% toluene from an n-heptane feed at 40 °C. For sulfolane an S/F ratio of 4 and for [mebupy]BF$_4$ an S/F ratio of 2 was used. In Figures 5.9 and 5.10, several areas can be discerned: flooding, the normal operating area and an area which is limited by the maximum rotor speed in the RDC. With [mebupy]BF$_4$, also an area exists, where the downcomer velocity is limited at low rotation speeds. From Figures 5.9 and 5.10, it can be concluded that the maximum achievable flux in the RDC for sulfolane is 15.5 m^3/m^2.hr (at 170 rpm) and for [mebupy]BF$_4$ 12.1 m^3/m^2.hr (at 50 rpm). For fluxes up to 10 m^3/m^2.hr for sulfolane and 10.8 m^3/m^2.hr for [mebupy]BF$_4$, every rotor speed lays within the operating regime. The difference in maximum flux can be explained by the difference in density and drop size. Since sulfolane has larger drop sizes and a higher density than [mebupy]BF$_4$: 1.26 g/cm^3 and 1.18 g/cm^3 respectively, a higher gravitational force and less resistance cause the sulfolane droplets to fall faster through the heptane and higher counteracting forces at higher fluxes can be overcome.

The limitation of the operating regime with the ionic liquid at low rotations is not caused by a large hold-up, since hold-up increases at higher rotation speeds and, therefore, cannot be the limiting factor. The drop size is relatively large at lower rotation speeds (Figure 5.7) and, therefore, the relative velocity is also large. It seems that a certain drop size is needed in order for the drops to fall past the internals. This was also found by others [6].

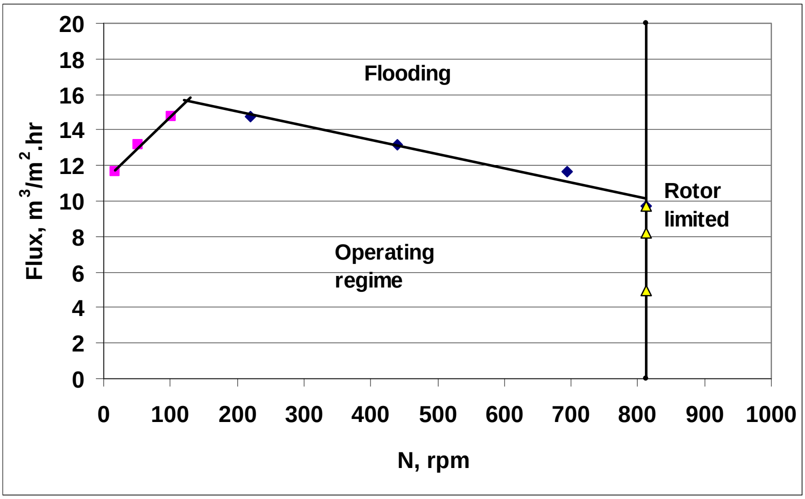

Figure 5.9. Operational regions for sulfolane as the dispersed and heptane as the continuous phase, ~10 wt% toluene in -n-heptane, T = 40 °C.

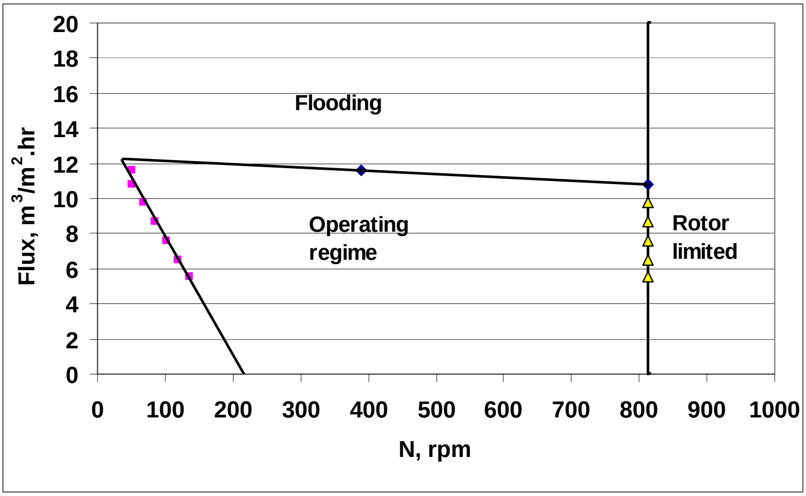

Figure 5.10. Operational regions for [mebupy]BF_4 as dispersed and heptane as the continuous phase, ~10 wt% toluene in n-heptane, T = 40 °C.

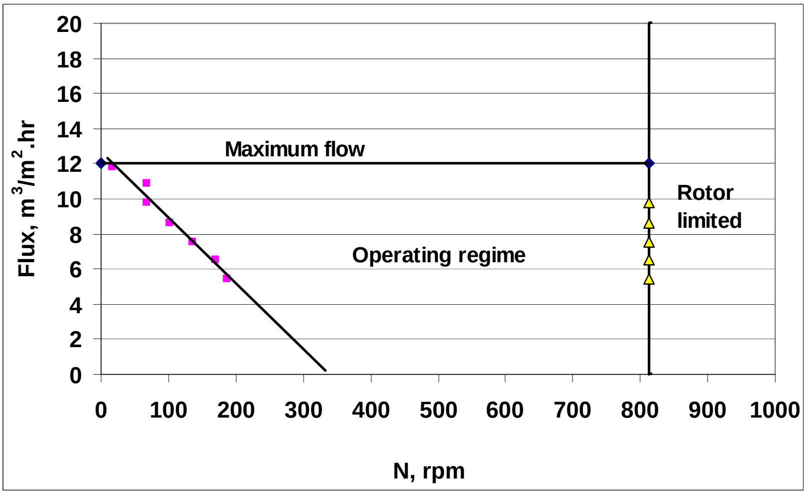

Figure 5.11. Operational regions for [mebupy]BF$_4$ as solvent and heptane as the continuous phase in a rotor speed versus flux graph in the RDC at 10 wt% toluene content, T = 75 ^{o}C.

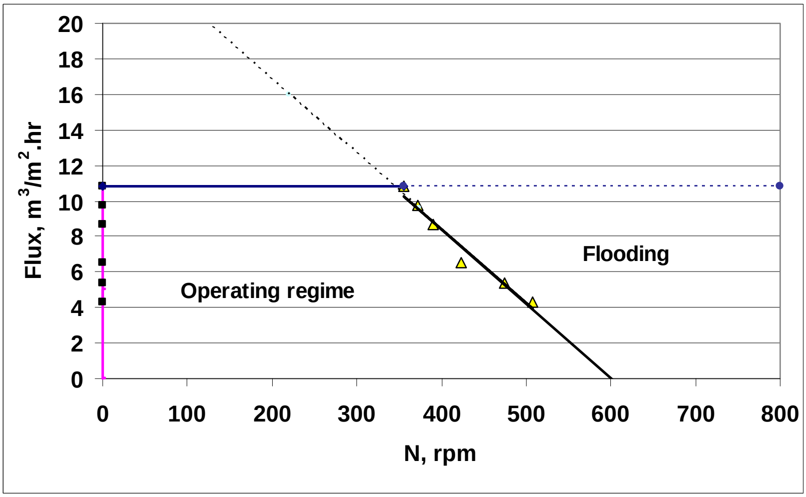

Figure 5.12. Operational regions for [mebupy]BF$_4$ as solvent and [mebupy]BF$_4$ as the continuous phase in a rotor speed versus flux graph in the RDC at 10 wt% toluene content, T = 40 ^{o}C.

In Figure 5.11, the results of tests with [mebupy]BF$_4$ as the dispersed phase at 75 °C are shown. The main difference between the operational regions of [mebupy]BF$_4$ at 40 ^{o}C and 75 ^{o}C is that, contrary to the measurements at 40 ^{o}C, no flooding regime could be determined at 75 ^{o}C. At 75 ^{o}C, the operating regime was limited by the maximum achievable flux instead of flooding, because the solvent pump had reached its limit due to the high viscosity of the solvent. The temperature increase does not cause a large density difference between the two phases and the density of ionic liquids is not highly temperature dependent [7]. Therefore, the increase in maximum flux could be a result from an increase in interfacial tension, which in turn causes an increase in drop size. The high temperature dependency of the interfacial tension is also reported in other literature [8,9]. The hold-up becomes lower and higher fluxes can be achieved before flooding occurs. With an increase in temperature, the drop size increases as well, as can be seen in Figure 5.7. Therefore, the downcomer velocity limit is shifted to higher rotation speeds at 75 °C.

The operating regime with [mebupy]BF_4 as the continuous phase does not show a lower limit for the rotor speed (Figure 5.12). The heptane droplets rise easily through the solvent, as the dispersed drops are much smaller in this configuration, and, therefore, the drops are not hindered so much by the internals. On the other hand, the operational area is limited at higher rotation speeds, because flooding occurs.

5.4.4 MASS TRANSFER

5.4.4.1 Extraction with sulfolane

The capacity of sulfolane as an extraction solvent can be expressed in terms of the total amount of toluene extracted and in terms of the number of equilibrium units. The concentration profiles of toluene over the column length in both the extract and raffinate phases are shown in Figure 5.13.

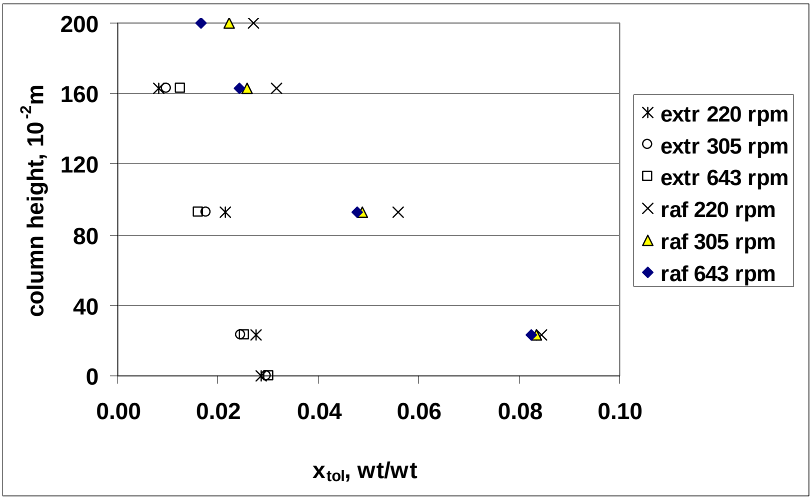

Figure 5.13. Concentration profiles of toluene over the column in the raffinate and extract phase for sulfolane with heptane as the continuous phase for different rotor speeds at 40 °C and F = 9.7 m^3/m^2 hr.

The concentration of heptane in the raffinate phase increases with the column length, because toluene is transferred to the sulfolane and, therefore, the toluene concentration decreases in the raffinate and as a result the heptane concentration increases. Sulfolane partly dissolves in heptane and, therefore, a small amount of sulfolane is present in the raffinate stream, up to 5 wt%.

The toluene concentration decreases in the raffinate phase and increases in the extract phase, because the toluene is transferred from the organic to the solvent phase. In this way, the feed stream is purified from toluene. The feed contained 9.72 wt% toluene, the raffinate at the top of the column 2.72 wt% toluene, the solvent 0.78 wt% toluene and the extract 2.87 wt % toluene at N = 220 rpm and a flux of 9.7 m^3/m^2.hr, as can be seen in Figure 5.13 and in Table 5.2. From this table can be concluded that the amount of toluene in the raffinate phase decreases as the rotation speed increases and the amount of toluene in the extract phase increases. This indicates a better solvent performance at higher rotation speeds, which corresponds to findings in the other literature [10,11].

Table 5.2. Concentrations of toluene with sulfolane as the solvent and heptane as the continuous phase, at 40 °C and F = 9.7 m^3/m^2.hr.

N [rpm]	x_F [wt/wt]	F [kg/hr]	x_S [wt/wt]	S [kg/hr]	x_R [wt/wt]	R [kg/hr]	x_E [wt/wt]	E [kg/hr]	Error [%]
220	0.0972	5.8	0.0078	24	0.0272	5.8	0.0287	24	12.8
305	0.0972	5.8	0.0078	24	0.0221	5.8	0.0296	24	11.9
643	0.0972	5.8	0.0078	24	0.0165	5.8	0.0301	24	9.1

5.4.4.2 Extraction with [mebupy] BF_4

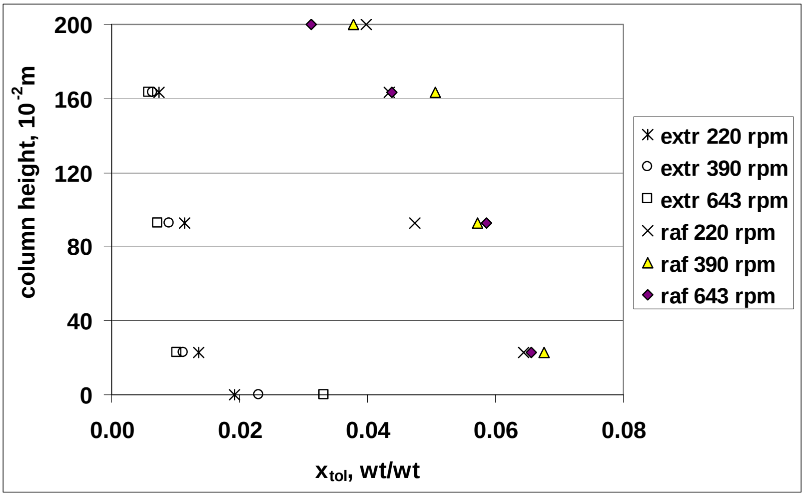

Figure 5.14. Concentration profiles of toluene over the column length in the raffinate and extract phase for [mebupy]BF_4 with heptane as the continuous phase at 40 ^oC and F = 5.6 m^3/m^{-2}.hr.

In Figure 5.14, the concentration profile of toluene is shown for the extraction of toluene with [mebupy]BF_4 at 40 °C and a flux of 5.6 m^3/m^2.hr. The toluene concentration decreases in the raffinate phase and increases in the extract phase, because of solute mass transfer. The feed contained 7.55 wt% toluene and the raffinate at the top of the column contained 3.97 wt%. The increase of toluene content in the solvent stream was from 0.53 to 1.92 wt% at N = 220 rpm, as can be seen in Figure 5.14 and Table 5.3. From Table 5.3, it can be concluded that with an increase in rotation speed, the final toluene concentration in the raffinate decreases and, therefore, the final toluene concentration in the extract phase increases.

With an increase of the flux, from 5.6 to 10.8 m^3/m^2.hr, the final toluene concentration in the raffinate decreases. While at a flux of 5.6 m^3/m^2.hr and a rotation speed of 220 rpm, the final toluene concentration in the raffinate was 3.97 wt%, at a flux of 10.8 m^3/m^2.hr and with the same rotation speed, the final toluene concentration was 3.75 wt%. From these results can be concluded that an increase in flux leads to a larger column capacity.

The influence of temperature on the solvent performance was also investigated. When increasing the temperature, the distribution coefficient of heptane increases. This will have a negative influence on the solvent performance. But on the other hand, the temperature also influences the physical properties of the liquids. In the hydraulic experiments, the influence of temperature on the drop size and hold-up was already determined. A rise in temperature resulted in larger drop size and smaller hold-ups. Therefore, an increase in temperature seems to lead to lower mass transfer and to a lower column capacity. The results from the extraction experiments at a temperature of 75 °C showed indeed a lower solvent performance, as is depicted in Figure 5.15.

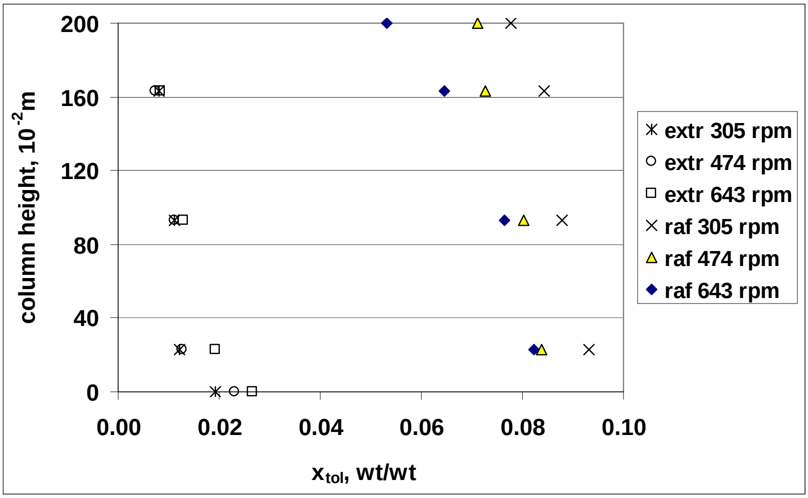

Figure 5.15. Concentration profiles of toluene over the column length in the raffinate and extract phase for [mebupy]BF_4 with heptane as the continuous phase at 75 °C and F = 5.6 m^3/m^2.hr.

The feed concentration of the extraction experiments performed at 75 °C was 9.82 wt%. For a flux of 5.6 m^3/m^2.hr and rotation speed of 643 rpm, the toluene concentration in the raffinate phase decreased from 9.82 to 5.32 wt%. For a flux of 8.7 m^3/m^2.hr and rotation speed of 643 rpm the final raffinate concentration was 4.87 wt%.

When carrying out the experiments with the ionic liquid as the continuous phase, the sample ports did not work well. Since the ionic liquid phase was now surrounding the inlets of the sample ports, the heptane had difficulty getting into the sample port. Therefore, the raffinate flow could only be measured at the top of the column, but not at the sample ports along the column. So no concentration profiles of toluene in the raffinate phase along the column could be determined. The toluene concentrations in the different streams in the column with the ionic liquid as the continuous phase at two flux rates are shown in Table 5.5.

In almost all of the experiments, an ionic liquid concentration of about 3 wt% in the raffinate phase was measured, which is too large compared to the equilibrium data. The concentration of the ionic liquid in the raffinate phase measured with the equilibrium experiments was 0.001 mole fraction or 0.24 wt%. Apparently, the phase separation in the top settler is not complete during the extraction. Therefore, the experiments in the extraction column should be repeated after the top settler section is adapted so that a correct phase separation could take place.

Table 5.3. Concentrations of toluene over in the different streams for [mebupy]BF_4 with heptane as the continuous phase at 40 °C for F = 5.6 and 10.8 m^3/m^2.hr.

N [rpm]	x_F [wt/wt]	F [kg/hr]	x_S [wt/wt]	S [kg/hr]	x_R [wt/wt]	R [kg/hr]	x_E [wt/wt]	E [kg/hr]	Error [%]
220	0.0755	5	0.0058	10	0.0397	5	0.0192	10	10.3
390	0.0755	5	0.0058	10	0.0379	5	0.0230	10	3.7
643	0.0755	5	0.0058	10	0.0311	5	0.0331	10	11.8
220	0.0755	10	0.0058	20	0.0375	10	0.0248	20	0.1
390	0.0755	10	0.0058	20	0.0357	10	0.0253	20	0.9
643	0.0755	10	0.0058	20	0.0301	10	0.0295	20	2.3

Table 5.4. Concentrations of toluene over in the different streams for [mebupy]BF_4 with heptane as the continuous phase at 75 °C for F = 5.6 and 8.7 m^3/m^2.hr.

N [rpm]	x_F [wt/wt]	F [kg/hr]	x_S [wt/wt]	S [kg/hr]	x_R [wt/wt]	R [kg/hr]	x_E [wt/wt]	E [kg/hr]	Error [%]
305	0.0982	5	0.0053	10	0.0777	5	0.0192	10	6.8
474	0.0982	5	0.0053	10	0.0712	5	0.0231	10	8.0
643	0.0982	5	0.0053	10	0.0532	5	0.0267	10	2.0
220	0.0982	8	0.0053	16	0.0579	8	0.0204	16	9.2
390	0.0982	8	0.0053	16	0.0509	8	0.0232	16	10.6
643	0.0982	8	0.0053	16	0.0487	8	0.0254	16	8.5

Table 5.5. Concentrations of toluene over in the different streams for [mebupy]BF$_4$ with [mebupy]BF$_4$ as the continuous phase at 40 °C for F =5.6 and 8.7 m^3/m^2.hr.

N [rpm]	x_F [wt/wt]	F [kg/hr]	x_S [wt/wt]	S [kg/hr]	x_R [wt/wt]	R [kg/hr]	x_E [wt/wt]	E [kg/hr]	Error [%]
220	0.1030	5	0.0057	10	0.0655	5	0.0210	10	6.1
305	0.1030	5	0.0057	10	0.0635	5	0.0220	10	6.0
220	0.1030	8	0.0057	16	0.0571	8	0.0263	16	4.2
305	0.1030	8	0.0057	16	0.0544	8	0.0282	16	3.2

5.4.4.3 Number of equilibrium stages

The column performance was evaluated using the number of equilibrium stages (N_S) over the column, by means of the graphical method, and the results were confirmed by using equation 5.13. In Figure 5.16, the N_S as function of the rotating speed is depicted. The highest N_S is obtained with [mebupy]BF$_4$ at high rotor speeds and at a flux of 10.8 m^3/m^2.hr. With sulfolane as the solvent, the feed flow was 5.8 kg/hr with a total flux of 9.7 m^3/m^2.hr and with [mebupy]BF$_4$ as the solvent, the feed flow was 10 kg/hr with a total flux of 10.8 m^3/m^2.hr. This means that more toluene can be extracted with the ionic liquid as solvent than with sulfolane.

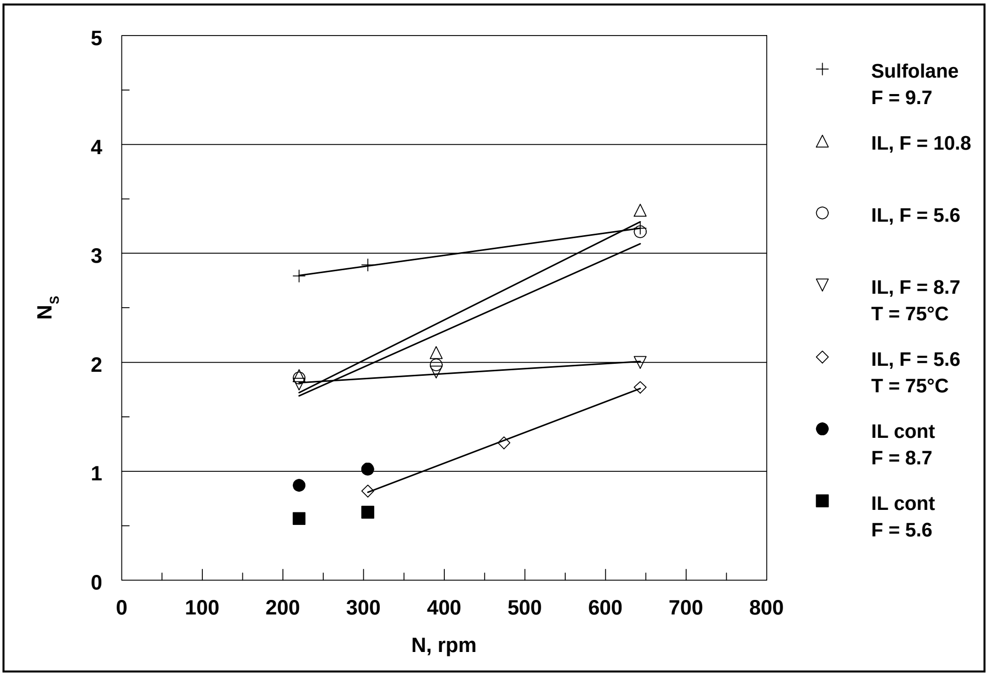

Figure 5.16. Number of equilibrium stages with sulfolane and [mebupy]BF$_4$ in the RDC, T = 40 °C, ~ 10 % toluene, flux in m^3/m^2.hr.

At 75 °C and at the configuration where the ionic liquid was the continuous phase, lower N_S's were obtained. At 75 °C, the heptane is more soluble in the ionic liquid, while the solubility of toluene remains at about the same level and the drop size is larger at this temperature. This means that the mass transfer is reduced due to a lower specific area. With the ionic liquid as the continuous phase, this phase flows faster than the dispersed heptane phase. Flooding occurs already at low rotor speeds (Figure 5.12).

5.5 CONCLUSIONS

In the pilot plant, the RDC provided good results for the toluene/heptane separation: small droplets were formed with the ionic liquid and the column capacity was high.

The extraction with the ionic liquid can very well be compared to the extraction with sulfolane in the RDC.

Due to the higher toluene distribution coefficient, lower S/F ratios were required to extract the same amount of toluene with the ionic liquid, while compared to sulfolane a 10% higher flux (volumetric throughput) and similar mass transfer efficiency were obtained. Also, the feed flow with [mebupy]BF_4 was higher (10 kg/hr) than with sulfolane (5.8 kg/hr) as the solvent.

The best performance (highest toluene extraction efficiency) was obtained at the highest rotation speed used (643 rpm). At a flux of 10.8 m^3/m^2.hr excellent hydrodynamic behaviour was observed and about three equilibrium stages were contained in the 1.80 m high active section of the column.

The top settler of the column should be adapted to enhance the phase separation of the incoming ionic liquid and the outgoing raffinate, resulting in lower ionic liquid concentrations in the raffinate phase.

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6 TERNARY LIQUID-LIQUID EQUILIBRIA FOR MIXTURES OF AN AROMATIC+AN ALIPHATIC HYDROCARBON+AN IONIC LIQUID

6.1 ABSTRACT

This research has been focused on a study of sulfolane and three ionic liquids as solvents in liquid-liquid extraction. Tie line data were obtained for mixtures of (sulfolane or [mmim]CH_3SO_4 or [emim]$C_2H_5SO_4$ or [mebupy]BF_4)+toluene+n-heptane and ([mebupy]BF_4+(benzene or ethylbenzene or m-xylene)+(hexane or n-octane) at T = 313.2 and 348.2 K (T = 313.2 and 333.2 K for the ternary mixtures with benzene) and p = 0.1 MPa.

Comparing the experimental and the fitted data in the ternary diagrams for the seven systems under investigation, it can be concluded that all the experimental data could very well be correlated with the NRTL model.

The aromatic/aliphatic selectivity values were higher with all three ionic liquids tested than with sulfolane, which is one of the most common solvents for extraction of aromatic hydrocarbons from mixtures of aromatic and aliphatic hydrocarbons used in industry. The ionic liquid [mebupy]BF_4 showed an optimal combination of a high toluene distribution coefficient and a high toluene/heptane selectivity. These values were for the range of toluene concentrations below 55 mole% at 313.2 K and below 45 mole% at 348.2 K higher than those with sulfolane. The ionic liquid [mebupy]BF_4 is, therefore, a suitable solvent for an industrial extraction process for the separation of aromatic and aliphatic hydrocarbons.

6.2 INTRODUCTION

The separation of aromatic hydrocarbons (benzene, toluene, ethylbenzene and xylenes) from C_4 – C_{10} aliphatic hydrocarbon mixtures is challenging since these hydrocarbons have boiling points in a close range and several combinations form azeotropes. The conventional processes for the separation of these aromatic and aliphatic hydrocarbon mixtures are liquid extraction, suitable for the range of 20 – 65 wt% aromatic content, extractive distillation for the range of 65 – 90 wt% aromatics and azeotropic distillation for high aromatic content, >90 wt% [1]. This implicates that there are no suitable separation processes available for process streams with an aromatic content below 20 wt%. Typical solvents used are polar components such as sulfolane [2-9], N-methyl pyrrolidone (NMP) [8], N-formyl morpholine (NFM), ethylene glycols [9-11], propylene carbonate [9]. This implicates additional distillation steps to separate the extraction solvent from both the extract and raffinate phases, and to purify the solvent, with, consequently, additional investments and energy consumption. Overviews of the use of extraction and extractive distillation for the separation of aromatic hydrocarbons from aliphatic hydrocarbons can be found elsewhere [12-15].

Replacement of volatile solvents in the separation of aromatic and aliphatic hydrocarbons by non-volatile ionic liquids can offer several advantages: less complex processes and a more simple regeneration of the solvent. In order to apply these ionic liquids in the chemical process industry, thermodynamic data need to be available for designing a proper separation process. We have investigated several combinations of ionic liquids and binary mixtures of aromatic and aliphatic hydrocarbons in order to determine thermodynamic data for the design of an extraction process suitable for separating aromatic and aliphatic hydrocarbons.

Liquid-liquid equilibrium (LLE) data are essential for the design of extraction equipment and/or for the calculation of the thermodynamic limit of a given separation. In the existing literature, hardly any data are found on LLE with ionic liquids [17-28]. There are only four references concerning liquid-liquid equilibria for an aromatic and an aliphatic hydrocarbon with ionic liquids [17-20]. Selvan et al. [18] use the ionic liquids [emim]I_3 and [[bmim]I_3 for the extraction of toluene from a mixture of toluene and heptane. However, these ionic liquids are very corrosive and, therefore, not suitable for industrial applications [16]. Letcher and Deenadayalu [19] have investigated ternary liquid-liquid equilibria for mixtures of [omim]Cl, benzene and an alkane at T = 298.2 K. Letcher and Reddy [20] have investigated ternary liquid-liquid equilibria for mixtures of the ionic liquids [hmim]BF_4 and [hmim]PF_6, and benzene and an alkane with the goal to find an alternative for [hmim]PF_6, which can decompose in the presence of water and at elevated temperatures to form HF. All benzene/heptane selectivities measured with these ionic liquids are too low ($S<10$) to be of industrial interest.

In Chapter 4 and in a previous paper [16], three suitable ionic liquids were identified for the separation of aromatic and aliphatic hydrocarbons, notably 1,3-dimethylimidazolium ([mmim]) methylsulfate, 1-ethyl-3-methylimidazolium ([emim]) ethylsulfate and 4-methyl-N-butylpyridinium ([mebupy]) tetrafluoroborate. The structures of these ionic liquids are given below:

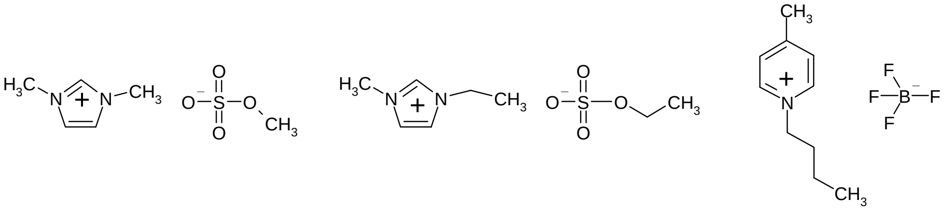


Figure 6.1. Structures of [mmim] methylsulfate, [emim] ethylsulfate and [mebupy]BF_4.

Since there are no thermodynamic data available for these IL’s, LLE data must be determined in order to evaluate the process performance. In this study, experimental LLE data over a wide composition range were gathered and the phase compositions were correlated by using the non-random two-liquid (NRTL) model for six ionic liquid systems: toluene+n-heptane+1,3-dimethylimidazolium methylsulfate, toluene+n-heptane+1-ethyl-3-methylimidazolium ethylsulfate, toluene+n-heptane+4-methyl-N-butylpyridinium tetrafluoroborate, ethylbenzene+n-octane+4-methyl-N-butylpyridinium tetrafluoroborate and m-xylene+n-octane+4-methyl-N-butylpyridinium tetrafluoroborate at T = 313.2 K and 348.2 K and p = 0.1 MPa and benzene+n-hexane+4-methyl-N-butylpyridinium tetrafluoroborate at T = 313.2 K and 333.2 K and p = 0.1 MPa.

The solvent sulfolane is used as a comparison for this separation, because it is one of the most common solvents for extraction of aromatic hydrocarbons from mixtures of aromatic and aliphatic hydrocarbons used in industry [2-9]. LLE experiments were also carried out with sulfolane, because relevant data for the range in toluene concentrations below 20 mole % were not available.

6.3 PROCEDURE

Before each experiment, the ionic liquids were dried at 348.2 K under reduced pressure in a rotary evaporator. Liquid-liquid equilibrium experiments were carried out in jacketed vessels with a volume of approximately 70 mL. The top of a vessel was closed using a PVC cover, through which a stirrer shaft passed. Two stainless steel propellers were used with an electronic stirrer (Heidolph RZR 2051 control). The vessels were jacketed to circulate water from a water bath (Julabo F32-MW) in order to maintain the temperature inside the vessels at either 313.2, 333.2 or 348.2 K.

For each experiment, 20 mL of the ionic liquid and 10 mL of a toluene/n-heptane mixture were placed into the vessel. The temperature and the ratio of toluene in n-heptane were varied. We established that equilibrium was reached within 5 minutes. This was done for one IL by taking samples after 5, 10, 15, 30, 65 and 120 minutes and analysing them. In order to avoid this procedure for the other ternary mixtures, the extraction experiment was continued for 20 minutes. After stirring, the two phases were allowed to settle for about one hour.

6.4 ANALYSIS

Samples (approximately 0.5 mL) were taken from both phases. 1-Butanol (0.5 mL) was added to each sample to avoid phase splitting and to maintain a homogeneous mixture, and n-hexane was added to samples as an internal standard for the GC analysis, 0.2 mL to the raffinate phase and 0.1 mL to the extract phase samples. For the analysis of n-hexane from the experiments with mixtures of benzene+n-hexane, acetone was used as solvent instead of 1-butanol and n-pentane was used as the internal standard.

The concentrations of toluene and n-heptane in the samples were analysed by a Varian CP-3800 gas chromatograph with an Alltech Econo-Cap EC-Wax column (30 m x 0.32 mm x 0.25 µm) and with a Varian 8200 AutoSampler. Because the ionic liquid has no vapour pressure, it cannot not be analysed by GC. The IL is collected in a pre-column in order not to disrupt the analysis. In a ternary mixture, one has to analyse only two components and the third one, the IL, can then be determined by subtracting the sum of the measured molar fractions of the aromatic and the aliphatic hydrocarbons from a value of 1.

Measurements were carried out in duplicate in order to exclude exceptions in the measurements that could lead to wrong conclusions. The deviance in the calibration curves of 1% and a possible contamination of the gas chromatograph can also cause a variance in the mole fractions (estimated on 1%). The averages of the two measurements were used in our results.

6.5 DATA CORRELATION

The determined phase equilibrium data for the described systems were correlated with the NRTL model. Several authors have used this model to describe their measurements of liquid-liquid equilibria and vapour-liquid equilibria with ionic liquids [18-29]. The binary interactions were calculated using equation 6.1:

$$\tau_{ij} = a_{ij} + \frac{b_{ij}}{T} \qquad G_{ij} = \exp(-\alpha_{ij}\tau_{ij}) \qquad \alpha_{ij} = \alpha_{ji} \tag{6.1}$$

where τ_{ij} and G_{ij} are NRTL parameters, which are calculated via the non-randomness parameter α_{ij} and the parameters a_{ij} and b_{ij}/K. The model parameters of the NRTL equation (α_{ij}, a_{ij}, a_{ji}, b_{ij}/K and b_{ji}/K) were determined via data regression using ASPEN Plus 12.1.

Seiler et al. [29] have also used ASPEN Plus to determine the model parameters for the NRTL equation for a VLE of ethanol, water and the ionic liquid [emim]BF_4. In their work, the ionic liquid is treated as a non-dissociating component. Since the ionic liquid has no vapour pressure and its concentration in the vapour phase is close to zero, the parameter regression is not asked to fulfil the equation for the equality of the fugacity for the ionic liquid.

The objective function for the regression of the NRTL-parameters is the equality of the activity for each component in both phases. With the assumption of an equilibrium in the liquid phase, the referring equation is:

$$x_R = \frac{\gamma_E}{\gamma_R} x_E \tag{6.2}$$

For the component ionic liquid, this equation contains two values, which are close to zero: its concentration in the raffinate phase (x_R) and the value of $1/\gamma_R$. The value of γ_R is very large because the concentration of the ionic liquid in the raffinate phase is very small and its concentration in the extract phase is very large. Therefore, to circumvent numerical problems, the constraints for the ionic liquid for the parameter regression are left out, just as in the parameter regression carried out by Seiler et al. [29]. Also, where the concentrations of the ionic liquid in the raffinate phase could not be detected, the concentrations were set to 10^{-6} mole fraction in order to avoid numerical problems.

The value of the non-random parameter α_{ij} was set to 0.3 for the aromatic-aliphatic system and was regressed for the combinations with the ionic liquids, because the standard value gave erroneous results. For ionic systems, α_{ij} has usually another value than 0.3. Other authors who investigated LLE data with IL's also used other values for α_{ij} than the standard value of 0.3 [18-21]. The binary interaction parameters for toluene+n-heptane for the ionic liquid systems were determined by regression of two data sets of the system toluene+n-heptane+[mebupy]BF_4 at T = 313.2 K and 348.2 K. These parameters were then used in the determination of the interaction parameters (toluene+ionic liquid and n-heptane+ionic liquid) of the other ternary systems with ionic liquids. The binary interaction parameters for toluene+n-heptane, obtained with [mebupy]BF_4 as solvent, were not suitable for the calculation of the tie lines for the ternary system toluene+n-heptane+sulfolane, probably because the ionic liquids are ionic and sulfolane is not. Therefore, the binary interaction parameters for the ternary mixture toluene+n-heptane+sulfolane were determined separately. Also, the values of the binary interaction parameters of toluene+n-heptane, obtained by regression for the mixture toluene+n-heptane+sulfolane, could not be used to calculate the tie lines of the ternary mixtures with the ionic liquids.

The binary interaction parameters for n-octane+[mebupy]BF_4 were determined by regression of two data sets of the ternary system m-xylene+n-octane+[mebupy]BF_4 at T =313.2 K and 348.2 K, because there were more experimental data points available for this ternary system than for the system ethylbenzene+n-octane+[mebupy]BF_4. These interaction parameters were then used in the determination of the other interaction parameters of the ternary system ethylbenzene+n-octane+[mebupy]BF_4.

6.6 RESULTS AND DISCUSSION

6.6.1 TERNARY MIXTURES WITH TOLUENE+HEPTANE+AN IONIC LIQUID OR SULFOLANE

The compositions of the conjugate phases, the toluene/heptane selectivity and the tie-line results of the ternary mixtures investigated at T = 313.2 and 348.2 K and 0.1 Mpa are given in the following tables (in Appendix 1) and figures:

- Toluene+n-heptane+sulfolane:	Table 6.1 and Figures 6.2 and 6.3
- Toluene+n-heptane+[mebupy]BF_4:	Table 6.2 and Figures 6.4 and 6.6
- Toluene+n-heptane+[emim]$C_2H_5SO_4$:	Table 6.3 and Figures 6.8 and 6.9
- Toluene+n-heptane+[mmim]CH_3SO_4:	Table 6.4 and Figures 6.10 and 6.11

The selectivity (*S*) of the ionic liquid (IL) or sulfolane was determined from the equation:

$$S = (x_1/x_2)_{\text{IL(sulfolane)-rich phase}}/(x_1/x_2)_{\text{alkane-rich phase}} \tag{6.3}$$

where x_1 and x_2 refer to the molar fractions of the aromatic hydrocarbon and the alkane, respectively.

The solvent sulfolane is used as a comparison for the extraction of aromatic hydrocarbons. The compositions of the conjugate phases and the toluene/heptane selectivity of the ternary mixture toluene+n-heptane+sulfolane T = 313.2 and 348.2 K and 0.1 Mpa are given in Table 6.1. The tie-line results have been plotted in Figure 6.2. In Figure 6.3, the toluene/heptane selectivities at T = 313.2 and 348.2 K are shown. In Figure 6.5, our own experimental data and LLE data from literature [2,3,4] are shown at T = 313.2 K and 348.2 K. Our experimental data and the data at 313.2 K from Tripathi [2] and Rawat and Gulati [3] are in good agreement with each other, but the data from De Fré [4] at 348.2 K differ from our own. Both the toluene and the heptane distribution coefficients are higher than our data at higher toluene concentrations and the toluene/heptane selectivity is lower than our data for all toluene concentrations.

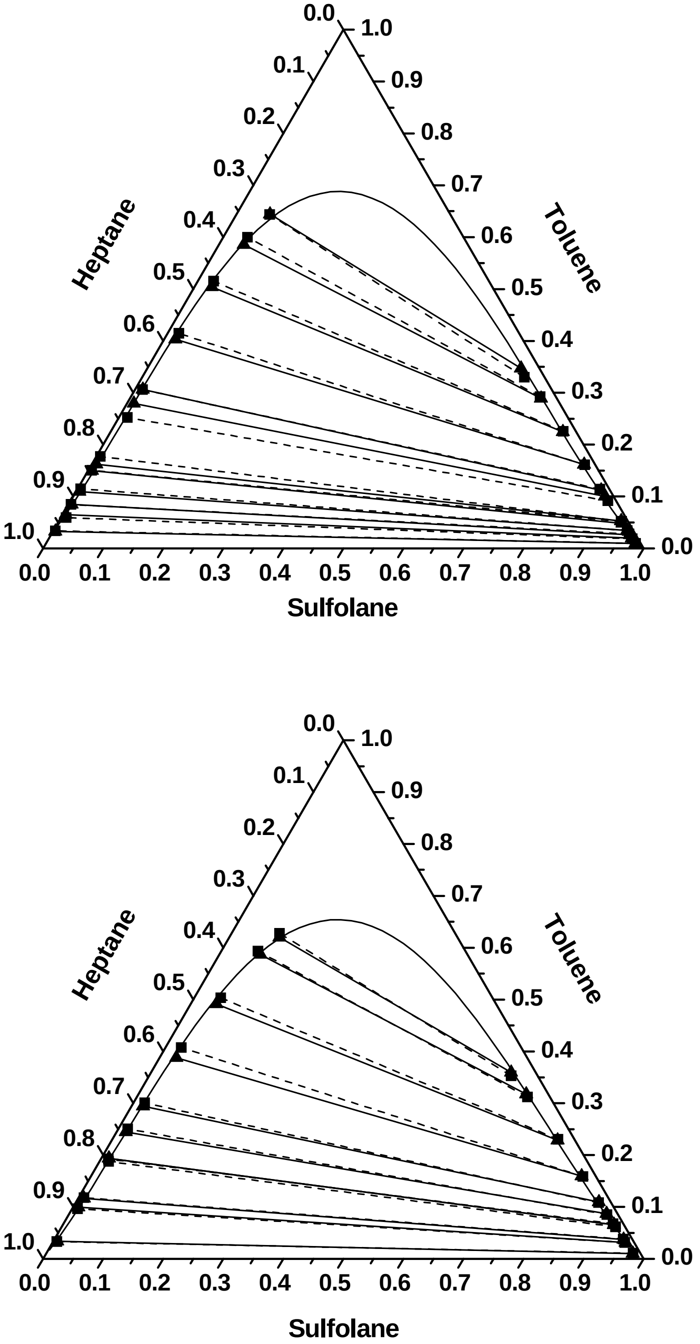


Figure 6.2. Tie lines for ternary mixture of toluene+n-heptane+sulfolane at 313.2 K (top) and 348.2 K (bottom) and p = 0.1 MPa. Experiments: ■, dashed lines; calculated: ▲, solid lines.

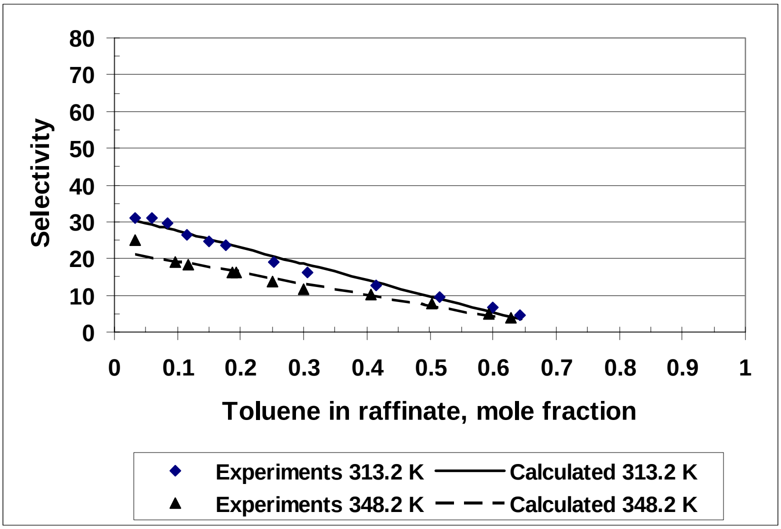


Figure 6.3. Experimental and calculated toluene/n-heptane selectivity with sulfolane at 313.2 and 348.2 K.

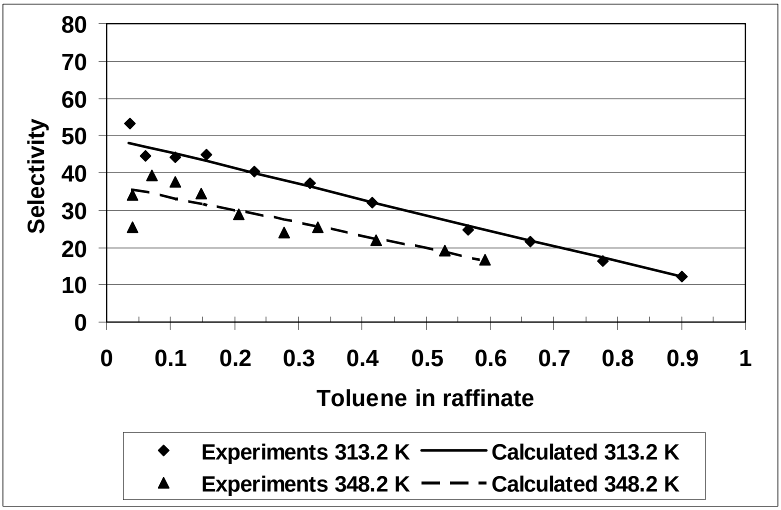
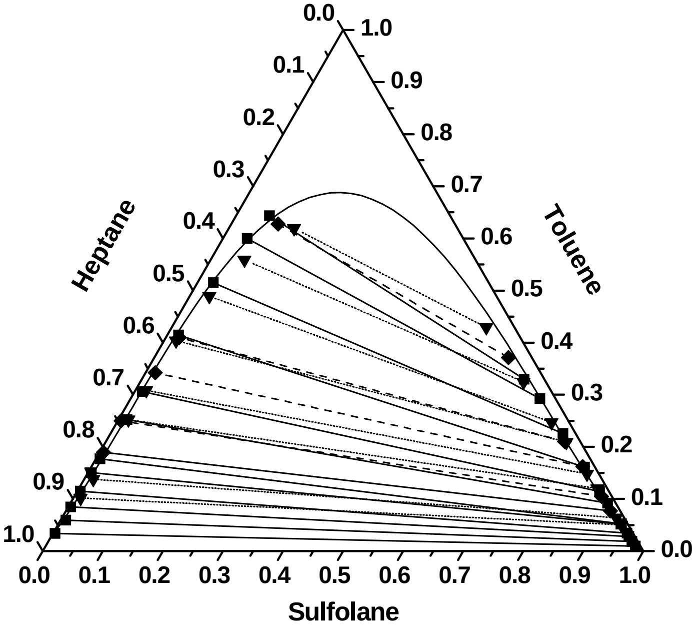


Figure 6.4. Experimental and calculated toluene/n-heptane selectivity with [mebupy]BF_4 at 313.2 and 348.2 K.



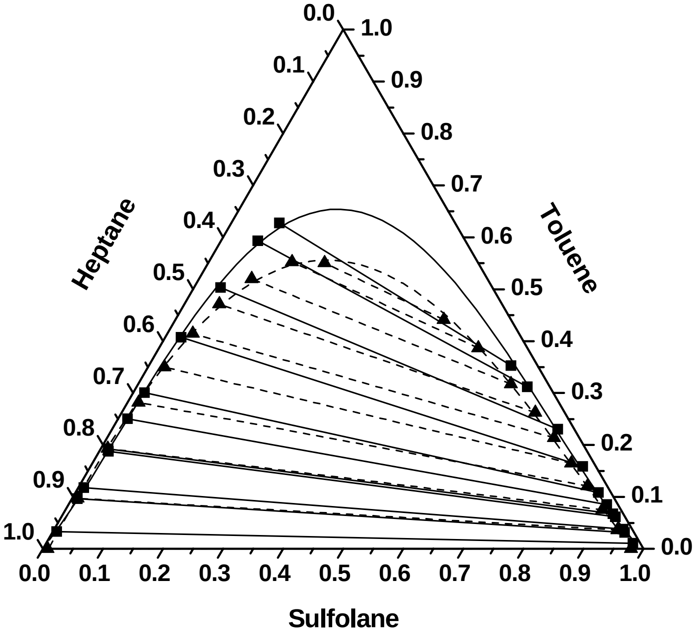


Figure 6.5. Tie lines for ternary mixture of toluene+n-heptane+sulfolane at 313.2 K (top) and 348.2 K (bottom) and p = 0.1 MPa. Experiments: ■, calculated binodal line: solid line. Literature data from [2]: ▼, [3]: ◆ (top); [4]: ▲ (bottom); binodal line: dashed line.

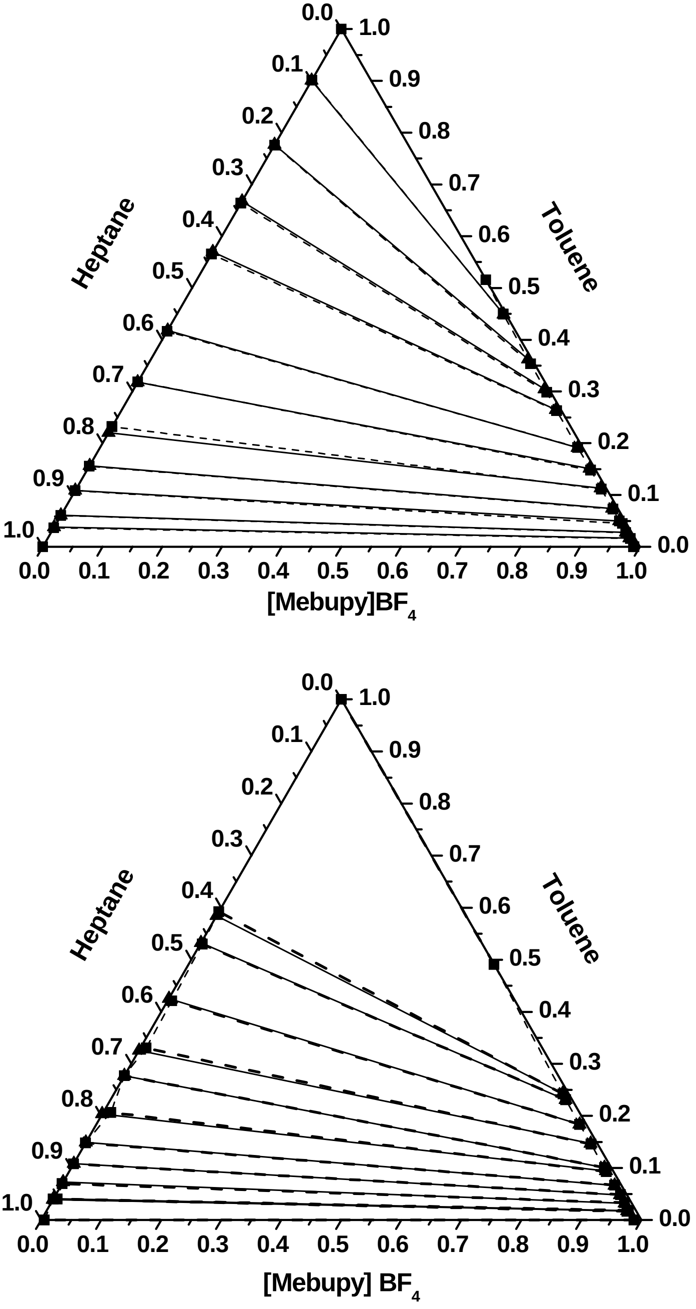


Figure 6.6. Tie lines for ternary mixture of toluene+n-heptane+[mebupy]BF_4 at 313.2 K (top) and 348.2 K (bottom) and p = 0.1 MPa. Experiments: ■, dashed lines; calculated: ▲, solid lines.

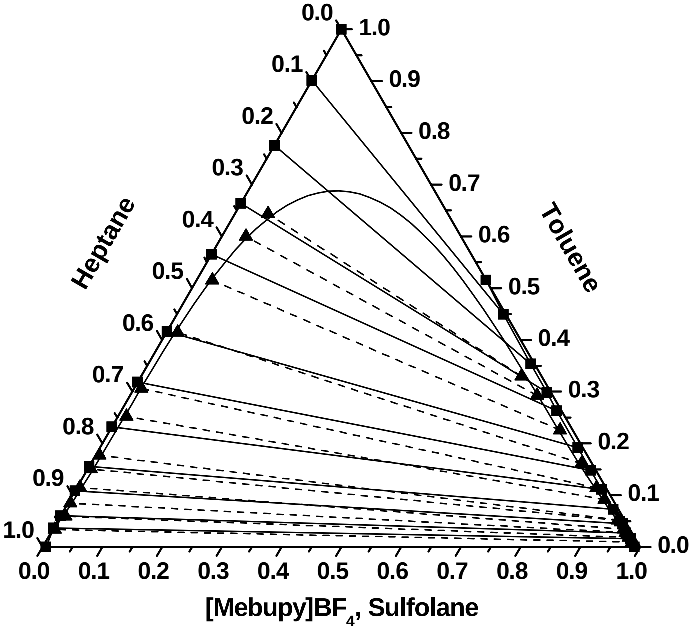


Figure 6.7. Ternary diagram of the system toluene+n-heptane+[mebupy]BF$_4$ (■), solid lines and toluene+n-heptane+sulfolane (▲), dashed lines at T = 313.2 K and p = 0.1 MPa.

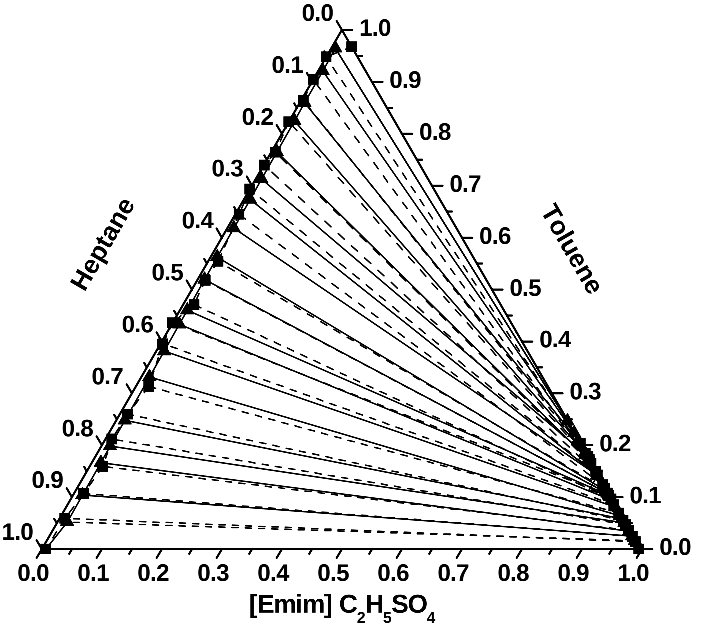
In Figure 6.7, the experimental tie lines of the ternary system toluene+n-heptane+ sulfolane and of the ternary system toluene+n-heptane+[mebupy]BF$_4$ and at T = 313.2 K and p = 0.1 MPa are shown in order to compare these two solvents for the separation of toluene from toluene/n-heptane mixtures.

From Figure 6.7, it is clear from the straight lines in the ternary diagram that with the IL [mebupy]BF$_4$ hardly dissolves in the heptane phase and that the concentration of heptane in the IL phase is very low. The toluene distribution coefficient with the IL remains at the same level, independent of the toluene concentration. The miscibility gap between heptane and sulfolane becomes smaller at higher toluene concentrations. This means that the toluene distribution coefficient with sulfolane increases with the toluene concentration, but the toluene/heptane selectivity with sulfolane decreases with increasing toluene concentration, as can be seen in Figure 6.3.

Comparing Figures 6.6, 6.8 and 6.11, it can be seen that the miscibility gap between the IL [mebupy]BF$_4$ and heptane is larger than for the two other ionic liquids. Furthermore, the solubility of toluene in [mebupy]BF$_4$ is higher (about 44 mole%) than in the other IL's (18 mole% in [emim]$C_2H_5SO_4$ and 8 mole% in [mmim]CH_3SO_4). The solubility of the ionic liquids in heptane is low: 0.0058 and 0.0146 mole fraction [mebupy]BF$_4$, 0.0066 and 0.0087 mole fraction [emim]$C_2H_5SO_4$ and 0.0025 and 0.0188 mole fraction

[mmim]CH_3SO_4 at 313.2 and 348.2 K respectively. This means that not much IL is lost in the raffinate phase. The solubility of the ionic liquids in heptane increases somewhat with temperature, as can be seen comparing the results at 313.2 K and 348.2 K. The solubility of heptane in all ionic liquids is very low: 0.0095 (313.2 K) and 0.0118 (348.2 K) mole fraction in [mebupy]BF_4, 0.0051 mole fraction in [emim]$C_2H_5SO_4$ and 0.0013 mole fraction in [mmim]CH_3SO_4. This the cause of the scattering of the experimental selectivity data, especially with [mmim]CH_3SO_4 (Figure 6.10), since small errors in the analyses of heptane in the IL-phase will then have a large effect on the selectivity.

Due to the low solubility of heptane in [mmim]CH_3SO_4, the toluene/heptane selectivities are higher with this IL than for both other IL's, which have approximately the same toluene/n-heptane selectivity, as can be seen by comparing Figures 6.4, 6.9 and 6.10. However, since the solubility of toluene in [mmim]CH_3SO_4 is very low, the toluene distribution coefficient in this IL is also low. Considering the relatively high solubility of toluene in [mebupy]BF_4 and the high toluene/heptane selectivity, [mebupy]BF_4 is the best solvent for the aromatic/aliphatic separation of the three ionic liquids investigated. Comparing Tables 6.1, 6.2, 6.3 and 6.4, and Figures 6.3, 6.4, 6.9 and 6.10, it is obvious that the toluene/heptane selectivity is much higher with the three IL's investigated than with sulfolane.



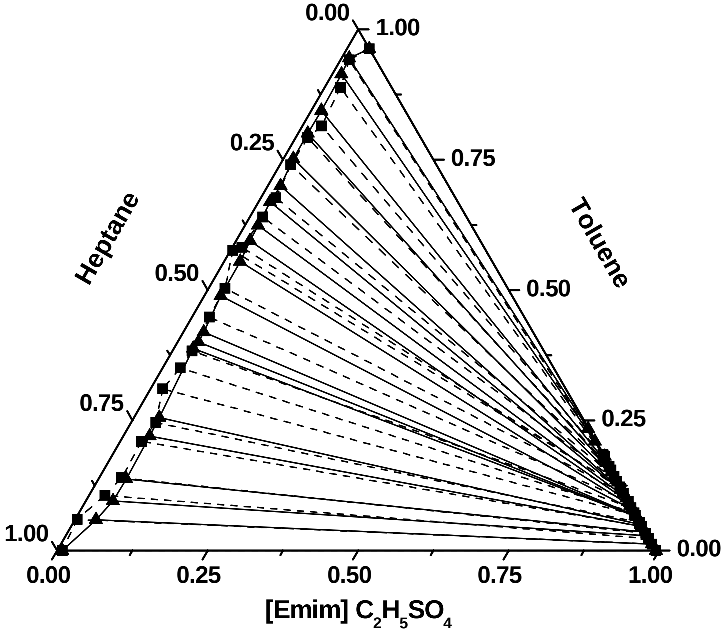


Figure 6.8. Tie lines for the ternary system toluene+n-heptane+[emim]$C_2H_5SO_4$ at T = 313.2 K (top) and 348.2 K (bottom). Experiments: ■, dashed lines; calculated: ▲, solid lines.

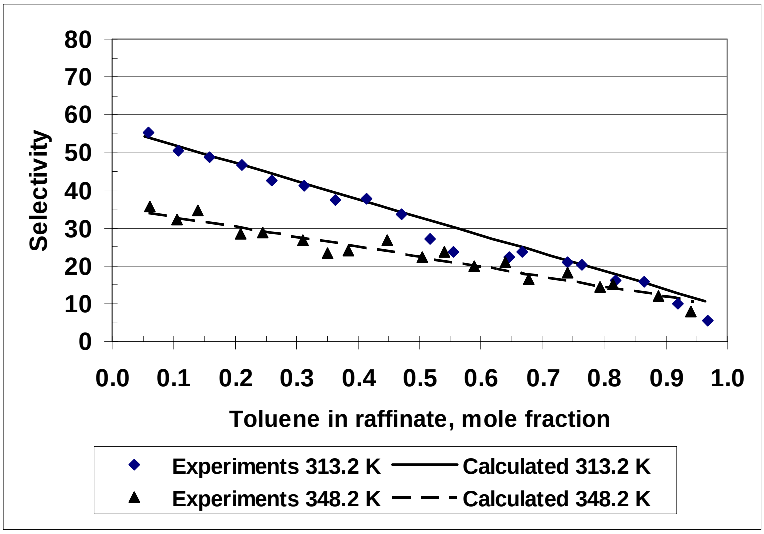


Figure 6.9 Experimental and calculated toluene/n-heptane selectivity with [emim]$C_2H_5SO_4$ at T = 313.2 and 348.2 K.

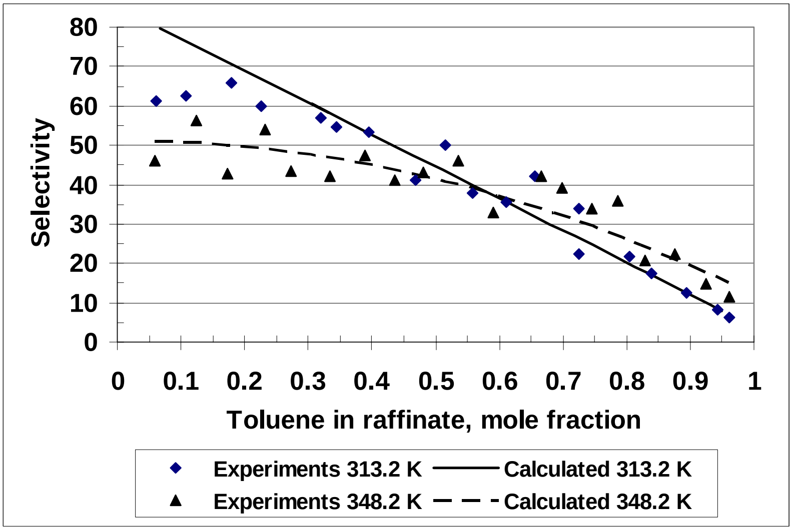
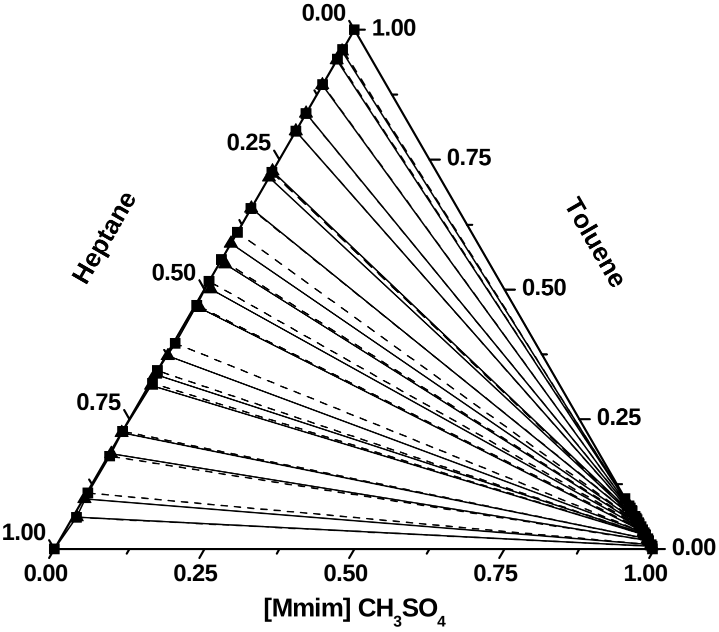


Figure 6.10. Experimental and calculated toluene/n-heptane selectivity with [mmim]CH_3SO_4 at 313.2 and 348.2 K.



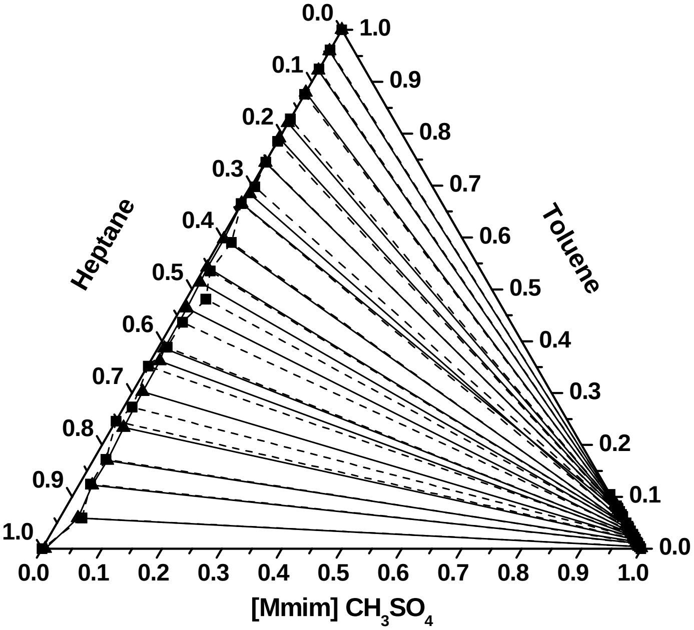


Figure 6.11. Tie lines for the ternary mixture toluene+n-heptane+[mmim]CH_3SO_4 at T=313.2 K (top) and 348.2 K (bottom). Experiments: ■, dashed lines; calculated: ▲, solid lines.

6.6.2 TERNARY MIXTURES WITH AN AROMATIC+AN ALIPHATIC HYDROCARBON +[MEBUPY]BF_4

Since the IL [mebupy]BF_4 was considered the best ionic liquid of the three ionic liquids investigated, further tests were carried out for other binary aromatic/aliphatic hydrocarbon mixtures, notably benzene/n-hexane, ethylbenzene/n-octane and m-xylene/n-octane. The experiments with benzene+n-hexane were carried out at T = 313.2 and 333.2 K, because of the low boiling point of n-hexane (342 K). The experiments with the two other mixtures were carried out at T = 313.2 and 348.2 K. The results can be found in the following Tables and Figures:

• Benzene+n-hexane+[mebupy]BF_4:	Table 6.5 and Figures 6.12 and 6.13
• Ethylbenzene+n-octane+[mebupy]BF_4:	Table 6.6 and Figures 6.14 and 6.15
• m-Xylene+n-octane+[mebupy]BF_4:	Table 6.7 and Figures 6.16 and 6.17

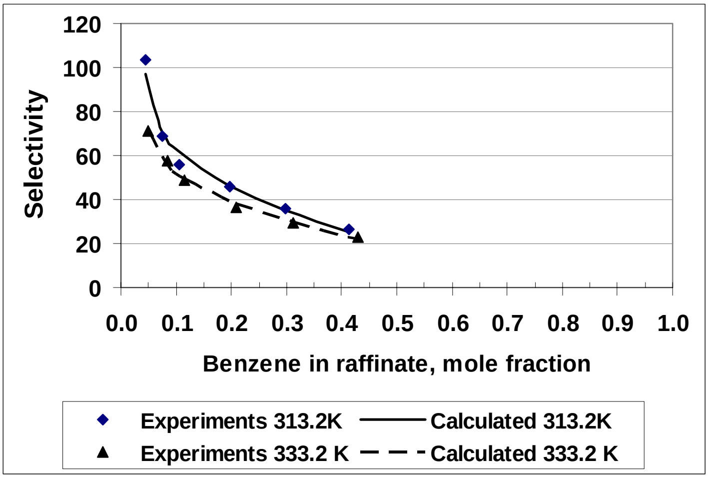
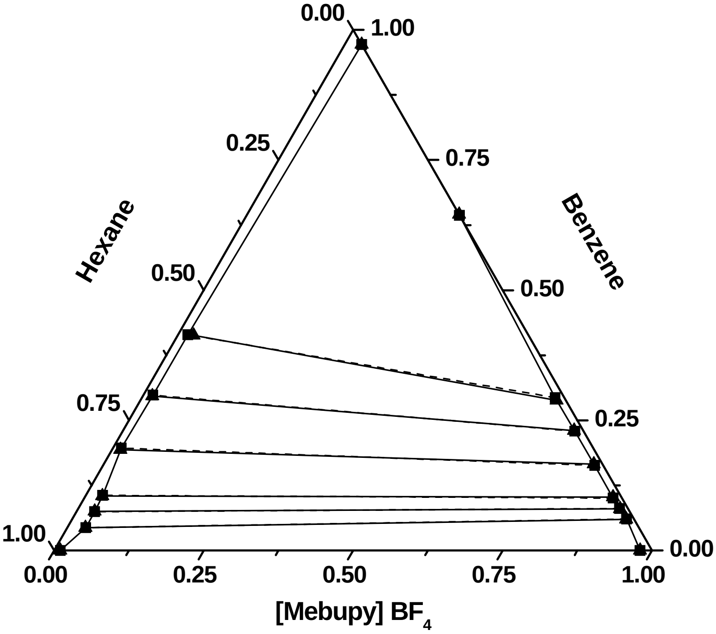


Figure 6.12. Experimental and calculated benzene/n-hexane selectivity with [mebupy]BF_4 at 313.2 and 333.2 K.



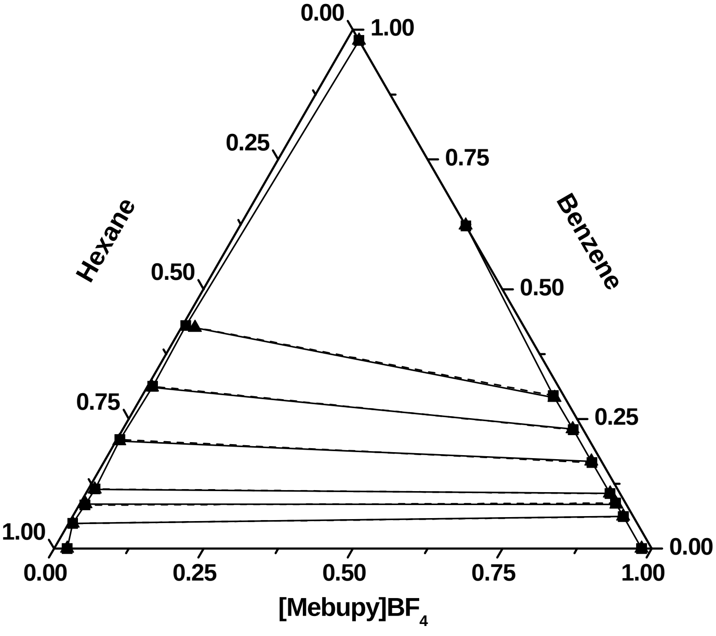
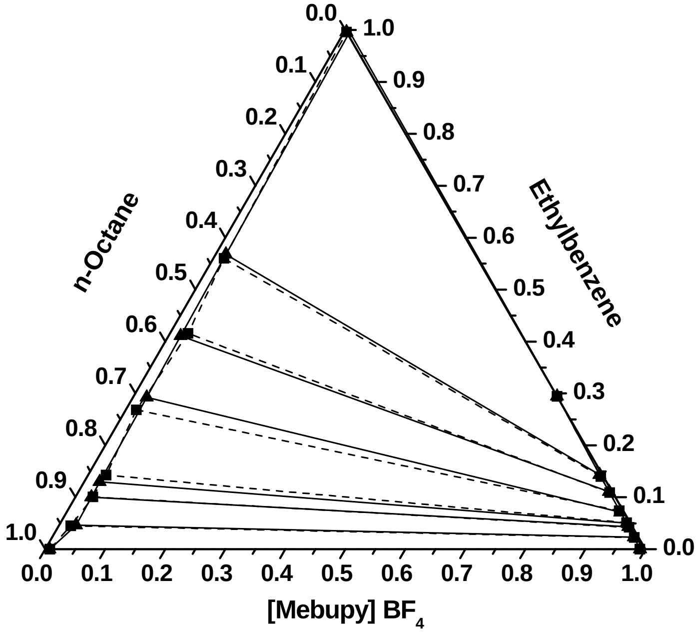


Figure 6.13. Tie lines for ternary mixture of benzene+n-hexane+[mebupy]BF4 at 313.2 K (top) and 333.2 K (bottom) and p = 0.1 MPa.
Experiments: ■, dashed lines; calculated: ▲, solid lines.



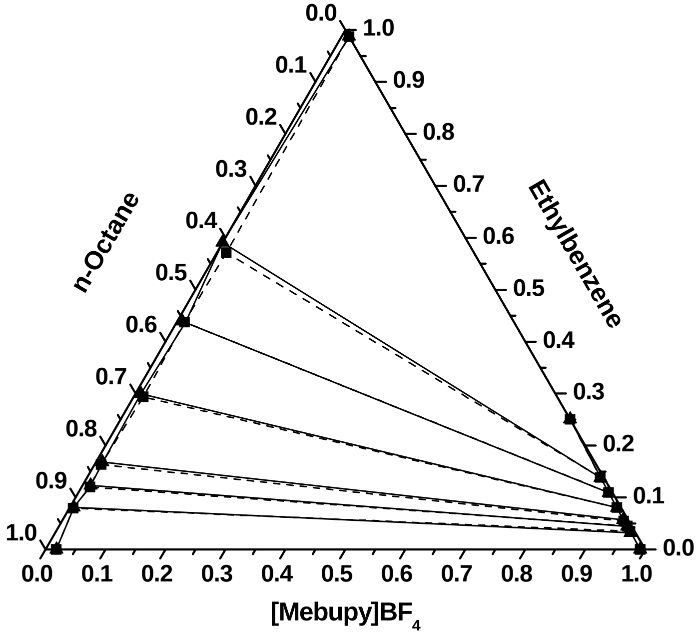


Figure 6.14. Tie lines for ternary mixture of ethylbenzene+n-octane+[mebupy]BF$_4$ at 313.2 K (top) and 348.2 K (bottom) and p = 0.1 MPa. Experiments: ■, dashed lines; calculated: ▲, solid lines.

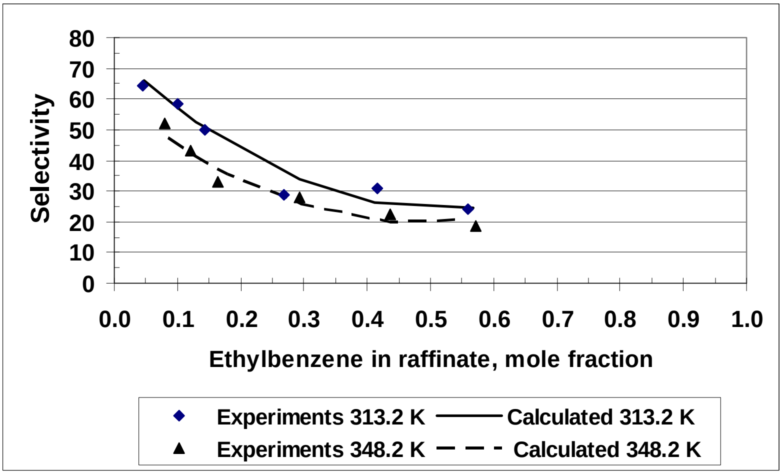


Figure 6.15. Experimental and calculated ethylbenzene/n-octane selectivity with [mebupy]BF$_4$ at 313.2 and 348.2 K.

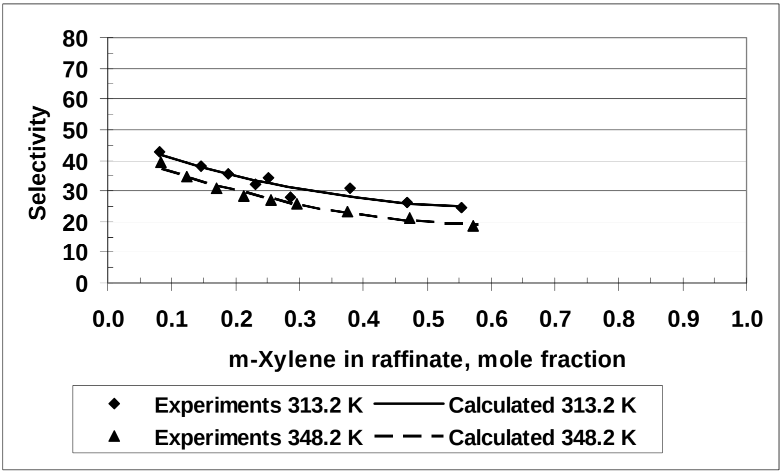
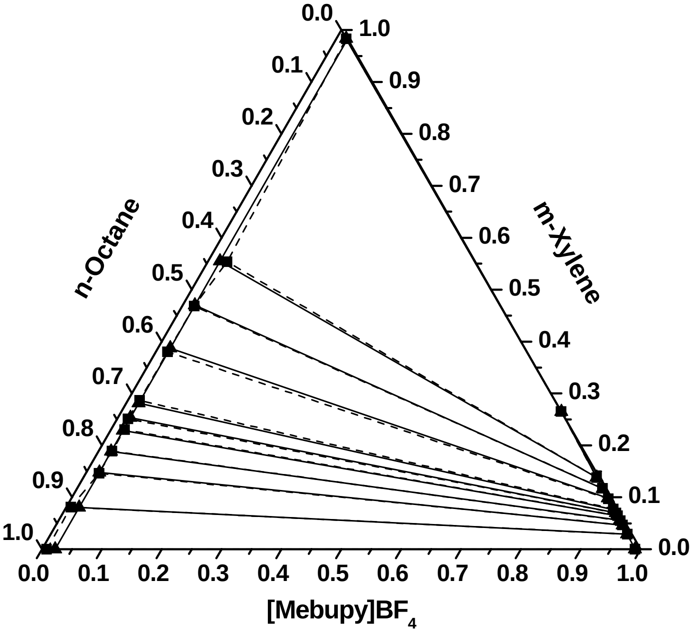


Figure 6.16. Experimental and calculated m-xylene/n-octane selectivity with [mebupy]BF$_4$ at 313.2 and 348.2 K.



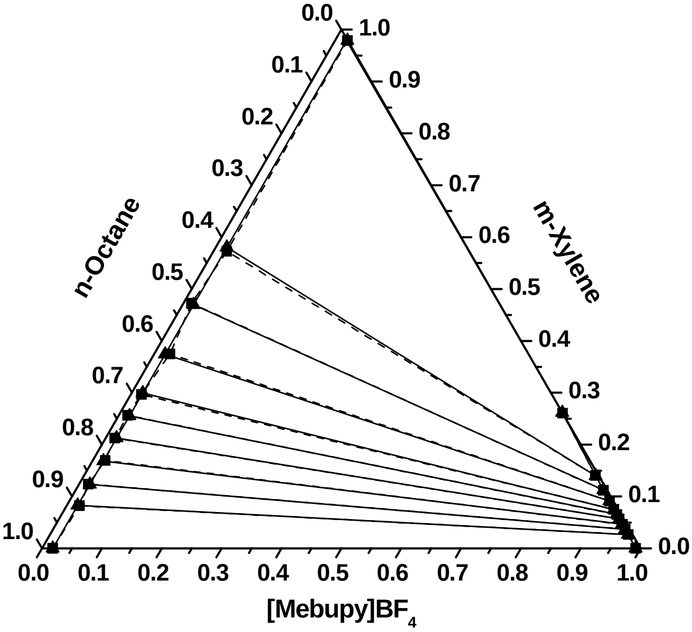


Figure 6.17. Tie lines for the ternary mixture of m-xylene+n-octane+[mebupy]BF$_4$ at 313.2 K (top) and 348.2 K (bottom) and p = 0.1 MPa.
Experiments: ■, dashed lines; calculated: ▲, solid lines.

Comparing the results of the four binary systems and [mebupy]BF_4, it can be seen that benzene has the highest solubility in this IL, notably 63 mole%. The solubility of toluene, ethylbenzene and m-xylene in [mebupy]BF_4 are around 44, 27 and 26 mole%, respectively. It can also be seen that n-hexane is more soluble in [mebupy]BF_4 than n-heptane or n-octane. The values are: 0.0199 and 0.0168 mole fraction n-hexane (at 313.2 and 333.2 K, resp.); 0.0095 and 0.0118 mole fraction n-heptane; 0.0094 and 0.0083 mole fraction n-octane at 313.2 and 348.2 K, respectively. The highest aromatic/aliphatic selectivity was observed for the binary system benzene/n-hexane, notably S = 104 at 6.04 mole% benzene at 313.2 K, due to the high solubility of benzene in [mebupy]BF_4. The benzene/n-hexane selectivity is significantly higher than the toluene/n-heptane, ethylbenzene/n-octane or m-xylene/n-octane selectivities, as is clear by comparing Figures 6.4, 6.12, 6.15 and 6.16.

6.6.3 COMPARISON OF EXPERIMENTAL AND CALCULATED DATA

As can be seen from the results as depicted in Figures 6.2, 6.6, 6.8, 6.11, 6.13, 6.14 and 6.17, the experimental and calculated data are very well consistent with each other. The tie-lines in the ternary diagrams coincide in many cases. Also, the experimental aromatic/aliphatic selectivity is very well described with the calculated data, as can be seen in Figures 6.3, 6.4, 6.9, 6.10, 6.12, 6.15 and 6.16. In Table 6.8, all interaction parameters determined by the NRTL model are given.

The root mean square deviation, rmsd, is defined as:

$$\mathrm{rmsd} = \left\{ \sum_{i} \sum_{l} \sum_{m} \left(x_{ilm}^{exp} - x_{ilm}^{calc} \right)^2 / 6k \right\}^{1/2} \tag{6.4}$$

where x is the mole fraction and the subscripts i, l and m provide a designation for the component, phase and the tie lines, respectively. The value k designates the number of interaction components. The values of the rmsd of the systems under investigation are listed in Table 6.9.

The values of rmsd in Table 6.9 provide a measure of the accuracy of the correlations. As can be inferred from these values, a good correlation of the experimental values with the NTRL model was obtained. Most of the rmsd values are below 0.01 with exceptions for toluene+n-heptane+[mebupy]BF_4 at 313.2 K and toluene+n-heptane+[emim]$C_2H_5SO_4$ at 348.2 K, caused by scattering in the experimental data points.

Table 6.8. Regressed NRTL Interaction Parameters for the description of the systems aromatic (1)+aliphatic (2)+ionic liquid (3) at (313.2 and 348.2) K.

Binary parameter	a_{ij}	a_{ji}	b_{ij}/K	b_{ji}/K	α_{ij}
Toluene+n-heptane (IL)	3.914	15.185	-880.0	-4673	0.3
Toluene+[mmim]CH_3SO_4	-34.065	43.029	6934	-8436	0.0074
n-Heptane+[mmim]CH_3SO_4	-25.010	14.476	6751	-2020	-0.3429
Toluene+[emim]$C_2H_5SO_4$	3.428	-0.815	737.2	51.69	0.1450
n-Heptane+[emim]$C_2H_5SO_4$	2.636	13.57	-1527	-2181	-0.3250
Toluene+[mebupy]BF_4	-11.704	21.989	4394	-6659	0.3519
n-Heptane+[mebupy]BF_4	-29.032	4.918	6364	1112	-0.0998
Benzene+n-hexane	0.0	0.0	208.04	-42.60	0.2999
Benzene+[mebupy]BF_4	4.075	-6.842	1536	1874	0.4474
n-Hexane+[mebupy]BF_4	1.567	4.877	458.23	-2620	-0.3137
Ethylbenzene+n-octane	2.413	30.671	-1256	-9852	0.3
Ethylbenzene+[mebupy]BF_4	9.699	-8.894	-3660	4264	0.380
n-Octane+[mebupy]BF_4	2.673	3.354	570.0	-2776	-0.185
m-Xylene+n-octane	-2.930	4.470	675.9	-843.9	0.3
m-Xylene+[mebupy]BF_4	7.651	-2.135	-349.5	78.52	0.0983
Toluene+ n-heptane (sulfolane)	0.269	-0.756	31.74	48.41	0.3
Toluene+ sulfolane	-1.057	0.428	1017	-165.7	0.3
n-Heptane+sulfolane	-0.039	-0.215	1365	1188	0.3

Table 6.9. Value of the root mean square deviation for the ternary mixtures of an aromatic (1)+ an alkane (2) + an ionic liquid (3).

Ternary system	Temperature, K	rmsd
Toluene+n-heptane+[mebupy]BF_4	313.2	0.0134
	348.2	0.0035
Toluene+n-heptane+[emim]$C_2H_5SO_4$	313.2	0.0091
	348.2	0.0134
Toluene+n-heptane+[mmim]CH_3SO_4	313.2	0.0084
	348.2	0.0088
Benzene_n-hexane+[mebupy]BF_4	313.2	0.0025
	333.2	0.0035
Ethylbenzne+n-octane+[mebupy]BF_4	313.2	0.0044
	348.2	0.0019
m-Xylene+n-octane+[mebupy]BF_4	313.2	0.0019
	348.2	0.0016
Toluene+n-heptane+sulfolane	313.2	0.0069
	348.2	0.0049

6.7 CONCLUSIONS

Ternary data for the systems toluene+n-heptane+an solvent were collected for the solvents sulfolane and the ionic liquids [mebupy]BF_4, [emim]$C_2H_5SO_4$ and [mmim]CH_3SO_4.

Ternary data for the systems aromatic+aliphatic hydrocarbon+[mebupy]BF_4 were gathered for the aromatic/aliphatic combinations of benzene/n-hexane at T = 313.2 and 333.2 K, ethylbenzene/n-octane and m-xylene/n-octane at T = 313.2 and 348.2 K.

All experimental data can very well be correlated with the NRTL model, as can be seen by comparing the experimental and the fitted data in the ternary diagrams for the seven systems under investigation. The rmsd values of the correlations are generally below 0.01.

The experimental and calculated aromatic/aliphatic selectivities are in good agreement with each other.

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APPENDIX 1.

TABLES OF EXPERIMENTAL TIE LINES OF AN AROMATIC+AN ALIPHATIC HYDROCARBON + SOLVENT

Table 6.1. Experimental tie lines of the system toluene (1) + n-heptane (2) + sulfolane (3) at T = 313.2 K and p = 0.1 Mpa.

n-Heptane-rich phase			Sulfolane-rich phase			Selectivity
Mole fractions						Exp.
1	2	3	1	2	3	
0.0335	0.9628	0.0037	0.0095	0.0088	0.9818	31.01
0.0591	0.9318	0.0091	0.0186	0.0095	0.9720	30.85
0.0845	0.9114	0.0042	0.0279	0.0102	0.9619	29.53
0.1149	0.8798	0.0054	0.0342	0.0099	0.9559	26.48
0.1503	0.8439	0.0059	0.0516	0.0118	0.9366	24.59
0.1772	0.8159	0.0069	0.0522	0.0102	0.9376	23.54
0.2521	0.7334	0.0145	0.0915	0.0139	0.8946	19.11
0.3064	0.6812	0.0125	0.1145	0.0156	0.8700	16.36
0.4142	0.5665	0.0193	0.1612	0.0173	0.8216	12.78
0.5149	0.4585	0.0266	0.2254	0.0213	0.7533	9.42
0.6001	0.3594	0.0405	0.2924	0.0261	0.6815	6.70
0.6437	0.3006	0.0557	0.3301	0.0333	0.6366	4.63

T = 348.2 K and p = 0.1 Mpa.

0.0330	0.9603	0.0067	0.0104	0.0121	0.9775	24.91
0.0967	0.8942	0.0091	0.0317	0.0155	0.9529	18.97
0.1178	0.8731	0.0091	0.0376	0.0153	0.9471	18.27
0.1878	0.7967	0.0155	0.0614	0.0160	0.9226	16.32
0.1922	0.7953	0.0125	0.0675	0.0172	0.9153	16.20
0.2506	0.7335	0.0159	0.0855	0.0180	0.8965	13.87
0.3005	0.6805	0.0189	0.1081	0.0207	0.8712	11.80
0.4073	0.5661	0.0266	0.1590	0.0214	0.8196	10.33
0.5032	0.4524	0.0444	0.2305	0.0272	0.7424	7.63
0.5933	0.3456	0.0612	0.3119	0.0375	0.6506	4.85
0.6274	0.2924	0.0802	0.3529	0.0443	0.6028	3.71

Table 6.2. Experimental tie lines of the system toluene (1) + n-heptane (2) + [mebupy]BF_4 (3) at T = 313.2 K and p = 0.1 Mpa.

n-Heptane-rich phase			[Mebupy]BF_4-rich phase			Selectivity
Mole fractions						Exp.
1	2	3	1	2	3	
0	1	0	0	0.0095	0.9905	-
0.0367	0.9633	0.0000	0.0162	0.0080	0.9758	53.09
0.0645	0.9306	0.0049	0.0290	0.0079	0.9631	52.91
0.1021	0.8979	0.0000	0.0448	0.0079	0.9473	49.63
0.1388	0.8590	0.0023	0.0594	0.0077	0.9328	47.67
0.1558	0.8442	0.0000	0.0730	0.0088	0.9182	45.22
0.2319	0.7681	0.0000	0.1112	0.0091	0.8798	40.57
0.3183	0.6817	0.0000	0.1481	0.0085	0.8433	37.13
0.4162	0.5838	0.0000	0.1916	0.0084	0.8000	32.05
0.5653	0.4347	0.0000	0.2630	0.0082	0.7288	24.63
0.6638	0.3362	0.0000	0.2982	0.0070	0.6948	21.48
0.7759	0.2241	0.0000	0.3538	0.0062	0.6400	16.43
0.9011	0.0989	0.0000	0.4496	0.0041	0.5464	12.14
1	0	0	0.5158	0	0.4842	-

T = 348.2 K and p = 0.1 Mpa.

0	0.9951	0.0049	0	0.0118	0.9882	-
0.0402	0.9598	0.0000	0.0166	0.0156	0.9678	26.15
0.0404	0.9531	0.0066	0.0182	0.0126	0.9692	34.26
0.0701	0.9299	0.0000	0.0334	0.0113	0.9553	39.32
0.1077	0.8923	0.0000	0.0483	0.0107	0.9410	37.43
0.1478	0.8522	0.0000	0.0669	0.0112	0.9218	34.33
0.2069	0.7804	0.0126	0.0929	0.0121	0.8950	28.98
0.2771	0.7229	0.0000	0.1008	0.0110	0.8882	23.87
0.3303	0.6600	0.0097	0.1455	0.0114	0.8431	25.59
0.4211	0.5719	0.0071	0.1836	0.0113	0.8050	22.04
0.5302	0.4668	0.0031	0.2307	0.0106	0.7587	19.15
0.5920	0.4080	0.0000	0.2420	0.0099	0.7481	16.85
1	0	0	0.4911	0	0.5089	-

Table 6.3. Experimental tie lines of the system toluene (1) + n-heptane (2) + [emim]$C_2H_5SO_4$ (3) at T = 313.2 K and p = 0.1 Mpa.

n-Heptane-rich phase			[Emim]$C_2H_5SO_4$-rich phase			Selectivity
Mole fractions						Exp.
1	2	3	1	2	3	
0	0.9934	0.0066	0	0.0051	0.9949	-
0.0590	0.9320	0.0090	0.0140	0.0040	0.9820	55.29
0.1070	0.8770	0.0160	0.0240	0.0039	0.9721	50.44
0.1590	0.8190	0.0220	0.0360	0.0038	0.9602	48.80
0.2120	0.7770	0.0110	0.0470	0.0037	0.9493	46.56
0.2600	0.7270	0.0130	0.0550	0.0036	0.9414	42.72
0.3131	0.6651	0.0218	0.0695	0.0036	0.9269	41.14
0.3634	0.6046	0.0144	0.0853	0.0039	0.9108	37.46
0.4139	0.5643	0.0139	0.1029	0.0038	0.8933	37.63
0.4705	0.5110	0.0185	0.0964	0.0031	0.9005	33.60
0.5174	0.4688	0.0137	0.1079	0.0036	0.8885	27.04
0.5542	0.4290	0.0168	0.1165	0.0038	0.8797	23.66
0.6446	0.3489	0.0065	0.1238	0.0030	0.8732	22.40
0.6664	0.3065	0.0114	0.1429	0.0029	0.8542	23.54
0.7396	0.2593	0.0011	0.1492	0.0025	0.8483	21.10
0.7646	0.2284	0.0070	0.1645	0.0024	0.8331	20.22
0.8179	0.1769	0.0099	0.1692	0.0022	0.8286	16.28
0.8646	0.1320	0.0034	0.1849	0.0018	0.8133	15.79
0.9189	0.0954	0.0089	0.1724	0.0013	0.8262	10.04
0.9694	0.0518	0.0084	0.2034	0.0008	0.7958	5.61
0.9675	0	0.0325	0.1790	0	0.8210	-

T = 348.2 K and p = 0.1 Mpa.

0	0.9913	0.0087	0	0.0052	0.9948	-
0.0601	0.9364	0.0035	0.0124	0.0054	0.9822	35.55
0.1059	0.8675	0.0266	0.0229	0.0058	0.9721	32.34
0.1395	0.8231	0.0375	0.0333	0.0056	0.9602	35.09
0.2096	0.7547	0.0357	0.0465	0.0059	0.9493	28.38
0.2456	0.7129	0.0415	0.0536	0.0054	0.9414	28.81
0.3102	0.6694	0.0204	0.0682	0.0055	0.9269	26.76
0.3504	0.6204	0.0292	0.0721	0.0055	0.9108	23.21
0.3829	0.5842	0.0328	0.0826	0.0052	0.8933	24.24
0.4482	0.5229	0.0289	0.0943	0.0041	0.9016	26.83
0.5033	0.4693	0.0274	0.1101	0.0046	0.8853	22.32
0.5391	0.4335	0.0274	0.1220	0.0042	0.8732	22.40
0.5876	0.3850	0.0274	0.1190	0.0039	0.8770	21.06
0.6401	0.3386	0.0213	0.1335	0.0034	0.8632	20.77
0.6766	0.2980	0.0254	0.1421	0.0038	0.8541	16.47
0.7399	0.2416	0.0185	0.1543	0.0028	0.8430	17.99
0.7922	0.1874	0.0203	0.1612	0.0026	0.8362	14.67
0.8150	0.1531	0.0320	0.1775	0.0022	0.8203	15.16
0.8888	0.0850	0.0262	0.1826	0.0015	0.8159	11.64
0.9417	0.0440	0.0143	0.1844	0.0011	0.8145	7.83
0.9627	0	0.0373	0.1808	0	0.8192	-

Table 6.4. Experimental tie lines of the system toluene (1) + n-heptane (2) + [mmim]CH_3SO_4 (3) at T = 313.2 K and p = 0.1 Mpa.

n-Heptane-rich phase			[Mmim]CH_3SO_4-rich phase			Selectivity
Mole fractions						Exp.
1	2	3	1	2	3	
0	1	0	0.0028	0	0.9972	-
0.0608	0.9325	0.0067	0.0052	0.0013	0.9936	61.35
0.1075	0.8902	0.0023	0.0083	0.0011	0.9895	62.48
0.1788	0.8183	0.0028	0.0158	0.0011	0.9826	65.74
0.2270	0.7725	0.0005	0.0194	0.0011	0.9786	60.02
0.3193	0.6768	0.0039	0.0268	0.0010	0.9721	56.81
0.3432	0.6568	0.0000	0.0285	0.0010	0.9700	54.54
0.3960	0.6007	0.0034	0.0316	0.0009	0.9675	53.26
0.4694	0.5278	0.0028	0.0365	0.0010	0.9625	41.04
0.5157	0.4843	0.0000	0.0427	0.0008	0.9565	50.12
0.5574	0.4426	0.0000	0.0478	0.0010	0.9512	37.96
0.6101	0.3899	0.0000	0.0501	0.0009	0.9490	35.58
0.6558	0.3442	0.0000	0.0560	0.0007	0.9433	41.99
0.7254	0.2746	0.0000	0.0591	0.0010	0.9400	22.37
0.7253	0.2747	0.0000	0.0628	0.0007	0.9365	33.98
0.8049	0.1951	0.0000	0.0629	0.0007	0.9360	21.78
0.8386	0.1614	0.0000	0.0721	0.0008	0.9271	17.35
0.8943	0.1057	0.0000	0.0740	0.0007	0.9253	12.49
0.9431	0.0569	0.0000	0.0830	0.0006	0.9164	8.35
0.9614	0.0386	0.0000	0.0790	0.0005	0.9207	6.34
1	0	0	0.0971	0	0.9029	-

T = 348.2 K and p = 0.1 Mpa.

0	0.9947	0.0053	0	0.0012	0.9988	-
0.0595	0.9036	0.0370	0.0039	0.0013	0.9948	45.56
0.1242	0.8571	0.0188	0.0101	0.0012	0.9886	58.08
0.1725	0.8072	0.0203	0.0126	0.0014	0.9860	42.11
0.2459	0.7534	0.0007	0.0184	0.0011	0.9805	51.25
0.2727	0.7133	0.0139	0.0219	0.0013	0.9768	44.06
0.3518	0.6466	0.0015	0.0266	0.0012	0.9722	40.74
0.3885	0.5972	0.0143	0.0278	0.0009	0.9713	47.48
0.4367	0.5473	0.0160	0.0346	0.0011	0.9643	39.42
0.4806	0.4862	0.0332	0.0404	0.0010	0.9583	40.87
0.5356	0.4519	0.0126	0.0434	0.0008	0.9558	45.77
0.5901	0.3889	0.0210	0.0423	0.0009	0.9562	30.97
0.6651	0.3349	0.0000	0.0499	0.0006	0.9495	41.88
0.6977	0.2965	0.0058	0.0616	0.0007	0.9377	37.40
0.7452	0.2540	0.0008	0.0622	0.0006	0.9372	35.33
0.7853	0.2143	0.0004	0.0659	0.0005	0.9336	35.97
0.8285	0.1715	0.0000	0.0716	0.0007	0.9277	21.17
0.8760	0.1240	0.0000	0.0768	0.0005	0.9227	21.74
0.9242	0.0758	0.0000	0.0787	0.0004	0.9209	16.14
0.9611	0.0389	0.0000	0.0826	0.0003	0.9171	11.14
1	0	0	0.1047	0	0.8953	-

Table 6.5. Experimental tie lines of the system benzene (1) + n-hexane (2) + [mebupy]BF$_4$ (3) at T = 313.2 K and p = 0.1 Mpa.

n-Hexane-rich phase			[Mebupy]BF$_4$-rich phase			Selectivity
Mole fractions						Exp.
1	2	3	1	2	3	
0	0.9895	0.0105	0	0.0199	0.9801	-
0.0439	0.9254	0.0307	0.0604	0.0123	0.9274	103.76
0.0747	0.8951	0.0302	0.0803	0.0140	0.9057	68.68
0.1059	0.8659	0.0282	0.1005	0.0147	0.8848	55.88
0.1967	0.7894	0.0139	0.1633	0.0143	0.8223	45.73
0.2987	0.6857	0.0157	0.2294	0.0146	0.7559	36.03
0.4143	0.5695	0.0162	0.2936	0.0154	0.6910	26.18
0.9716	0	0.0284	0.6438	0	0.3562	-

T = 333.2 K and p = 0.1 Mpa.

0	0.9781	0.0219	0	0.0168	0.9832	-
0.0488	0.9442	0.0070	0.0614	0.0167	0.9218	71.09
0.0841	0.9061	0.0098	0.0879	0.0164	0.8957	57.91
0.1146	0.8742	0.0112	0.1060	0.0165	0.8774	48.85
0.2100	0.7845	0.0055	0.1660	0.0170	0.8171	36.52
0.3129	0.6786	0.0085	0.2289	0.0168	0.7543	29.54
0.4300	0.5644	0.0056	0.2950	0.0169	0.6881	22.94
0.9793	0	0.0207	0.6218	0	0.3782	-

Table 6.6. Experimental tie lines of the system ethylbenzene (1) + n-octane (2) + [mebupy]BF$_4$ (3) at T = 313.2 K and p = 0.1 MPa.

n-Octane-rich phase			[Mebupy]BF$_4$-rich phase			Selectivity
Mole fractions						Exp.
1	2	3	1	2	3	
0	0.9921	0.0079	0	0.0094	0.9906	-
0.0452	0.9349	0.0199	0.0227	0.0073	0.9700	64.32
0.1006	0.8704	0.0290	0.0418	0.0062	0.9520	58.33
0.1425	0.8273	0.0302	0.0507	0.0059	0.9435	49.89
0.2681	0.7144	0.0176	0.0739	0.0068	0.9193	28.96
0.4159	0.5543	0.0298	0.1092	0.0047	0.8861	30.97
0.5602	0.4219	0.0179	0.1399	0.0044	0.8557	23.95
0.9961	0	0.0039	0.2942	0	0.7058	-

T = 348.2 K and p =0.1 MPa.

0	0.9822	0.0178	0	0.0083	0.9917	-
0.0794	0.9139	0.0067	0.0347	0.0077	0.9576	51.87
0.1205	0.8657	0.0139	0.0450	0.0075	0.9476	43.11
0.1637	0.8254	0.0108	0.0547	0.0084	0.9370	32.83
0.2937	0.6899	0.0164	0.0808	0.0068	0.9123	27.91
0.4374	0.5497	0.0129	0.1098	0.0062	0.8840	22.26
0.5716	0.4125	0.0159	0.1385	0.0054	0.8561	18.51
0.9874	0	0.0126	0.2503	0	0.7497	-

Table 6.7. Experimental tie lines of the system m-xylene (1) + n-octane (2) + [mebupy]BF_4 (3) at T = 313.2 K and p = 0.1 MPa.

n-Octane-rich phase			[Mebupy]BF_4-rich phase			Selectivity
Mole fractions						Exp.
1	2	3	1	2	3	
0	0.9921	0.0079	0	0.0094	0.9906	-
0.0810	0.9114	0.0076	0.0288	0.0076	0.9652	42.64
0.1463	0.8315	0.0221	0.0469	0.0070	0.9461	38.08
0.1888	0.7889	0.0223	0.0550	0.0065	0.9386	35.36
0.2303	0.7468	0.0229	0.0644	0.0065	0.9292	32.13
0.2513	0.7309	0.0178	0.0696	0.0059	0.9244	34.31
0.2865	0.6935	0.0200	0.0774	0.0067	0.9159	27.96
0.3803	0.6003	0.0195	0.0973	0.0050	0.8977	30.72
0.4684	0.5116	0.0201	0.1171	0.0049	0.8779	26.10
0.5535	0.4141	0.0324	0.1380	0.0042	0.8579	24.58
0.9833	0	0.0167	0.2654	0	0.7346	-

T = 348.2K and p = 0.1 MPa.

0	0.9822	0.0178	0	0.0083	0.9917	-
0.0822	0.8963	0.0215	0.0266	0.0074	0.9660	39.20
0.1237	0.8606	0.0157	0.0366	0.0073	0.9561	34.88
0.1695	0.8097	0.0208	0.0464	0.0072	0.9464	30.79
0.2123	0.7723	0.0154	0.0569	0.0073	0.9358	28.35
0.2565	0.7288	0.0147	0.0650	0.0068	0.9282	27.16
0.2969	0.6851	0.0179	0.0754	0.0067	0.9179	25.97
0.3750	0.5987	0.0264	0.0910	0.0062	0.9027	23.43
0.4727	0.5140	0.0133	0.1120	0.0058	0.8822	21.00
0.5727	0.4050	0.0223	0.1405	0.0053	0.8542	18.75
0.9791	0	0.0209	0.2607	0	0.7393	-

7 CONCEPTUAL PROCESS DESIGN FOR THE EXTRACTION OF AROMATIC COMPOUNDS WITH IONIC LIQUIDS

7.1 ABSTRACT

With the NRTL interaction parameters determined for the combinations of aromatic and aliphatic hydrocarbons with the ionic liquid [mebupy]BF_4, a process model could be developed using the flow sheeting program of ASPEN Plus 12.1. The results of the simulations for extraction of toluene from a 10% toluene in heptane feed were that for a toluene recovery of at least 98% and a heptane purity of more than 98%, twelve stages and an S/F ratio of 2.3 were required.

A conceptual separation process, consisting of an extractor and an evaporator only, was developed using a toluene/heptane mixture. It was not possible to develop a complete process, due to severe errors occurring in the flow sheeting program.

With the crude results of the process simulation of the separation of toluene from a mixed toluene/heptane stream, the investments of an extraction process with the ionic liquid [mebupy]BF_4 were estimated to be M€ 56, including an ionic liquid inventory of M€ 20, using an ionic liquid price of € 20/kg. The total investment costs in the sulfolane extraction were estimated by UOP, the supplier of this process, to be about M€ 86 for a naphtha feed of 300 ton/hr containing 10% aromatic hydrocarbons.

A high aromatic distribution coefficient is the key factor for a feasible extraction process with ionic liquids, provided the aromatic/aliphatic selectivity is high enough, around 30 or higher, because the price of the ionic liquids will probably always be higher than that of sulfolane. With an aromatic distribution coefficient of 1.8 and a reasonable aromatic/aliphatic selectivity the investment costs of the aromatic/aliphatic separation could be reduced to about M€ 25 – 30.

7.2 INTRODUCTION

The objective of this thesis was the development of a separation technology for the selective recovery and purification of aromatic compounds benzene, toluene, ethylbenzene and xylenes (BTEX) from liquid ethylene cracker feeds by means of extraction, adsorption/desorption on zeolites or a membrane separation with zeolite membranes, or a combination of these technologies. Most ethylene cracker feeds contain 10 – 25% of aromatic components, depending on the source of the feed (naphtha or gas condensate). The aromatic compounds are not converted to olefins and even small amounts are formed during the cracking process in the cracker furnaces [1]. Therefore, they occupy a part of the capacity of the furnaces and they put an extra load on the separation section of the C_5^+-aliphatic compounds. If a major part of the aromatic compounds present in the feed to the crackers could be separated up stream of the furnaces, it would offer several advantages: higher capacity, higher thermal efficiency and less fouling. The energy requirement of a thermal cracker is about 8.5 GJ/ton feed. The improved margin will be around € 20/ton of feed or € 48 million per year for a naphtha cracker with a feed capacity of 300 ton/hr, due to the lower operational costs, as was indicated by DSM.

The recovery of the aromatic hydrocarbons should be at least 98%. The purity of product streams, one containing mainly aliphatic hydrocarbons and the other aromatic hydrocarbons, should be at least 98%. The extraction of toluene from mixtures of toluene and heptane is used as a model for the aromatic/aliphatic separation. The solvent sulfolane is used as a benchmark for this separation.

In the previous chapters, several separation technologies were evaluated: pervaporation/vapour permeation of aromatic compounds with zeolite membranes and extraction of aromatic compounds from aromatic/aliphatic mixtures with aqueous cyclodextrins, ionic liquids and sulfolane. Membrane permeation is possible, but in order to arrive at a reasonable membrane area required to carry out this separation, the flux rates must be increased by at least a factor of 25 compared to the present flux rates. Also, the current cost price of the zeolite membranes must be lowered by a factor of 10. Since it is very probable that these two requirements are not being met, this option was not pursued further. Extraction of aromatic compounds from aromatic/aliphatic mixtures with aqueous cyclodextrins is possible, but the experimentally determined toluene distribution coefficients were far too low for industrial application. Therefore, also this separation was not considered suitable for this separation.

The application of ionic liquids for extraction processes is promising because of their non-volatile nature [2]. This facilitates solvent recovery using techniques as simple as flash distillation or stripping. A large number of ionic liquids with different cations and anions were tested and three suitable ionic liquids were identified for a more detailed screening for the separation of aromatic and aliphatic hydrocarbons, notably 1,3-dimethylimidazolium methylsulfate, 1-ethyl-3-methylimidazolium ethylsulfate and 4-methyl-N-butylpyridinium tetrafluoroborate ([mebupy]BF_4), because they all showed a higher aromatic/aliphatic selectivity than sulfolane. Since the ionic liquid [mebupy]BF_4 showed both a higher toluene distribution coefficient and a higher toluene/heptane selectivity ($D_{tol} = 0.44$ and $S_{tol/hept} = 53$ at 313.2 K) than sulfolane ($D_{tol} = 0.31$ and $S_{tol/hept} = 31$ at 313.2 K), this ionic liquid was selected for testing the extractive removal of toluene from a toluene/heptane mixture in a pilot scale RDC extraction column, as is described in Chapter 5. Since the feed stream to the naphtha cracker also contains other aromatic and aliphatic hydrocarbons than toluene and heptane, equilibrium tests with other aromatic/aliphatic combinations and [mebupy]BF_4 were carried out. The systems investigated were: benzene/n-hexane at T = 313.2 K and 333.2 K, ethylbenzene/n-octane at T = 313.2 K and 348.2 K and m-xylene/n-octane at T = 313.2 K and 348.2 K.

The contribution of this chapter is the development of a conceptual process design for the extraction of aromatic compounds with ionic liquids, for which estimations of the energy required, investment costs and variable costs can be made. In the previous chapter, the interaction parameters for use in the NRTL model were determined for four aromatic/aliphatic combinations with [mebupy]BF_4 and for toluene, n-heptane and sulfolane by regression the experimental equilibrium data with ASPEN Plus 12.1. With these interaction parameters, an extraction model using the flow sheeting program ASPEN Plus 12.1 is developed. Since ionic liquids are not present in the ASPEN data bank, the values of parameters for several physical properties of the ionic liquid [mebupy]BF_4 will have to be estimated, guessed or simply left out. This means that it is not possible to design a complete process for the recovery of aromatic and aliphatic hydrocarbons using this program.

The model will be validated with the experimental data for the extraction in the extraction pilot plant. Subsequently, the model is used to determine the optimal process conditions in extraction, such as the number of stages and the solvent-to-feed ratio. With these data, a conceptual process for the extraction of aromatic and aliphatic hydrocarbons is generated for which an economic evaluation of the process is made.

7.3 PILOT PLANT EXTRACTION COLUMN SIMULATION

7.3.1 EXTRACTION OF TOLUENE FROM TOLUENE/HEPTANE MIXTURES WITH SULFOLANE

The solvent sulfolane is used as a comparison for this separation, because it is one of the most common solvents for extraction of aromatic hydrocarbons from mixtures of aromatic and aliphatic hydrocarbons used in industry. In Table 7.1, the experimental data form the pilot plant described in Chapter 5 are compared with the calculated data from ASPEN Plus 12.1, using the NRTL interaction parameters determined in Chapter 6. Since it was established that the pilot plant had about three equilibrium stages, this number of stages was also used in the simulation with ASPEN Plus 12.1.

The sulfolane stream entering the pilot plant contains a small amount of toluene, because regenerated sulfolane was used for the extraction. Comparing the data in Table 7.1, it can be concluded that the pilot plant provides somewhat different results than the model with three stages, but the trends are similar. The sulfolane concentration in the raffinate in the pilot plant is higher than the calculated value, probably due to a not optimal operating top settler, as was explained earlier. The heptane concentration in the raffinate in the pilot plant experiments is about 96% and this value is also calculated by the model. The final toluene concentration in the raffinate is, however, lower and in the extract phase higher for the pilot plant experiments than calculated by the model. One explanation for the differences is that the mass balance of the data in the pilot plant has an error of about 13%. The differences in the toluene concentrations in the raffinate and extract phases may also be explained by the amount of water added to the sulfolane in the pilot plant. In order to decrease the viscosity of the sulfolane 5 v/v% water was added to the solvent stream. However, when in ASPEN Plus this 5 v/v% water was taken into account, the extraction column gave an even lower performance. This is also reported in literature: adding water to a solvent reduces its capacity and increases its selectivity. A third explanation for the differences between the pilot plant data and the calculated data could be that model uses CISTR's in series to simulate the experiments, while the RDC is a differential contactor.

Table 7.1. Input and output parameters for the extraction with sulfolane in three stages in the pilot plant and for the simulation in ASPEN Plus 12.1 in an extraction column.

Parameters	Feed	Sulfolane	Raffinate	Extract
Pilot plant				
T, °C	40	40	40	40
P, atm	1	1	1	1
Flow, kg/hr	5.8	24	n.a.	n.a.
Toluene, wt%	9.72	0.78	2.72	2.87
Heptane, wt%	90.28	-	96.02	0.79
Sulfolane, wt%	-	99.22	1.27	96.34
ASPEN				
T, °C	40	40	40	40
P, atm	1	1	1	1
Flow, kg/hr	5.8	24	5.411	24.389
Toluene, wt%	9.72	0.78	3.88	2.22
Heptane, wt%	90.28	-	95.82	0.21
Sulfolane, wt%	-	99.22	0.30	97.57

7.3.2 EXTRACTION OF TOLUENE FROM TOLUENE/HEPTANE MIXTURES WITH [MEBUPY]BF_4

In Table 7.2, the experimental and calculated data of the extraction with the ionic liquid [mebupy]BF_4 are shown. The experimental data from the extraction with the ionic liquid in the RDC in this table are different from those in Chapter 5. The amount of ionic liquid in the raffinate was too high in most of the experiments, due to a not optimal operating top settler, as was explained earlier. However, in one experiment there was a low concentration of ionic liquid in the raffinate and the results of this experiment are now shown in Table 7.2. The number of stages in the pilot plant for this extraction is about three with the highest rotation speed and the highest flux. Therefore, this number of stages was also used in the simulation.

The ionic liquid used for the extraction of toluene contains a small amount of toluene, because regenerated ionic liquid was used. Comparing the experimental and calculated data in Table 7.2, it can be concluded that the measured and calculated data are in reasonable agreement with each other. The largest differences are the concentration of the ionic liquid in the raffinate, the concentration of toluene and heptane in the extract phase. The average concentration of the ionic liquid in the raffinate phase measured with the equilibrium experiments was 0.001 mole fraction or 0.24 wt% and this value compares very well with the one measured during the extraction in the column (0.26 wt%). The experimental concentration of toluene in the extract phase is lower than expected. If the feed and raffinate phases in the pilot plant RDC were in equilibrium, a toluene concentration of 1.59 wt% in the raffinate was expected, instead of 1.38 wt%. The expected heptane concentration in the raffinate is 0.36 wt%, instead of 0.14 wt%. The expected concentrations of toluene and heptane in the raffinate phase are quite similar to the ones calculated with the flow sheeting program. Therefore, the ASPEN Plus flow sheeting program can be used to generate reasonably accurate data for process evaluation.

Table 7.2. Experimental and calculated data for the extraction of toluene with [mebupy]BF_4 in three stages.

Parameters	Feed	[mebupy]BF_4	Raffinate	Extract
Pilot plant				
T, °C	40	40	40	40
P, atm	1	1	1	1
Flow, kg/hr	10	20	n.a.	n.a.
Toluene, wt%	7.55	0.58	5.91	1.38
Heptane, wt%	92.45	-	93.83	0.14
[mebupy]BF_4, wt%	-	99.42	0.26	98.48
ASPEN				
T, °C	40	40	40	40
P, atm	1	1	1	1
Flow, kg/hr	10	20	9.728	20.272
Toluene, wt%	7.55	0.58	5.71	1.56
Heptane, wt%	92.45	-	94.28	0.36
[mebupy]BF_4, wt%	-	99.42	0.01	98.08

7.4 PROCESS SIMULATIONS

7.4.1 EXTRACTION OF TOLUENE FROM TOLUENE/HEPTANE MIXTURES WITH [MEBUPY]BF_4

Several process simulations were carried out with the ionic liquid [mebupy]BF_4 as the solvent, with the objective to establish the minimum solvent-to-feed ratio and the number of stages for a toluene recovery of at least 98% and a heptane purity in the raffinate of at least 98%.

The input data for all simulations were:

T = 40 °C
P = 1.013 bar
Toluene concentration in the feed: 10 wt%
Toluene content in the IL: 0 wt%

Only one temperature was used (40 °C), because the heptane distribution coefficient is lower at 40 °C than at higher temperatures, while the toluene distribution coefficient is relatively unaffected by the temperature in the range measured (40 and 75 °C).

In Table 7.3, the results of the simulation of the extraction with [mebupy]BF_4 in twelve stages is given. In order to achieve a toluene recovery of at least 98%, the number of stages must be higher than six, as can be seen in Figure 7.1. For a purity of heptane in the raffinate of at least 98%, the S/F ratio must be above 2.33 with three stages, 1.78 with six and 1.65 with ten or twelve stages, as can be seen in Figure 7.2. Since the S/F ratio will be in the range of 2.45 with ten stages or 2.31 with twelve stages in order to achieve a toluene recovery of at least 98%, the obtained heptane purity will always be higher than 99.5%.

In Figure 7.3, the heptane recovery in the raffinate is given. As the S/F ratio increases, the heptane recovery will decrease, because the solubility of heptane in the pure ionic liquid is 0.40 wt% (0.95 mole %) and the solubility of heptane in the extract stream is 0.36 wt% (0.83 mole %). The solubility of heptane in the mixture is lower, because also toluene is present in the extract stream.

In Figure 7.4, the purity of toluene in the extract stream is given on a solvent-free basis. Due to the fact that with an increasing S/F ratio the amount of heptane increases in the extract, the toluene purity will, of course, decrease. With an S/F = 2.45 and ten stages, the toluene purity in the extract stream will be 81.7% and with an S/F = 2.31 and twelve stages the toluene purity in the extract stream will be 82.6%.

Table 7.3. Results of the extraction of toluene and n-heptane with [mebupy]BF_4 in twelve stages.

	Feed	IL	Raffinate	Extract	Split ratio, %	
					Raff.	Extr.
Temperature, °C	40	40	43.9	41.3		
Pressure, bar	1.013	1.013	1.013	1.013		
Mole flow, kmol/hr	10	23.1	8.738	24.362		
Mass flow, kg/hr	993.347	5475.855	875.488	5593.715		
Volumetric flow, m^3/hr	1.452	4.664	1.313	4.803		
Mass flow, kg/hr						
Toluene	99.335		1.947	97.388	1.96	98.04
N-heptane	894.013		873.488	20.525	97.70	2.30
[mebupy]BF_4	0	5475.855	0.053	5475.802	0.00	100.00

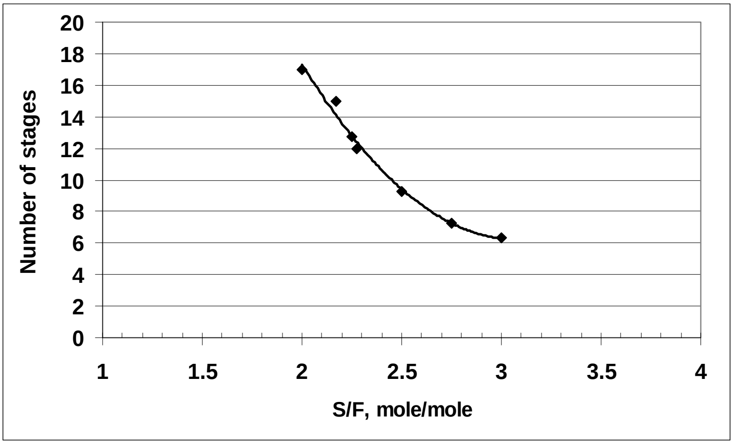

Figure 7.1. Number of stages vs. S/F ratio for the recovery of toluene of 98%.

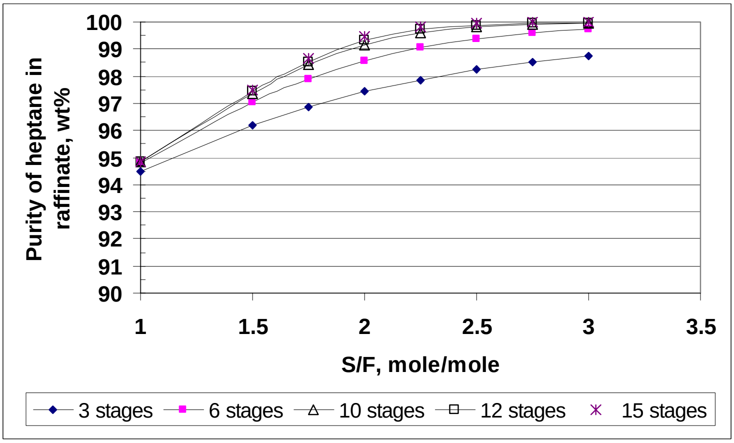

Figure 7.2. Purity of heptane in the raffinate.

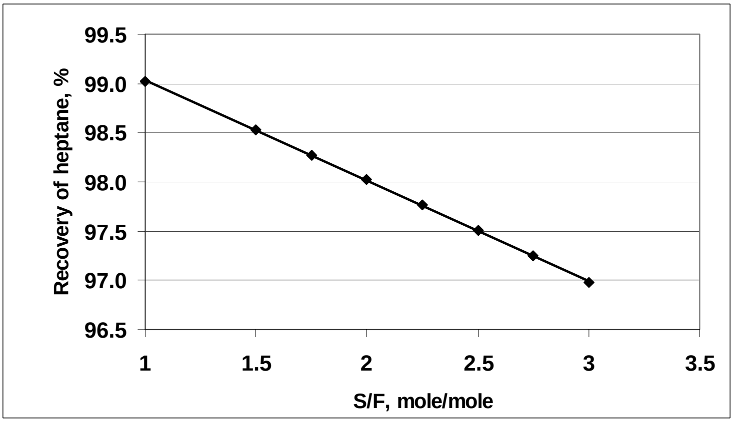

Figure 7.3. Recovery of heptane in the raffinate.

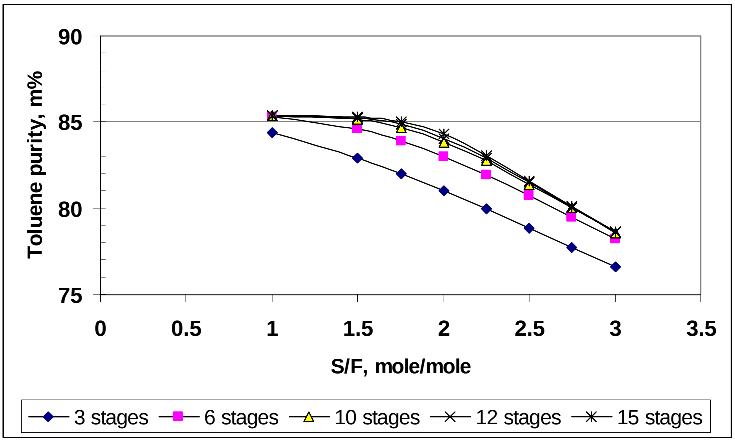

Figure 7.4. Toluene purity in the extract, solvent free basis.

For the toluene/heptane separation, an extraction with ten to twelve stages and a solvent-to-feed ratio of 2.45 to 2.31, respectively, is sufficient to obtain a toluene recovery of at least 98% and a heptane purity in the raffinate of at least 99.5%. The toluene purity in the extract stream on a solvent free basis is 81.7 to 82.6%. There is a very small loss of ionic liquid in the raffinate, 0.053 kg/hr, as can be seen from Table 7.3.

7.4.2 SEPARATION OF AROMATIC AND ALIPHATIC MIXTURES

The separation of a mixture of aromatic and aliphatic hydrocarbons can also be simulated with ASPEN Plus 12.1, since the NRTL-interaction parameters of the aromatic compounds benzene, toluene, ethylbenzene and m-xylene with the ionic liquid [mebupy]BF_4 were determined by regression of ternary equilibrium data, as was described in Chapter 6. Also, the interaction parameters of the aliphatic hydrocarbons n-hexane, n-heptane and n-octane with [mebupy]BF_4 and the interaction parameters of benzene/n-hexane, toluene/n-heptane, ethylbenzene/n-octane and m-xylene/n-octane were determined by regression of the equilibrium data, as was described in Chapter 6. The interaction parameters of the other combinations of aromatic and aliphatic hydrocarbons were not determined, but the NRTL parameters present in the ASPEN data bank (VLE-IG data) were used. The composition of the model naphtha feed is the following, in wt%:

benzene	1.8	n-hexane	43.2
toluene	3.3	n-heptane	15.8
ethylbenzene	2.0	n-octane	31.0
m-xylene	2.9		
Total	10		90

The total aromatic content is 10 wt% and the compositions of the aromatic hydrocarbons resemble that of a typical naphtha feed, see Table 1.1 in Chapter 1. The concentration of m-xylene in the model feed is that of all the xylenes present in the naphtha feed. The hexane concentration in the model feed is the sum of all the $C_4 – C_6$ - compounds in the naphtha feed, just as the heptane concentration is the sum of all the C_7 - compounds and octane the sum of all the C_8^+- compounds.

The results of the simulation with the flow sheeting program are given in Table 7.4. From this table, it is clear that the simulation of the aromatic/aliphatic separation gives erroneous results. The recovery of toluene in the extract stream is, even at an S/F mole ratio of 3, now 71.7%, instead of 98% in the toluene/heptane extraction. The toluene distribution coefficient at the bottom of the extraction column is lower than was measured with the equilibrium experiments with toluene and heptane only: 0.23 and 0.44, respectively. Apparently, the binary interaction parameters from the ASPEN data bank for those combinations which were not measured, are not suitable to model the separation of mixed aromatic and aliphatic hydrocarbons.

The loss of the ionic liquid in the raffinate with the mixed aromatic/aliphatic stream is higher than with the extraction of toluene from toluene/heptane mixtures, because the solubility of $[mebupy]BF_4$ in hexane is higher than in heptane. The average solubility of the ionic liquid in heptane/toluene mixtures is 0.001 mole fraction and the solubility in hexane is around 0.02 mole fraction.

Table 7.4. Results of the extraction of aromatic and aliphatic hydrocarbons with $[mebupy]BF_4$ in twelve stages.

	Feed	IL	Raffinate	Extract	Split ratio, %	
					Raff.	Extr.
Temperature, °C	40	40	48.3	42.8		
Pressure, bar	1.013	1.013	1.013	1.013		
Mole flow, kmol/hr	10	30	8.884	31.116		
Mass flow, t/hr	0.966	7.111	0.871	7.206		
Volumetric flow, m^3/hr	1.412	6.057	1.299	6.170		
Mass flow, kg/hr						
Benzene	17.385		0	17.385	0	100
Toluene	31.873		9.021	22.852	28.30	71.70
Ethylbenzene	19.317		1.439	17.878	7.45	92.55
M-xylene	28.009		7.792	20.217	27.82	72.18
N-hexane	417.245		397.015	20.23	95.15	4.85
N-heptane	152.603		147.677	4.926	96.77	3.23
N-octane	299.412		290.964	8.448	97.18	2.82
$[mebupy]BF_4$	0	7111.5	16.975	7094.525	0.24	99.76

Table 7.5. Distribution coefficients and selectivities.

Measured	Distribution coefficient	$S_{benzene}$	$S_{toluene}$	$S_{m\text{-}xylene}$	$S_{ethylbenzene}$
Benzene	0.9188	1	0.58	0.40	0.35
Toluene	0.5288	1.74	1	0.69	0.61
m-Xylene	0.3630	2.53	1.46	1	0.89
Ethylbenzene	0.3224	2.85	1.64	1.13	1
N-hexane	0.0198	46.32	26.66	18.30	16.25
N-heptane	0.0131	70.03	40.30	27.66	24.57
N-octane	0.0074	124.99	71.94	49.37	43.85
Calculated					
Benzene	0.3182	1	0.72	0.73	0.87
Toluene	0.2286	1.39	1	1.01	1.22
m-Xylene	0.2308	1.38	0.99	1	1.20
Ethylbenzene	0.2778	1.15	0.82	0.83	1
N-hexane	0.0165	19.25	13.83	13.96	16.81
N-heptane	0.0132	24.18	17.37	17.54	21.11
N-octane	0.0076	41.68	29.94	30.23	36.39

There was one equilibrium experiment carried out with a mixture of aromatic and aliphatic hydrocarbons. The results of this experiment and the calculated data from the simulation with an S/F = 3 and twelve stages are shown in Table 7.5. Comparing the measured and the calculated data, it is clear that the measured distribution coefficients are generally larger than the calculated ones. Also, the measured selectivities are higher than the calculated ones. From Table 7.5, it is also clear that experimental order of extraction is: benzene>toluene>m-xylene>ethylbenzene>n-hexane>n-heptane>n-octane. However, the order of extraction in the ASPEN simulation is: benzene>ethylbenzene> m-xylene>toluene>n-hexane>n-heptane>n-octane. According to the simulation, toluene is extracted to a lesser extent than ethylbenzene and m-xylene, hence the lower split ratio in the simulation. Therefore, it can be concluded that the NRTL interaction parameters used in the simulation did not generate the right results. Hence, more experimental data are required, especially in the range of 60 – 100% aromatic content, for the ternary combinations already investigated and for the generation of NRTL interaction parameters for the ternary combinations which were not yet investigated, such as benzene+heptane+IL or toluene+hexane+IL. Furthermore, it is necessary to determine more physical properties of the ionic liquid used over a wide range of temperatures, such as density, viscosity, surface tension and heat capacity, both for the pure ionic liquid and for combinations of the ionic liquid and the organic compounds to be separated. Presently, only limited data are available. Therefore, simulations of the extraction with mixtures of multiple aromatic and aliphatic hydrocarbons with an ionic liquid with the flow sheeting program of ASPEN Plus will probably generate erroneous results until these matters are resolved.

7.5 CONCEPTUAL PROCESS DESIGN

A conceptual process for the extractive separation of aromatic compounds from a mixed aromatic/aliphatic stream with the ionic liquid [mebupy]BF_4 was designed (Figure 7.5) in order to evaluate the separation process of aromatic and aliphatic hydrocarbons. Since the simulations with a model naphtha feed produced somewhat erroneous results, the conceptual design is calculated with a feed stream of toluene and heptane only. The process flow sheet was simulated in ASPEN Plus 12.1. The process specifications are given in Table 7.6 and the results of the simulation in Table 7.7.

Table 7.6. Operating specifications for the extraction column.

Operating pressure, bar	1.013
Operating temperature, °C	40
Number of stages	12
Feed stage	11
Recycle stage	12
S/F ratio, mole/mole	2.235

The feed stream with a flow rate of 300 ton/hr with 10 wt% toluene enters the extraction column at the bottom (stage 11) and the ionic liquid with a flow rate of 1600 ton/hr enters the extraction column at the top. The raffinate contains heptane with a purity of 99.6 wt% and is fed to a wash column, where the small amount of ionic liquid (0.006 wt% or 17.4 kg/hr) in the raffinate is removed by a water wash. The final product, a heptane product stream with a purity of 99.6 wt% leaves the column at the top. The bottom product, containing water and ionic liquid, is recycled to the extraction column (stage 12).

Table 7.7. Process simulation with simplified flow sheet.

	Feed	IL	Raffinate	Extract	Aromatic product	Reflux
T, °C	40	40	43.9	41.3	40	40
P, bar	1.013	1.013	1.013	1.013	1.013	1.013
Total flow, t/hr	300	1600	268	1675	32	44
Toluene, t/hr	30	-	1	68	29	39
Heptane, t/hr	270	-	267	7	3	4
IL, t/hr	-	1600	0.0174	1600	-	-
Mass concentrations, %						
Toluene	10	-	0.43	4.07	89.99	89.99
Heptane	90	-	99.56	0.45	10.01	10.01
IL	-	100	0.006	95.48	-	-

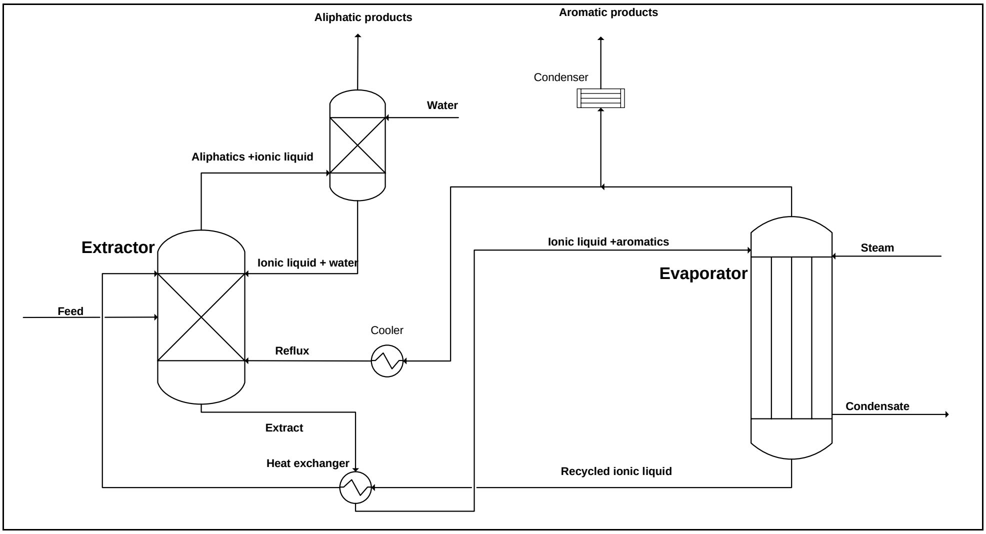

Figure 7.5. Conceptual flow scheme for the separation of aromatic and aliphatic hydrocarbons.

The extract phase from the extraction column contains ionic liquid, toluene and a small amount of heptane. This stream is heated and fed to an evaporator or stripper, where the volatile hydrocarbons are evaporated or stripped by for instance nitrogen from the non-volatile ionic liquid. The evaporator operates under reduced pressure, 0.3 bar, and at a temperature of 135 °C. The ionic liquid is then cooled to 40 °C and recycled to the extraction column. The top stream of the evaporator or stripper is partly recycled to the bottom of the extraction column in order to increase the purity of the extract stream. The aromatic product stream has a flow of 29 t/hr and contains 89.99 % toluene and 10.01 % heptane. The recovery of toluene in the extraction column is 98.3 %.

7.5.1 LOSS OF IONIC LIQUID IN THE RAFFINATE

The presence of ionic liquid in the raffinate will be unacceptable in an industrial plant, because the ionic liquid can cause contamination of other processes and fouling of equipment. Therefore, the ionic liquid must be completely recovered from the raffinate. The ionic liquid [mebupy]BF_4 is soluble in water and, hence, water can be used to wash the raffinate for removal of the ionic liquid. However, the effect of water on the extraction process must be determined. One preliminary experiment showed that the toluene distribution coefficient and the toluene/heptane selectivity increased with [mebupy]BF_4 containing 1 – 5% water.

If the ionic liquid is not recovered from the raffinate stream, the annual loss of ionic liquid for the toluene/heptane extraction will be 8000 $*$ 17.4 kg/hr = 139 ton/year. With a future price of the ionic liquid of around € 20/kg, the loss will be M€ 2.8/year. However, with a naphtha feed, the loss of the ionic liquid will probably be higher because the ionic liquid is more soluble in hexane than in heptane. Even if the ionic liquid price is around € 1/kg, the loss will also from an economic point of view be unacceptable.

7.5.2 PURITY AND RECOVERY OF PRODUCTS

The recovery of the toluene is 98.3% and the purity of the heptane product is 99.6%. The purity of toluene in the aromatic product stream is still too low (90%). This is caused by the fact that heptane dissolves slightly in the ionic liquid phase. In order to increase the purity of the aromatic product stream, several options are possible. The first one is to choose an ionic liquid in which aliphatic hydrocarbons do not or almost not dissolve. A second option is to install an extractive stripper which removes the heptane selectively from the extract stream and a third option is to purify the product stream after the evaporation.

In order to obtain an aromatic purity of at least 98%, the ionic liquid must have a high aromatic/aliphatic selectivity, notably S = 440 or higher. If the toluene distribution coefficient remains 0.44, as is the case with [mebupy]BF_4, then the required aliphatic distribution coefficient should be 0.001 or lower. Of all the ionic liquids investigated, none has a heptane distribution coefficient of 0.001. There are three ionic liquids of the ones investigated which show a heptane distribution coefficient lower than 0.002, notably [emim]HSO_4: 0.00104, [mmim]CH_3SO_4: 0.00120 and [emim]SCN, which was not reported before: 0.00192. The ionic liquid [emim]SCN has also a very high toluene/heptane selectivity: 139.2 at 40 °C. Since the highest selectivity measured was around 140, achieving a selectivity of 440 in order to obtain an aromatic purity of at least 98% is unrealistic. Therefore, the two other options for a higher aromatic purity must be investigated further. However, the process simulation including an extractive stripper in the ASPEN flow sheeting program produced erroneous results and a severe error was reported: most stages in the extractive stripper received no flow and the extractive stripper was bypassed. Since it was not known what exactly caused the error and since more detailed data were not available at this stage, only the extractor and the evaporator were used in the simulation.

7.5.3 COMPARISON OF THE SULFOLANE AND IONIC LIQUID EXTRACTION PROCESSES

The sulfolane process is one of the most used processes for the separation of aromatic and aliphatic hydrocarbons. Therefore, the cost of an extraction with an ionic liquid is estimated by comparing the sulfolane process with an ionic liquid process. According to UOP, the extraction of aromatics from naphtha cracker feed is feasible with the Sulfolane (Figure 7.6) or Carom processes [3]. Normally, this process is used for feed streams containing 68% aromatics or more (reformed petroleum naphtha, pyrolysis gasoline or coke oven light oil). UOP has made a rough estimate for the Sulfolane process for a feed stream of 300 t/hr with 10% aromatics in the feed.

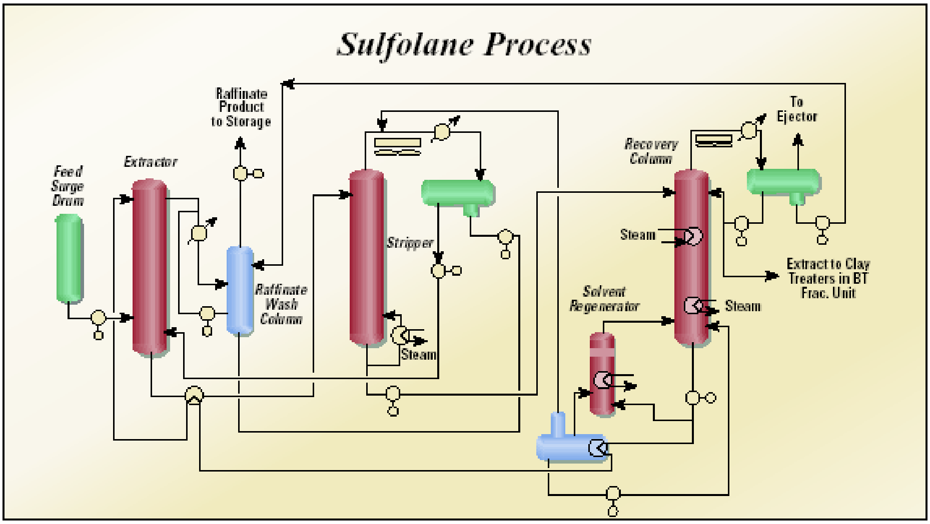

Figure 7.6. UOP Sulfolane process[3].

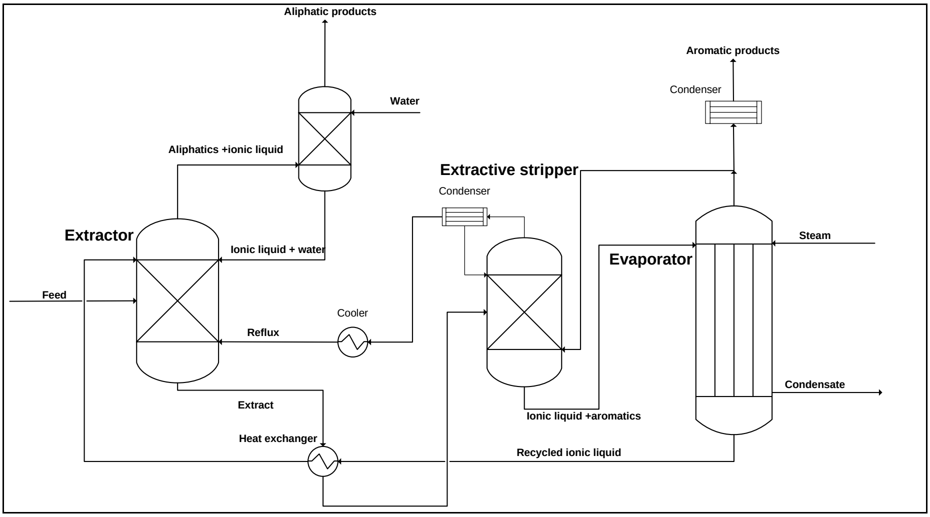

Figure 7.7. Conceptual flow scheme for the separation of aromatic and aliphatic hydrocarbons.

Comparing the extraction processes with sulfolane and with [mebupy]BF_4, including the extractive stripper (Figure 7.7), it can be stated that the extraction column will have about the same dimensions, because the flow of the ionic liquid is about the same as that with sulfolane. The solvent to feed ratio on mole basis is lower with the ionic liquid than for sulfolane, but the molecular weight of the ionic liquid is almost twice as high as that of sulfolane and, therefore, the about same amount of solvent is used on a weight basis.

The most expensive equipment in the sulfolane process is not the columns, vessels etc., but the heat exchangers, reboilers and coolers, which make up almost 65% of the total investment. The investment in the columns is about 28% of the total investment costs. The high share of the heat equipment is caused by the following reasons: the extraction is carried out at 100 °C, the extractive stripper and the recovery column operate at 190 °C and sulfolane, which has a boiling point of 287.3 °C, is taken from the top of the solvent regenerator column. These high temperatures require the use of high-pressure steam at several places, as can be seen in Figure 7.6. The high temperature has also another adverse effect: sulfolane decomposes at high temperatures and the decomposition products cause unacceptably high corrosion in the paraffin stripper and aromatics stripper if oxygen intrusion occurs [4].

In Table 7.8, extraction with sulfolane and with the ionic liquid [mebupy]BF_4 is compared. Of course, the estimations for the extraction with [mebupy]BF_4 are crude in this stage and they will require more detailed investigation. But due to the fact that an ionic liquid has no vapour pressure, the regeneration of this solvent is much simpler than that of, for instance, sulfolane and low pressure steam can be used. Instead of two distillation columns required for the recovery of the aromatics and the regeneration of the solvent sulfolane, only one flash column or stripper with for instance nitrogen is required for the ionic liquid process. Therefore, also the process temperatures are lower in the ionic liquid process than in the sulfolane process. The amount of energy required in the ionic liquid process is calculated by the flow sheeting program of ASPEN.

Assuming that the investments in the heat exchangers, reboilers and coolers are proportional to the duty, the investment in heat equipment in the ionic liquid process will then be about 20% of that of the sulfolane process. In the IL process, the recovery column and the solvent regenerator are replaced by one flash column and it is assumed that the investment in the extractor, extractive stripper and the flash column for the IL process will be lower than the investment in the extractor, extractive stripper, sulfolane regenerator column and recovery columns of the sulfolane process. The investments in the other equipment will be in the same range, because the flows will also be in the same range. The total investment in equipment in the IL process is then estimated to be about 45% of that of sulfolane. In Table 7.9, the investments of these two processes are compared. The costs of the inventory sulfolane and the ionic liquid are entered as separate items.

The annual variable capital costs (depreciation, 10%; ROI, 20% and other investment related costs, such as maintenance, 10%) are estimated to be 40% of the investment costs. The energy costs for the sulfolane process are estimated by UOP to be € 10/ton feed, which will amount to M€ 24/year.

Table 7.8. Comparison between extraction with sulfolane and IL.

Equipment	Sulfolane	T, °C	[mebupy]BF_4	T, °C
Extractor	x	100	x	40
Raffinate wash	x	40	x	40
Extractive stripper	x	190	x	135
Recovery column	x	190	-	-
Solvent regenerator	x	190	-	-
Flash column or stripper	-	-	x	135
Total heat load, MW	160		32	

Table 7.9. Estimated investment and variable costs in M€.

	Sulfolane (UOP)	[mebupy]BF_4
Materials and labour	46	21
Engineering	15	6
Inside battery limits	61	27
Outside battery limits	20	9
Solvent inventory	5	20
Total investment costs	86	56
Annual costs, 40% of total I	34.4	22.4
Energy costs	24	5
Total annual costs	58.4	27.4

The improved margin for removing the aromatic hydrocarbons from the feed to the naphtha cracker is € 20/ton feed, which amounts to M€ 48/year, resulting in a loss of around M€ 10/year for the sulfolane process and a profit of M€ 20/year for the ionic liquid process. Therefore, it is obvious that the sulfolane extraction process is not in operation anywhere for removing aromatic compounds from streams containing relatively low concentrations of aromatic compounds. Although the calculations for the investment and energy costs for the IL process are very crude, the margin between the sulfolane and the IL process is large enough to recommend further research in this process.

7.5.4 OPPORTUNITIES FOR PROCESS IMPROVEMENT

The ionic liquid [mebupy]BF_4 is not the most optimal ionic liquid for this separation, because the capacity compared to that of sulfolane is not that much higher. From the screening tests in Chapter 4, the ionic liquid [mebupy]CH_3SO_4 showed a higher toluene distribution coefficient, but a somewhat lower toluene/heptane selectivity than [mebupy]BF_4 ([mebupy]CH_3SO_4: $D_{tol} = 0.61$ on mole basis and $S_{tol/hept} = 42.3$; [mebupy]BF_4: $D_{tol} = 0.44$ and $S_{tol/hept} = 53$). If the ionic liquid [mebupy]CH_3SO_4 is used in the extraction, about 20% less ionic liquid on weight basis will be required. This means smaller equipment and less ionic liquid inventory. The required amount of ionic liquid can even decrease more if ionic liquid [emim]$AlCl_4$ from BASF could be used ($D_{tol} = 1.795$ and

$S_{tol/hept}$ = 69.6 at 40 °C). The amount of ionic liquid can then be decreased by about 70% on weight basis, resulting in smaller equipment and less ionic liquid inventory. Due to the higher toluene/heptane selectivity, the amount of heptane in the extract phase will be lower, also resulting in smaller equipment. However, the ionic liquid [emim]$AlCl_4$ cannot be used in practise because it reacts violently with water. The same argument is valid for the ionic liquid [bmim]$AlCl_4$, which shows a toluene distribution coefficient of 1.65 and a toluene/heptane selectivity of 38.5 at 40 °C. However, this proves that ionic liquids exist with high toluene distribution coefficients.

In Figure 7.8, the toluene/heptane selectivity as function of the toluene distribution coefficient for sulfolane and the ionic liquids [emim]SCN, [mebupy]BF_4, [mebupy]CH_3SO_4. [bmim]$AlCl_4$ and [emim]$AlCl_4$ at 40 °C is shown. Further research is required to identify ionic liquids which show high aromatic distribution coefficients and a reasonable aromatic/aliphatic selectivity. In Table 7.10, the estimated investment and total annual costs for the different ionic liquids are shown. From this table, it is obvious that a higher aromatic distribution coefficient has a tremendous effect on the feasibility of the extraction process with ionic liquids.

From Figure 7.9 can be seen that with a toluene distribution coefficient of about 0.2 the annual costs for an ionic liquid extraction are still about M€ 10 lower than the improved margin for the naphtha cracker. The investment and annual costs will probably not decrease much more at toluene distribution coefficients above 2.

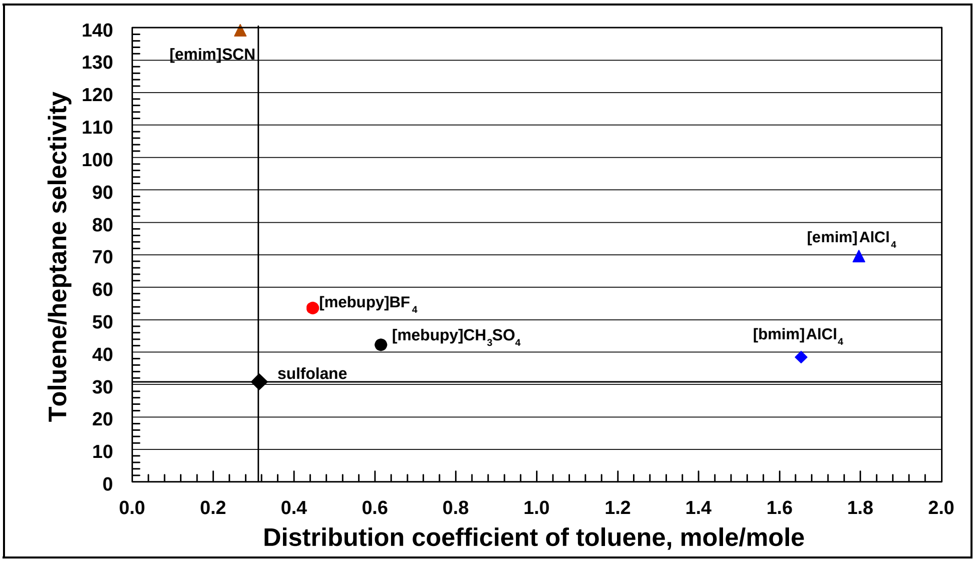

Figure 7.8. Toluene/heptane separation with selected ionic liquids, 10 v/v% toluene, T = 40 °C.

Table 7.10. Estimated investment and total annual costs for extraction with ionic liquids in M€.

	[mebupy]BF_4	[mebupy]CH_3SO_4	[bmim]$AlCl_4$	[emim]$AlCl_4$
Hardware investments	36	32	23	21
IL inventory	20	16	7	6
Total investments	56	48	30	27
Annual capital costs	22.4	19.2	12	10.8
Energy	5	5	5	5
Total annual costs	27.4	24.2	17	15.8

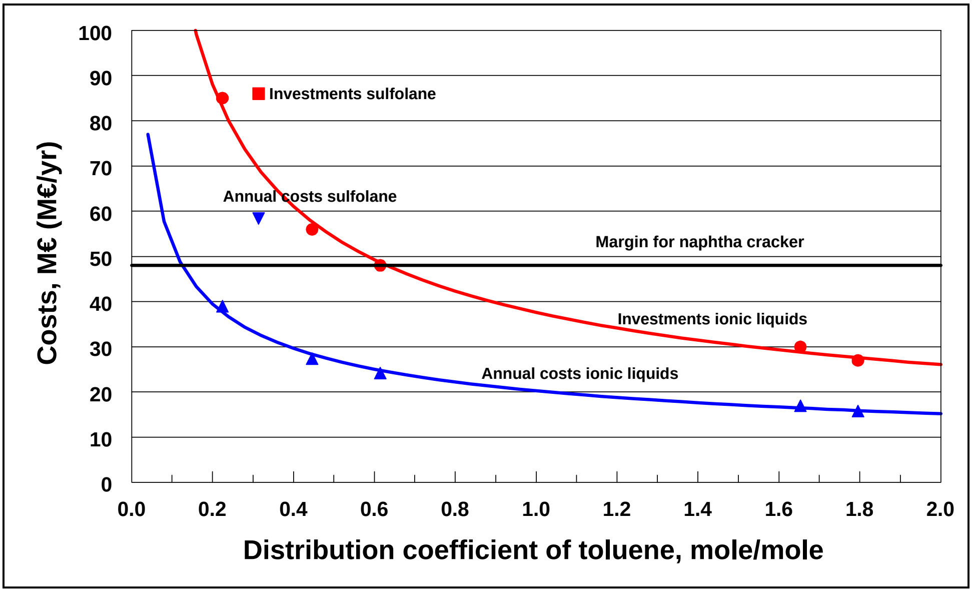

Figure 7.9. Investment and variable costs for extraction with ionic liquids.

7.6 CONCLUSIONS

A high aromatic distribution coefficient is the key factor for a feasible extraction process with ionic liquids, provided the aromatic/aliphatic selectivity is high enough, around 30 or higher, because the price of the ionic liquids will probably always be higher than that of sulfolane.

The toluene/n-heptane extraction can be simulated by the flow sheeting program in ASPEN Plus 12.1. The results of this simulation and the actual results obtained in a pilot plant extraction column are in reasonable agreement with each other. However, the simulation of an extraction with a mixture of aromatic and aliphatic hydrocarbons resembling the composition of a naphtha feed gave somewhat erroneous results.

With the process simulation, the following results are obtained: heptane purity of 99.6%, toluene recovery of 98.3% and toluene purity of 90%. The requirements for the heptane purity and the toluene recovery are met, but the toluene purity is still too low.

The complete removal of the ionic liquid from the raffinate stream is a prerequisite for an economically feasible aromatic/aliphatic separation. For water-soluble ionic liquids, washing with water is a possibility, but this must be experimentally proven.

The energy requirement for an extraction process with an ionic liquid as solvent is much lower than that with sulfolane, due to the lower process temperatures in the extraction with the ionic liquid process and the simpler recovery of the ionic liquid.

The investment costs are about 35% lower for the extraction with [mebupy]BF_4 than with sulfolane. If ionic liquids are used with higher aromatic distribution coefficients, the investment costs can even be decreased by almost 70% compared to the sulfolane process.

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8 CONCLUSIONS AND OUTLOOK

8.1 CONCLUSIONS

The objective of this study was the development of a separation technology for the selective recovery and purification of aromatic compounds benzene, toluene, ethylbenzene and xylenes (BTEX) from liquid ethylene cracker feeds. Most ethylene cracker feeds contain 10 – 25% of aromatic components, depending on the source of the feed (naphtha or gas condensate). The aromatic compounds are not converted to olefins and even small amounts are formed during the cracking process in the cracker furnaces [1]. Therefore, they occupy a part of the capacity of the furnaces and they put an extra load on the separation section of the C_5^+-aliphatic compounds. If a major part of the aromatic compounds present in the feed to the crackers could be separated up stream of the furnaces, it would offer several advantages: higher capacity, higher thermal efficiency and less fouling.

The current technologies for the separation of aromatic and aliphatic hydrocarbons are either suitable for aromatic concentrations of 20% or more, such as extraction, extractive distillation and azeotropic distillation, or show low aromatic/aliphatic selectivities and/or have low capacities. Therefore, it was investigated in this thesis whether and how the performance of adsorption/desorption, membrane separation and extraction could be drastically improved at low aromatic content by using new separating agents. After a short literature study, adsorption/desorption was discarded for further work, because suitable zeolite adsorbents, for instance X and Y types, would result in tremendous technical problems during desorption and its scale-up to large capacities appeared unfavourable.

8.1.1 MEMBRANE SEPARATION

Zeolite membranes exhibit high aromatic selectivities and are preferred for organic/organic separations because of their robustness in organic solvents and their application at higher temperatures. Furthermore, desorption is much less difficult as in adsorption/desorption, because a partial pressure difference is the driving force in pervaporation and vapour permeation. The performed feasibility study indicated that, although benzene/cyclohexane selectivities are high enough (S = 20 – 260), the flux rates are still too low for a feasible separation. Therefore, the flux rates must be increased by at least a factor of 25 to obtain a reasonable membrane area for this separation. The increase in flux is, in principle, possible, if the used zeolite membrane top layer of 30 μm can be reduced to a defect-free thickness of 1.2 μm. Another problem for zeolite membrane permeation is their current price, which can vary from € 2,000 – 10,000/m^2. Even when a 25 times increase in membrane flux is considered, the pay back time for this process with these prices for zeolite membranes will be 10 years or more. Combined with the fact that a defect-free top layer of 1.2 μm is extremely difficult to manufacture, it is clear that zeolite membrane permeation is presently not a feasible option.

8.1.2 EXTRACTION

The only way to improve the economic feasibility of extraction technology at low aromatics content is the development of new solvent systems that exhibit a dramatically higher aromatic distribution coefficient and/or a higher aromatic/aliphatic selectivity than the known solvents, such as sulfolane. To achieve this objective, aqueous solutions of cyclodextrins (CD) seemed a possible solution, because cyclodextrins can incorporate several organic compounds and the separation of the aqueous solution of complexed cyclodextrins from the organic feed is simple. Cyclodextrins are not soluble in organic liquids, but cyclodextrin derivatives are highly soluble in water. Unfortunately, the aromatic distribution coefficients (D = 0.05 for toluene at [m-ß-CD (1.7)] = 0.22 mole/L and D = 0.023 for o-xylene at [HP-ß-CD (0.8)] = 0.25 mole/L) and the aromatic/aliphatic selectivity were low (S = 6 for toluene/heptane with m-ß-CD (1.7)). Therefore, aqueous cyclodextrin solutions are not suitable for the extraction of aromatic compounds from aliphatic hydrocarbons.

Aromatic hydrocarbons are reported to have low activity coefficients at infinite dilution in several ionic liquids, while aliphatic hydrocarbons show high activity coefficients in the same ionic liquids. This means that ionic liquids are promising solvents for the extraction of aromatic hydrocarbons from aliphatic hydrocarbons. Several ionic liquids were screened on basis of activity coefficients at infinite dilution, solubility and extraction data. The cations were mostly imidazolium and pyridinium, and the anions were hydrogensulfate, methylsulfonate, methylsulfate, ethylsulfate, dimethylphoshate, diethylphosphate and tetrafluoroborate. A shorter alkyl group on the imidazolium cation of the ionic liquids generally results in a more aromatic character of the ionic liquid and, hence, to a higher toluene distribution coefficient and to a higher toluene/heptane selectivity. With an aromatic cation, such as pyridinium, both the toluene distribution coefficient and the toluene/heptane selectivity were higher than with other IL’s. IL’s with HSO_4^--anions showed a low toluene distribution coefficient and IL’s with a BF_4^--anion usually showed a relatively high toluene distribution coefficient.

Based on initial screening results, [mmim]CH_3SO_4, [emim]$C_2H_5SO_4$ and [mebupy]BF_4 were chosen for more detailed equilibrium tests, because the toluene distribution coefficient and/or the toluene/heptane selectivity were high. Of these ionic liquids, [mebupy]BF_4 appeared to be the most suitable, because of a combination of a high toluene distribution coefficient (D_{tol} = 0.44) and a high toluene/heptane selectivity ($S_{tol/hept}$ = 53). Therefore, with [mebupy]BF_4 also extraction experiments with other aromatic/aliphatic combinations (benzene/n-hexane, ethylbenzene/n-octane and m-xylene/n-octane) were carried out. It was found that the distribution coefficients of the aliphatic hydrocarbons decrease with increasing length of the compound and just as the distribution coefficients of the aromatic compounds decrease with an increasing alkyl chain on the benzene ring. Furthermore, the aromatic/aliphatic selectivities (benzene/hexane, toluene/heptane, ethylbenzene/octane and m-xylene/octane) using [mebupy]BF_4 increased with decreasing concentration of the aromatic compound in the raffinate phase. The aromatic/aliphatic selectivities were all in the same range of each other. Therefore, the selection of toluene/heptane as a model for aromatic/aliphatic separations is a valid one. In order to generate a conceptual process design, the obtained liquid-liquid equilibrium data were correlated with the NRTL model in ASPEN Plus 12.1. Comparison of the experimental and fitted data demonstrated that excellent agreement between the calculated and experimental data was obtained with rmsd values generally below 0.01.

Evaporating the organic compounds from the extract phase in a rotary evaporator at 75 °C could easily regenerate the ionic liquids used. Visible inspection of the NMR spectra of both the original ionic liquid and the regenerated product showed no differences between the two samples. The results of the equilibrium experiments were obtained with regenerated ionic liquids. The ionic liquid used in the pilot RDC was regenerated in the extraction column by stripping with nitrogen at 80 °C. Furthermore, several ionic liquids were continuously heated in an oven at 150 °C during 7.5 weeks and no degradation of the ionic liquid could be detected. This confirmed the assumption that the regeneration and recycling of the ionic liquids are indeed simple.

Since the ionic liquid [mebupy]BF_4 showed both a higher toluene distribution coefficient and a higher toluene/heptane selectivity than sulfolane, this ionic liquid was selected for testing the extractive removal of toluene from a toluene/heptane mixture in a pilot scale Rotating Disc Contactor (RDC) extraction column. The pilot plant RDC provided good results for the toluene/heptane separation: small droplets were formed with the ionic liquid and the column capacity was high. The extraction with the ionic liquid was more or less comparable to the extraction with sulfolane in the RDC. Due to the higher toluene distribution coefficient, lower S/F ratios were required to extract the same amount of toluene with the ionic liquid, while compared to sulfolane a 10% higher flux (volumetric throughput) and similar mass transfer efficiency was obtained. Also, the feed flow with [mebupy]BF_4 was higher (10 kg/hr) than with sulfolane (5.8 kg/hr) as the solvent. The best performance (highest toluene extraction efficiency) was obtained at the highest rotation speed used (643 rpm) during the extraction experiments. At a flux of 10 m^3/m^2.hr excellent hydrodynamic behaviour was observed and about three equilibrium stages were contained in the 1.80 m high active section of the column.

With the NRTL interaction parameters determined for the combinations of aromatic and aliphatic hydrocarbons with the ionic liquid [mebupy]BF_4, a process model could be developed using the flow sheeting program of ASPEN Plus 12.1. The model was validated with the experimental data from the RDC pilot plant for both sulfolane and the ionic liquid [mebupy]BF_4 as the solvent. Therefore, the ASPEN Plus flow sheeting program could be used to generate reasonably accurate data for a process evaluation. Several simulations for the extraction of toluene from a toluene (10%)/heptane mixture with the flow sheeting program were carried out in order to determine the optimal number of stages and the S/F ratio. For a toluene recovery of at least 98% and a heptane purity of more than 98%, twelve stages and an S/F ratio of 2.3 were required.

With the crude results of the process simulation of the separation of toluene from a mixed toluene/heptane stream, an economic evaluation of the process was made and compared to the extraction process with sulfolane. The total investment costs in the sulfolane extraction were estimated by UOP, the supplier of this process, to be about M€ 86 for a naphtha feed of 300 t/hr, containing 10% aromatic hydrocarbons. The extraction process with the ionic liquid [mebupy]BF_4 was estimated to be M€ 56, including an ionic liquid inventory of M€ 20. The lower investment in the ionic liquid process is mainly due to the fact that the regeneration of the ionic liquid is much simpler than that of sulfolane. Since also the energy costs are lower, the total annual costs with the ionic liquid process are estimated to be M€ 27.4, compared to M€ 58.4 for sulfolane. The improved margin for the naphtha cracker, if 10% aromatics are removed from the feed stream, is M€ 48/year. Therefore, it is obvious that a sulfolane process is not in operation to remove aromatics from a naphtha feed stream anywhere, but that an ionic liquid process seems to have a distinct advantage.

The aromatic distribution coefficient has a larger impact on the investment costs than the aromatic/aliphatic selectivity because the price of the ionic liquid will probably remain high. A higher aromatic distribution coefficient means a lower S/F ratio and, hence, a lower investment in the ionic liquid inventory. If the ionic liquids [mebupy]CH_3SO_4 or [emim]$AlCl_4$ are used as a solvent, which both have a higher toluene distribution coefficient than [mebupy]BF_4, the total investment costs could decrease to M€ 48 or even M€ 27, respectively. However, the ionic liquid [emim]$AlCl_4$ cannot be used in industrial practice because it reacts violently with water.

The main conclusion of the process evaluation is that ionic liquids which show a high aromatic distribution coefficient with a reasonable aromatic/aliphatic selectivity could reduce the investment costs of the aromatic/aliphatic separation to about M€ 25 – 30.

8.2 OUTLOOK

8.2.1 SELECTION OF IONIC LIQUIDS

One of the major conclusions of the conceptual process design was that a high toluene distribution coefficient is essential for an economic feasible extraction process with ionic liquids. Therefore, improved ionic liquids with an aromatic distribution coefficient on mole basis of 1 or higher with a reasonable aromatic/aliphatic selectivity of around 30 or higher must be found. One of the tools to obtain such an ionic liquid is the use of the program COSMO-RS (COnductor-like Screening MOdel for Real Solvents), which can predict activity coefficients at infinite dilution of ionic liquids with variations of the cation and the anion [2-6]. A significant difference between Group Contribution Methods (GCM), like UNIFAC, and COSMO is that the predictive ability of GCM's is dependent on the availability of group interaction parameters, whereas COSMO-RS is only limited by the availability of individual component parameters. On the basis of the preselection by COSMO-RS, the most promising ionic liquids can then be tested in equilibrium experiments.

Furthermore, essential physical data of the ionic liquids used in the extraction of aromatic and aliphatic hydrocarbons must be known, either from own experiments or from literature data, which then can be used in process simulations in ASPEN Plus.

8.2.2 EQUIPMENT

The measured concentration of the ionic liquid in the raffinate phase in almost all of the experiments in the pilot plant RDC was too large compared to the equilibrium data. Apparently, the phase separation in the top settler is not complete during the extraction. Therefore, the experiments in the extraction column should be repeated after the top settler section is adapted so that a correct phase separation can take place. The best performance (highest toluene extraction efficiency) was obtained at the highest rotation speed (643 rpm) that was applied for the extraction experiments in the pilot RDC column. However, not many experiments were carried out at the highest rotation speed of 810 rpm and, therefore, these experiments must be repeated in order to establish if indeed the performance increases compared to experiments at lower rotations. Also, the internals of the column could be replaced by, for instance, Kühni internals, which consists of a turbine mixer and stator plates. The Kühni contactor can be designed to obtain minimal axial mixing, constant hold-up of the dispersed phase, and maximum capacity for each column section. This design capability provides a large degree of flexibility and an overall high efficiency for the apparatus [7].

The number of equilibrium stages in the present 1.8 m long column was about three. With an additional element, the number of stages will be increased and, possibly, a more accurate column performance could be determined.

The regeneration of the ionic liquid, which was used in the pilot plant column, should be improved, as not all the toluene is removed with the present procedure. Besides, the present procedure takes a long time, about 20 hours.

After the pilot plant column has been adapted, an extraction with a model naphtha feed should be carried out in order to determine the performance of the column with this feed.

8.2.3 PROCESS SIMULATIONS

The flow sheeting program of ASPEN Plus 12.1 produced sometimes erroneous results. One of the possible reasons is that the ionic liquids are not present in the ASPEN data bank and that not all the necessary physical properties are known. The interaction parameters present in the ASPEN data bank for combinations of aromatic and aliphatic hydrocarbons are different from those determined by regression of equilibrium data. However, the interaction parameters obtained by regression of equilibrium data also produces sometimes erroneous results. Hence, more experimental data are required, especially in the range of 60 – 100% aromatic content, for the ternary combinations already investigated and for the generation of NRTL interaction parameters for the ternary combinations which were not yet investigated, such as benzene+heptane+IL or toluene+hexane+IL. With an improved set of interaction parameters and necessary physical properties data, the simulation with the model naphtha feed should be carried out without any errors. The conceptual process design could then also be optimised and a more accurate analysis of the process could be obtained.

8.2.4 INDUSTRIAL APPLICATION OF IONIC LIQUIDS

For the acceptance of ionic liquids in industrial practice, it is a prerequisite that enough toxicological data about ionic liquids are known. Without these data, no ionic liquid will be applied in industry [8,9].

Furthermore, the current price of ionic liquids, ranging from € 200 – 3,000/kg is too high for industrial use. Of course, the current prices are based on laboratory use and, hence, the scale of production is small. A reasonable price would be in the range of € 10 – 25/kg. BASF, who is a major producer of imidazole, one of the primary products for ionic liquids, has indicated that it is indeed possible to reach that level if ionic liquids are produced on a large scale [10,11].

For the application of ionic liquids for the removal of aromatic hydrocarbons from naphtha feed, the recovery of the ionic liquids from the raffinate phase must be investigated further, as the presence of ionic liquids in the naphtha cracker feed will not be acceptable and because loss of expensive ionic liquid involves loss of capital and their non-volatile nature will cause tremendous fouling.

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CURRICULUM VITAE

Geert Wytze Meindersma was born on 4th of August 1947 in Tilburg. At the age of 3, his family moved to Djakarta (Java, Indonesia). In February 1955, his family moved back to The Netherlands. He attended four different primary schools: in Surubaja (Java, Indonesia), Oisterwijk, Haaksbergen and Deventer, and two secondary schools: in Deventer and Gorinchem. After his graduation from Gymnasium Camphusianum in Gorinchem in 1965, he was an exchange student for one year in Dearborn Heights, Michigan, USA. He started to study Chemical Engineering at the Technical University of Delft in 1966 and graduated in 1974 on "The influence of pH and oxygen pressure on the morphology of Penicillium *chrysogenum* during fermentation." From 1974 to 1981, he was employed by AVEBE in Veendam, a potato starch company, where he started to work with membranes. His main achievement was the development of membrane filtration in the potato starch industry from laboratory scale (0.36 m^2) to industrial scale (6200 m^2). In 1981, he continued his work in membranes at DSM Research, where he became the membrane specialist. He worked with almost all membrane processes: membrane filtration (MF, UF, NF and RO), gas separation, pervaporation and electrodialysis. He was involved in the development of several industrial membrane processes at DSM: purification of hydrogen, ultrafiltration for the recovery of enzymes in the aspartame process, separation of propylene and nitrogen for a polypropylene plant, nanofiltration for the separation of salts and low-molecular weight organic compounds, microfiltration for the recovery of a catalyst and microfiltration for the recovery and purification of a conducting polymer. From May 1998, he worked in the Sector Industrial Services of DSM Research with the main focus on water management.

In July 2000, he started to work as an assistant professor and as a PhD student in the Separation Technology group of the University of Twente, supervising projects on membrane technology and presently also on ionic liquids.

Wytze is married to Rolanda since March 1970, and they have one son, two daughters and two granddaughters.