Invited Review
Application of Task-specific Ionic Liquids for Intensified Separations

G. Wytze Meindersma[1,*], **Lara M. Galán Sánchez**[2], **Antje R. Hansmeier**[1], and **André B. de Haan**[1]

[1] Department of Chemical Engineering and Chemistry/Process Systems Engineering,
   Eindhoven University of Technology, Eindhoven, The Netherlands
[2] University of Twente, Enschede, The Netherlands

Summary. Ionic liquids offer tremendous opportunities to intensify reactions and separations in process technologies by tuning their physical and chemical properties. Several ionic liquids are suitable for the separation of aromatic and aliphatic hydrocarbons. CO_2 absorption behavior was influenced by the functionalized chains appended to the room temperature ionic liquid (RTIL) cation. Ionic liquids seem able to combine the chemical features of amine solutions with the characteristic advantages of the physical solvents used for CO_2 absorption.

Keywords. Aromatic/aliphatic hydrocarbon separation; CO_2 absorption; Design of ionic liquids; Solvent effect; Simulation.

Introduction

The use of ionic liquids (ILs) in separations can be advantageous because of their specific properties, such as a negligible vapor pressure, high liquidus range, and thermal stability. Presently, there are more than 1000 different ILs commercially available, but it has been shown that there are $>10^{14}$ combinations possible. The type of anion and the *R* groups in the different cations may be used to adjust the properties of the ILs. Therefore, the possibility arises to functionalize the IL for a specific application by stepwise tuning the relevant solvent properties. For this reason ionic liquids have been referred to as "designer solvents".

   At the Eindhoven University of Technology and at the University of Twente, ILs are used as extractants for the separation of aromatic hydrocarbons from aliphatic hydrocarbons and for selective absorption of CO_2.

Results and Discussion

Aromatic/Aliphatic Separations

The separation of aromatic hydrocarbons (benzene, toluene, ethylbenzene, and xylenes) from C_4 to 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*-methylpyrrolidone (*NMP*) [5], *N*-formylmorpholine (*NFM*), ethylene glycols [6–8], or 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].

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* Corresponding author. E-mail: g.w.meindersma@tue.nl

According to *Weissermel* and *Arpe* [1], no feasible processes are available for the separation of aromatic and aliphatic hydrocarbons in the range below 20% aromatics in the feed mixture. The feed stream of naphtha crackers may contain up to 25% aromatic hydrocarbons, which must be removed. Preliminary calculations, with confidential 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 vapor [14].

Extraction with Ionic Liquids

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. The extraction of toluene from mixtures of toluene and *n*-heptane is used as a model for the aromatic/aliphatic separation. A mixture of 10% (*v*/*v*) toluene in *n*-heptane is taken as a reference for the selection of ionic liquids for the aromatic/aliphatic separation [16–18]. 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 $D_{toluene} \geq 0.3$ at 40°C.

Liquid–liquid equilibrium data were collected for mixtures of 10% (*v*/*v*) toluene in *n*-heptane at 40°C with the selected ionic liquids [19–20]. 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 *n*-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:

$$D_{tol} = C^{IL}_{tol}/C^{org}_{tol} \text{ and } D_{hept} = C^{IL}_{hept}/C^{org}_{hept}$$
$$(1)$$

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

$$S_{tol/hept} = D_{tol}/D_{hept}$$
$$= (C^{IL}_{tol}/C^{org}_{tol})/(C^{IL}_{hept}/C^{org}_{hept}) \quad (2)$$

The results of the experiments with 10% (*v*/*v*) toluene in the feed at 40°C are shown in Fig. 1. In this figure, the toluene/*n*-heptane selectivity is shown as function of the distribution coefficient of toluene.

Comparing the results with the different ionic liquids tested, it is apparent that the ionic liquids 4-methyl-*N*-butylpyridinium tetrafluoroborate ([*mebupy*][BF$_4$]), 1-butyl-3-methylimidazolium tetrafluoroborate ([*bmim*][BF$_4$]) and 4-methyl-*N*-butyl-

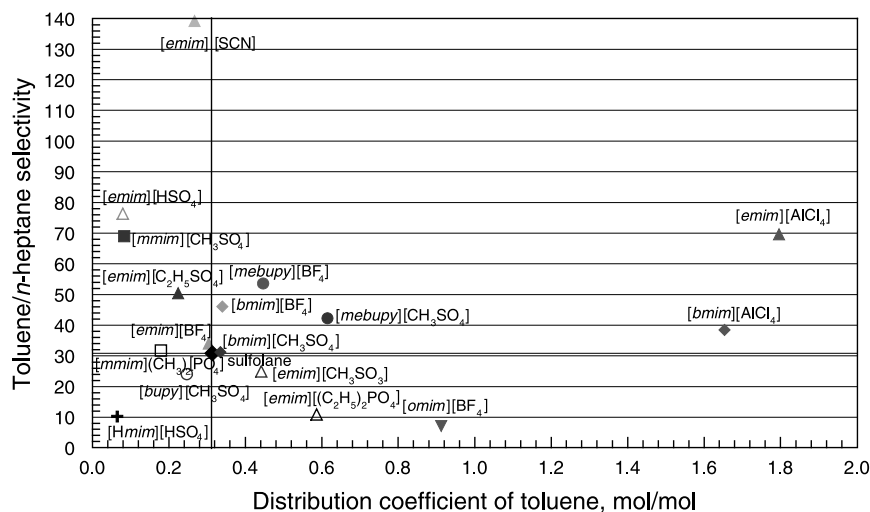**Fig. 1.** Toluene/*n*-heptane separation with ionic liquids, 10% (*v*/*v*) toluene, $T = 40$°C

pyridinium methylsulfate ([*mebupy*][CH$_3$SO$_4$]) show all a higher toluene distribution coefficient and a higher toluene/*n*-heptane selectivity than sulfolane. Although 1-ethyl-3-methylimidazolium aluminum-chloride ([*emim*][AlCl$_4$]) and 1-butyl-3-methylimida-zolium aluminumchloride ([*bmim*][AlCl$_4$]) showed even higher toluene distribution coefficients and higher toluene/*n*-heptane selectivities, these ionic liquids are not suitable due to their reaction with water.

Pilot Plant Experiments

The IL [*mebupy*]BF$_4$ exhibited the best combination of a high toluene distribution coefficient (0.44) and a high toluene/*n*-heptane selectivity (53) at 10% (*v/v*) toluene and 40°C [16–18]. Therefore, this IL was selected for the extractive removal of toluene from a toluene/*n*-heptane mixture in a pilot scale Rotating Disc Contactor (RDC) (Fig. 2) [21].

Until this date, no pilot plant scale experiments with extraction with ionic liquids have been carried out. The RDC was chosen because it is the most commonly used extractor in petrochemical proces-sing. The pilot RDC provided good results for the toluene/*n*-heptane separation: small droplets (high mass transfer rates) were obtained and the column capacity was high. Lower solvent to feed ratios were
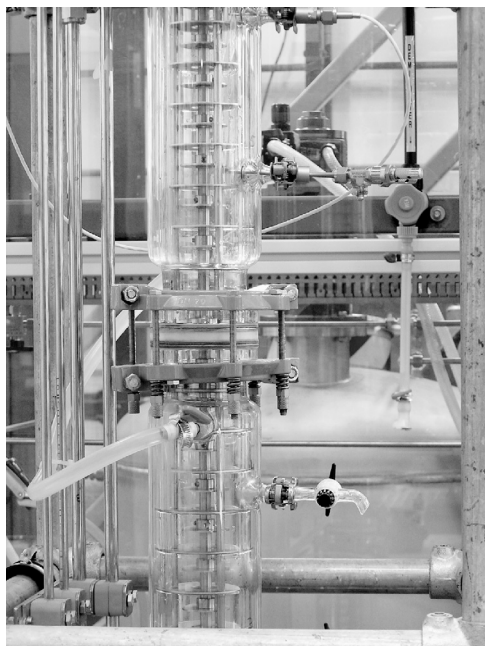

Fig. 2. Pilot Rotating Disc Column for extraction of toluene, inside column diameter 60 mm, 40 stirred compartments, total active length 1800 mm
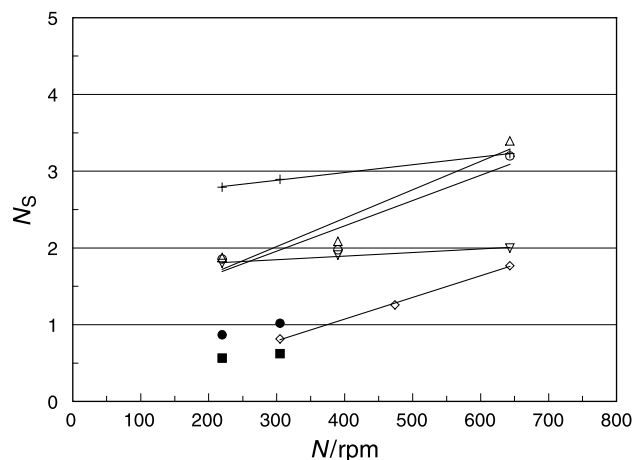

Fig. 3. Number of equilibrium stages with sulfolane and [*mebupy*][BF$_4$] in the RDC, *n*-heptane as continuous phase, $T = 40$°C, ~10% toluene, F flux in m^3/m$^2 \cdot$ h; + Sulfolane, $F = 9.7$; △ IL, $F = 10.8$; ○ IL, $F = 5.6$; ▽ IL, $F = 8.7$, $T = 75$°C; ◇ IL, $F = 5.6$, $T = 75$°C; ● IL, cont. $F = 8.7$; ■ IL, cont. $F = 5.6$

required with the IL than with sulfolane to extract the same amount of toluene, while a 10% higher flux (volumetric throughput) and a similar mass transfer efficiency were obtained. The best performance proved to be at the highest rotation speed used (643 rpm). In Fig. 3, the number of equilibrium stages, 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$^2 \cdot$ h. Excellent hydrodynamic behavior was observed and about three equilibrium stages were contained in the 1.80 m high active section of the column.

With sulfolane as the solvent, the feed flow was 5.8 kg/h with a total flux of 9.7 m^3/m$^2 \cdot$ h and with [*mebupy*][BF$_4$] as the solvent, the feed flow was 10 kg/h with a total flux of 10.8 m^3/m$^2 \cdot$ h. This means that more toluene can be extracted with the ionic liquid as solvent than with sulfolane.

Economic Evaluation

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 pro-cess in the cracker furnaces [22]. Therefore, they occupy a part of the capacity of the furnaces and they put an extra load on the separation section of the stream containing C$_5$–C$_{10}$ aliphatic compounds.
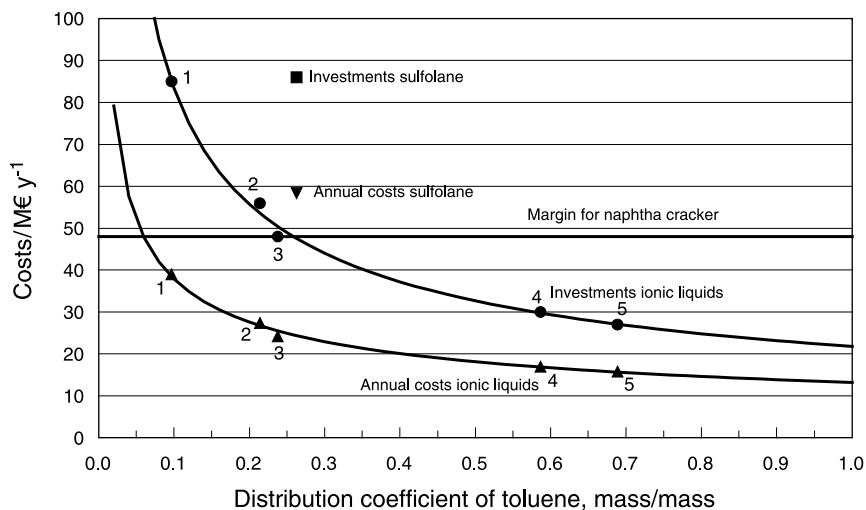
Fig. 4. Investment and variable costs for extraction with ionic liquids; *1* [*emim*][$C_2H_5SO_4$], *2* [*mebupy*][BF_4], *3* [*mebupy*][CH_3SO_4], *4* [*bmim*][$AlCI_4$], *5* [*emim*][$AlCI_4$]

If a major part of the aromatic compounds present in the feed to the crackers could be separated upstream of the furnaces, it would offer several advantages: higher capacity, higher thermal efficiency, and less fouling. 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/h, due to lower operational costs.

An economic evaluation was made for the separation of toluene from a mixed toluene/*n*-heptane stream with [*mebupy*][BF_4] and compared to that with sulfolane. For a naphtha feed of 300 ton/h containing about 10% aromatic hydrocarbons, the total investment costs in the sulfolane extraction were estimated to be about M€ 86 and with [*mebupy*][BF_4] about M€ 56, including an IL inventory of M€ 20. In the calculations, an ionic liquid price of € 20/kg was used and BASF, a major producer of imidazole, one of the primary products for ionic liquids, has indicated that it is indeed possible to reach a level of € 10–25/kg with production on a large scale [23–25]. The lower investment in the IL process is mainly due to the fact that the regeneration of the IL is much simpler than that of sulfolane. Since also the energy costs are lower, the total annual costs with the IL process are estimated to be M€ 27.4, compared to M€ 58.4 for sulfolane. The investment and annual costs for the separation of 10% aromatics from a cracker feed with sulfolane and ionic liquids are shown in Fig. 4. The loss of ionic liquid to the raffinate phase is minimal, estimated to be 0.006%. However the ionic liquid can be recovered with an extraction with water.

Suitability of Ionic Liquids for Extraction

Several ionic liquids are suitable for the separation of aromatic and aliphatic hydrocarbons. The ILs [*mebupy*][BF_4], [*mebupy*][CH_3SO_4], and [*bmim*][BF_4] show all a higher toluene distribution coefficient and a higher toluene/*n*-heptane selectivity than sulfolane. The ionic liquid [*mebupy*][BF_4] showed the best combination of both a high toluene distribution coefficient and a high toluene/*n*-heptane selectivity.

The main conclusion of the process evaluation is that ILs 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.

Design of Task-specific Ionic Liquids [26]

Since the properties of an IL are defined by the combination of the cation and anion, so called tailoring offers the possibility to create a special solvent for a specific task. The most suitable ionic liquids for the aromatic/aliphatic separation should have a high aromatic distribution coefficient with a reasonable aromatic/aliphatic selectivity. Because of the large number of combinations ($>10^{14}$), it is impossible to synthesize all ionic liquids and measure their properties [27]. Thus, to determine suitable ionic liquids for a certain problem, simulation tools will be very useful. The use of group contribution methods like UNIFAC is difficult because the specific interaction energy parameters of ionic liquids are

not available yet. Therefore, a dielectric continuum model (COSMO-RS) was chosen. Various ionic liquids have been screened with COSMO-RS. The predicted results were compared with the results obtained by experiments. The ionic liquids investigated were: [*emim*][AlCl$_4$], [*mebupy*][BF$_4$], [*bmim*][BF$_4$], and 1-ethyl-3-methylimidazolium methylsulfonate [*emim*][CH$_3$SO$_3$].

COSMO-RS is a quantum chemical approach, recently proposed by *Klamt* [28], for the *a priori* prediction of activity coefficients and other thermophysical data using only structural information of the molecules. By this method, it is possible to screen ionic liquids based on the surface charge, the polarity. Also, it is possible to calculate activity coefficients at infinite dilution.

Application of COSMO-RS

COSMO-RS screens the surface of the molecule and the location of the electrons is calculated. Concerning the surface energy and surface charge distribution, an ideally screened molecule is created (σ-surface), see Fig. 5. Within the water molecule, most electrons are concentrated at the oxygen atom, toluene has an electron cloud above the aromatic ring, and *n*-heptane has a homogenous distribution of the electrons over the whole surface. The polarity decreases from water (highly polar) to *n*-heptane (non-polar).

The σ-profile is derived from the σ-surface. Thereby, a mirror image of the molecule is created. The result is the so called σ-profile which describes the charge distribution above the molecule surface: (partial) positive surface charge gets a peak in the negative region and (partial) negative surface has a peak in the positive region.

With COSMO-RS, conventional solvents, such as *NMP* and sulfolane, and several ionic liquids have been screened quantitatively on their suitability to separate aromatic from aliphatic hydrocarbons. Anions have a positive peak in the σ-profile, due to their negative charge. It corresponds to the negative part of the toluene peak at $\sigma = -0.005\,\mathrm{e/A^2}$,
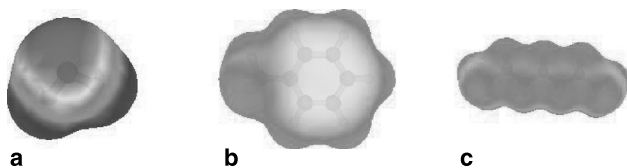

Fig. 5. σ Surface of: a) water; b) toluene; c) *n*-heptane
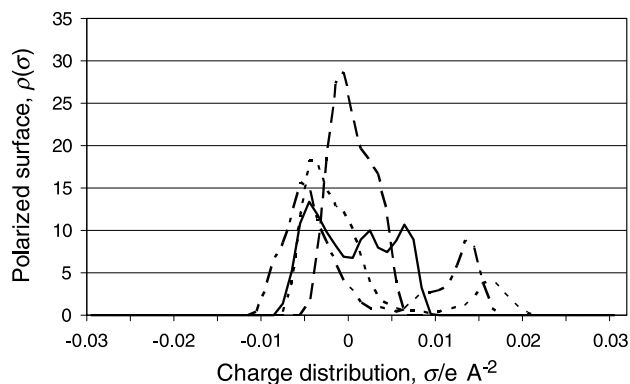

Fig. 6. σ-Profiles of toluene —, *n*-heptane – – –, sulfolane – – –, and *NMP* - - - -

which is derived of the partial positive charge of the π-orbital. Cations have peaks in the negative σ region, *e.g.*, [*mebupy*]$^+$ ($\sigma = -0.003\,\mathrm{e/A^2}$), that correspond to the peak of the toluene molecule ($\sigma = +0.007\,\mathrm{e/A^2}$) in the positive σ region.

The more the peaks correspond with each other, the higher the affinity of the molecules is to each other. That means the better the peaks of ionic liquid and aromatic hydrocarbon correlate, the better the separation between aromatic and aliphatic hydrocarbons will be. The results of the COSMO peaks for toluene, *n*-heptane, sulfolane, and *NMP* are shown in Fig. 6. It shows clearly that an interaction exists between sulfolane and *NMP* with the positive peak of toluene and no or little interaction with the negative peak of toluene.

With this method, good results have been obtained for [*emim*][AlCl$_4$], see Fig. 7. According to COSMO simulations, the anion [AlCl$_4$]$^-$ has a rather high selectivity for toluene and a high distribution coeffi-
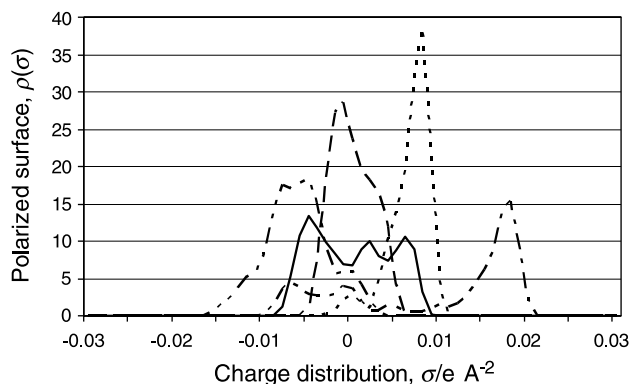

Fig. 7. σ-Profiles of toluene —, *n*-heptane – – –, [*emim*] ---, [AlCl$_4$]$^-$ - - - -, and [CH$_3$SO$_3$]$^-$ – – –
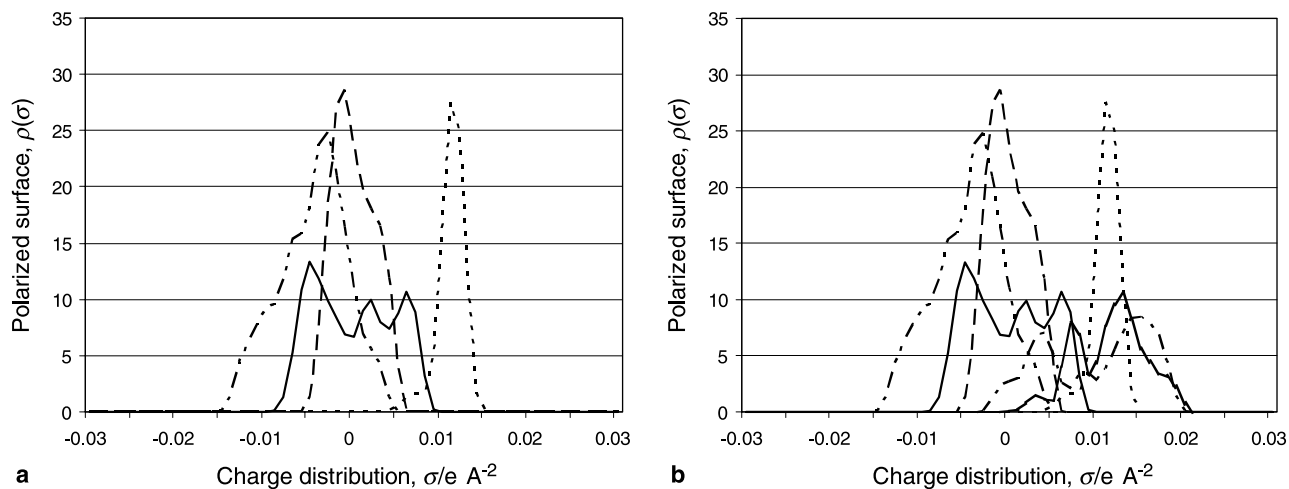
Fig. 8. σ-Profiles of a) toluene —, *n*-heptane - - -, [*mebupy*]$^+$ – – –, and [BF$_4$]$^-$ - - - -; b) toluene —, *n*-heptane – – –, [*mebupy*]$^+$ – – –, [BF$_4$]$^-$ - - - -, [*DCA*]$^-$ – – –, and [SCN]$^-$ —

cient which both could be verified by experiments. Also the cation [*emim*]$^+$ shows an interaction with toluene. Since both the cation and the anion show interaction with toluene, this ionic liquid shows both a high distribution coefficient and a high selectivity. However, one disadvantage is its instability in water. Also less suitable and completely improper ionic liquids are well predicted. As can be seen in Fig. 7, much poorer results are obtained for the anion [CH$_3$SO$_3$]$^-$.

Therefore, other anions were investigated: thiocyanate [SCN]$^-$ and dicyanamide [*DCA*]$^-$. In Fig. 8a, the σ-profiles of toluene, *n*-heptane, and the ionic liquid [*mebupy*][BF$_4$] are depicted. Figure 8b describes the σ-profiles of toluene, *n*-heptane, and [*mebupy*]$^+$

in combination with the anions ([BF$_4$]$^-$, [*DCA*]$^-$, [SCN]$^-$).

According to COSMO, they seem to have a high aromatic selectivity combined with good distribution coefficients as well. All the simulation results have been validated with experiments, see Figs. 1 and 9.

Activity coefficients at infinite dilution, γ_i^∞ ($D_i = 1/\gamma_i$), for toluene and *n*-heptane, which were calculated with COSMO-RS are depicted in Fig. 10. The predicted values of the *n*-heptane distribution coefficients at infinite dilution are much higher than the experimental data, as can be seen in Fig. 10. In comparison, the predicted toluene distribution coefficients match better with the experimental values, but there are still large deviations.
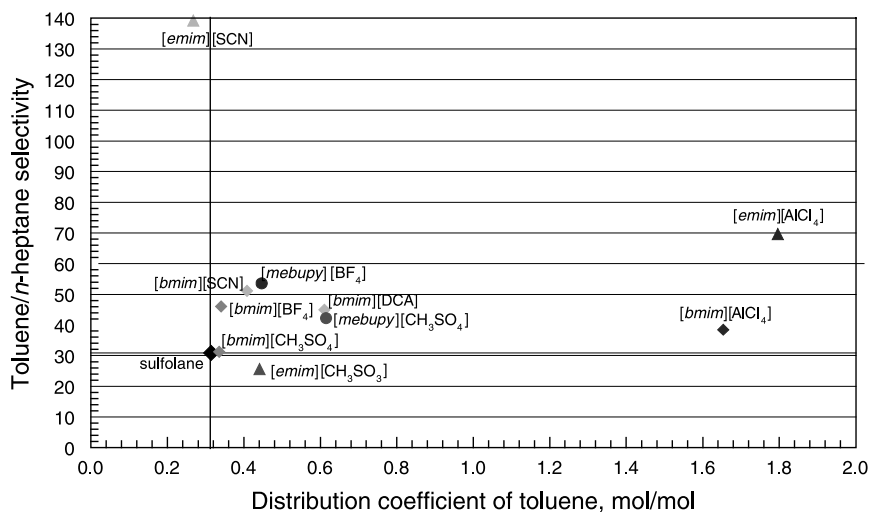

Fig. 9. Extraction performance of several ionic liquids compared to sulfolane at $T = 40°$C
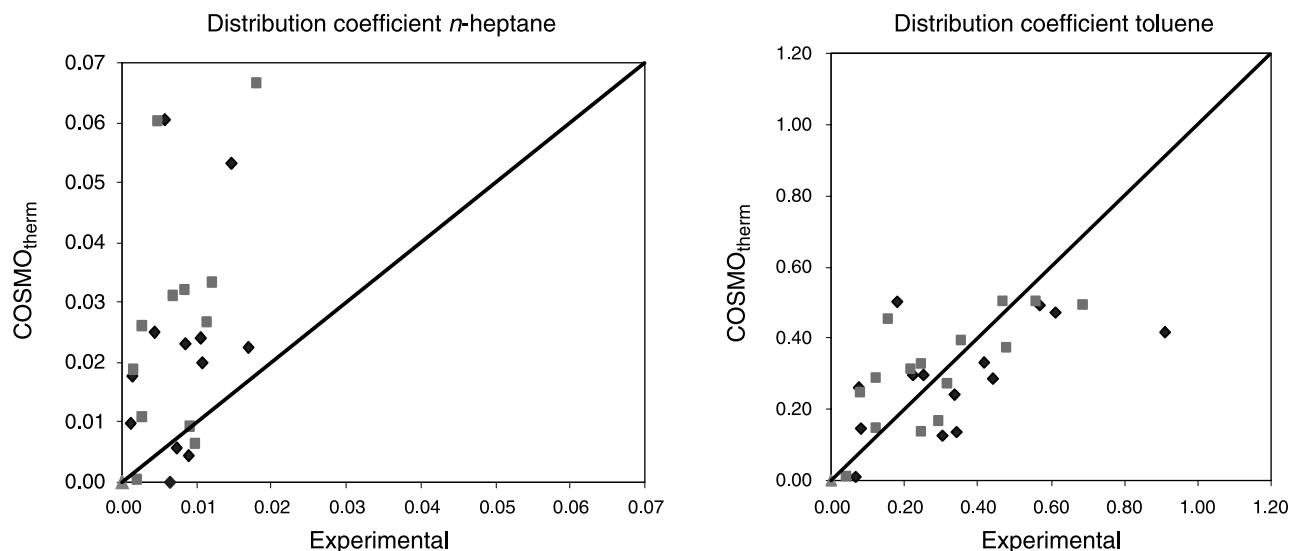
Fig. 10. Correlation between distribution coefficients at infinite dilution determined with COSMO-RS and experimental data at 10% toluene in *n*-heptane. ◆ 313 K, ■ 348 K

COSMO-RS as Design Tool

For the toluene/*n*-heptane system, COSMO-RS is used to determine suitable ionic liquids by predicting the interaction of the molecules based on the charge distribution above their surfaces. The results of the program are validated by experimental tests with the predicted ionic liquids. It could be shown that both good and poor candidates are well predicted and that there is a strong correlation between COSMO predictions and experimental observations: *e.g.*, anions like [SCN]⁻ and [*DCA*]⁻ will give much better results than [BF₄]⁻.

Besides polarity, also γ^∞-values determined with COSMO-RS can be used for a first screening. However, quantitative predictions are still inaccurate and COSMO-RS does not give sound predictions of γ-values for finite concentrations. Therefore, it cannot be used for calculation of distribution coefficients and selectivities yet. In general, COSMO-RS appeared to be a very promising tool to support the design of suitable ionic liquids for specific (separation) problems.

Gas Separations [29]

Chemical and physical absorption processes are extensively used in the natural gas, petroleum, and chemical industries for the separation of CO_2 [30]. Physical absorption is preferred when acid gases (H_2S, CO_2) are present at elevated concentration in the gas stream. Physical solvents are non-reactive polar organic compounds with an acid gas affinity. Chemical absorption is typically used for the removal of remaining acid impurities and when gas purity is a down-stream constraint. For chemical CO_2 removal, aqueous solutions of primary, secondary, tertiary, hindered amines and formulated amine mixtures are the most widely used solvents. About 75–90% of the CO_2 is captured using a *MEA*-based technology producing a gas stream of high CO_2 content (>99%) after desorption [31].

However, there is still a strong incentive for the development of low cost and efficient alternatives. The major drawbacks of the traditional gas absorption separation processes are mainly caused by the nature of the solvent and by the type of interactions given between the solute and the solvent. In an industrial gas absorption process, it is desirable to achieve fast absorption rates and high solute capacities into a solvent that is easily regenerated and which volume make-up is minimized.

CO₂ Absorption

ILs can be used as solvents for gas absorption in order to improve the process economy and general efficiency of gas separations. The ionic liquids used were: [*bmim*][BF₄], [*bmim*][*DCA*], and four functionalized ionic liquids, in which the cation was functionalized with either a primary, tertiary amine or a hydroxyl group, as is shown in Scheme 1.

[Am-im][BF$_4$]

[3Am-im][BF$_4$]

[OH-im][BF$_4$]

[3Am-im][DCA]
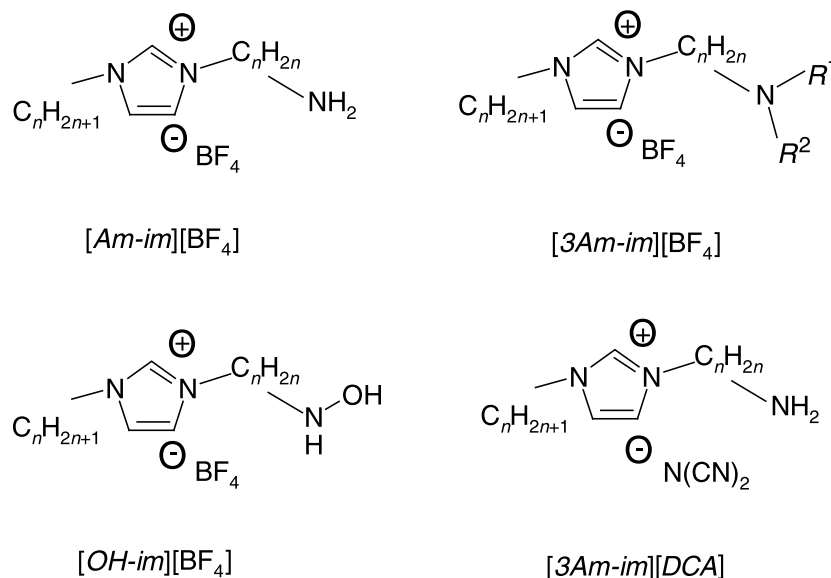
Scheme 1

Physical Properties

The density of the ionic liquids used is higher than those of conventional solvents and decreases linearly with an increase in temperature, as is shown in Fig. 11. On the other hand, the measured densities of [bmim][BF$_4$] and [bmim][DCA] at 20°C are comparable to the density of the classical physical CO_2 absorption solvents like sulfolane ($\rho \approx 1.26$ g/cm^3) and propylene carbonate ($\rho \approx 1.19$ g/cm^3). The measured densities are in agreement with published data [32, 33].

It is well known that viscosities of RTILs are relatively high compared to those of traditional solvents and water [32]. The large differences in viscosity are illustrated in Fig. 12, where the viscosity of one of the tested ionic liquids, [bmim][BF$_4$], is compared to the viscosity of an aqueous solution of 30% MEA [34]. With an increasing the temperature from 303 K to 343 K the viscosity of [bmim][BF$_4$] decreased by a factor of 4.5, whereas for a similar temperature change the viscosity of a 30% MEA solution decreased only by a factor of 2.7.

The surface tension of the screened ionic liquids decreases with higher temperatures. The measured values for [bmim][BF$_4$] varied from 44.6 mN · m^{-1} to 40.3 mN · m^{-1}, when temperature was increased from 293 K to about 360 K. The surface tension of a solution of 30% DEA changed from 61.94 mN · m^{-1} to 58.92 mN · m^{-1} when temperature was increased from 293 K to 333 K [35]. In Fig. 13, the surface
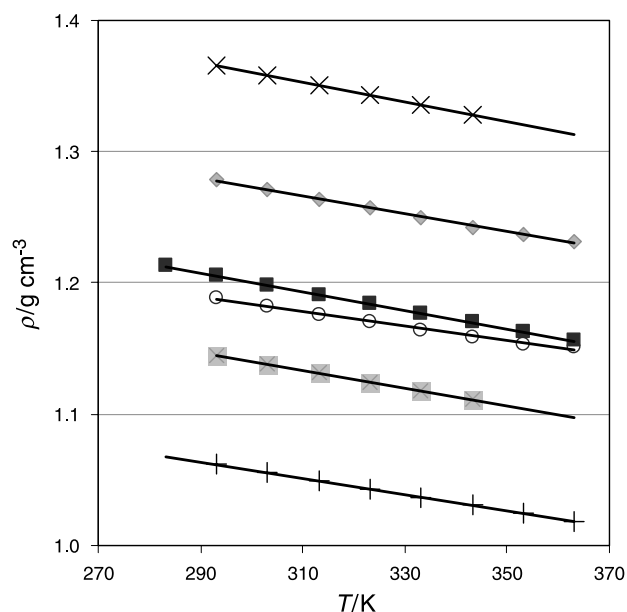

Fig. 11. RTILs density as function of temperature. ■ [bmim][BF$_4$], + [bmim][DCA], ◆ [Am-im][BF$_4$], ⊠ [3Am-im][BF$_4$], × [OH-im][BF$_4$], and ○ [Am-im][DCA]

tension of [bmim][BF$_4$] and [bmim][DCA] are compared with their respective primary amine functionalized IL.

CO$_2$ Solubility

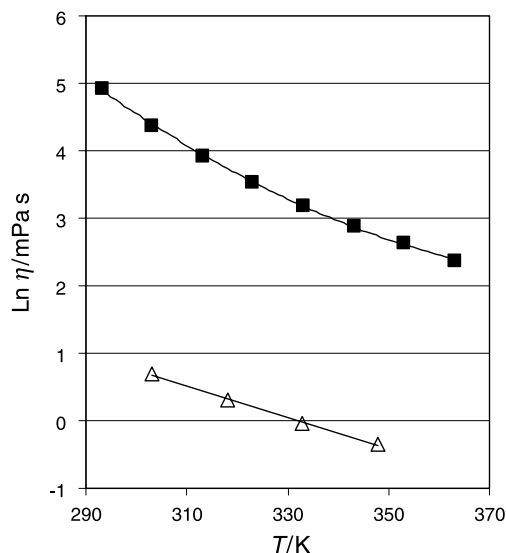The obtained CO_2 solubility results were reproducible (deviations in mole fraction <0.01) and they

Fig. 12. Viscosity of [*bmim*][BF₄] and 30% *MEA* solution. ■ [*bmim*][BF₄]. △ 30% *MEA* solution, taken from *Little et al.* [34] Lines were plotted as a view aid
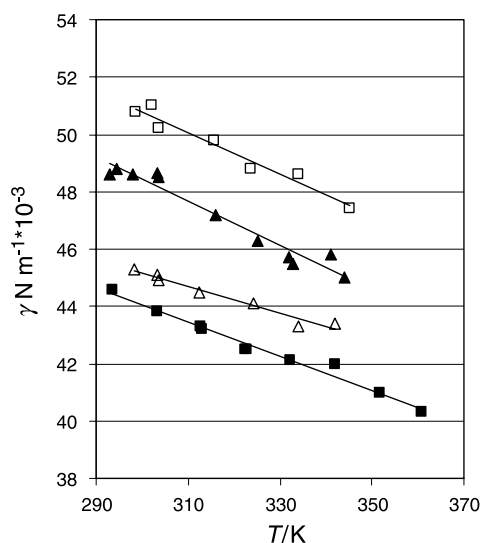

Fig. 13. Surface tension as a function of temperature. ■ [*bmim*][BF₄], □ [*Am-im*][BF₄], ▲ [*bmim*][DCA], △ [*Am-im*][DCA]

compare well with reported values found in literature [36, 37]. The ionic liquid samples were easily regenerated overnight by heating the CO_2-loaded RTILs up to around 353 K at vacuum (10^2 Pa). The regeneration temperature was dependent on the ionic liquid type. The regenerated liquid was used for carrying out further absorption experiments. It was observed that results obtained with a regenerated liquid did not differ significantly from those obtained with a fresh sample.
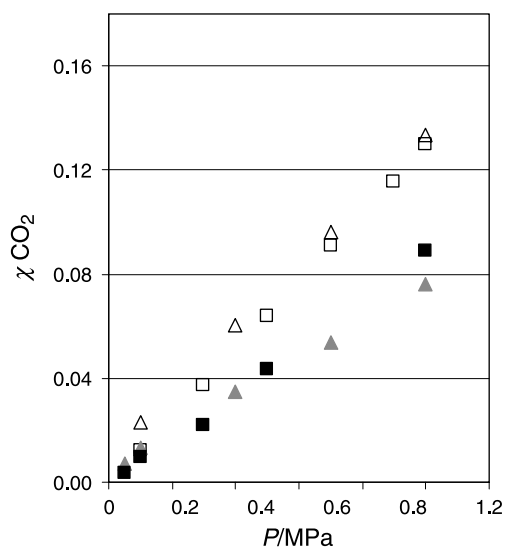

Fig. 14. CO_2 solubility in non-functionalized RTILs. [*bmim*][BF₄]: □ 303 K, ■ 344 K. [*bmim*][DCA]: △ 303 K, ▲ 345 K

The CO_2 solubility into the tested non-functionalized ionic liquids at 303 K and 345 K is depicted in Fig. 14. The CO_2 absorption for both [*bmim*][DCA] and [*bmim*][BF₄] increased at higher pressures and decreased at higher temperatures, as expected.

The CO_2 absorption into non-functionalized and functionalized ionic liquids at 303 K is compared in Figs. 15 and 16. By far the bigger increments on CO_2 absorption were obtained with the two ILs
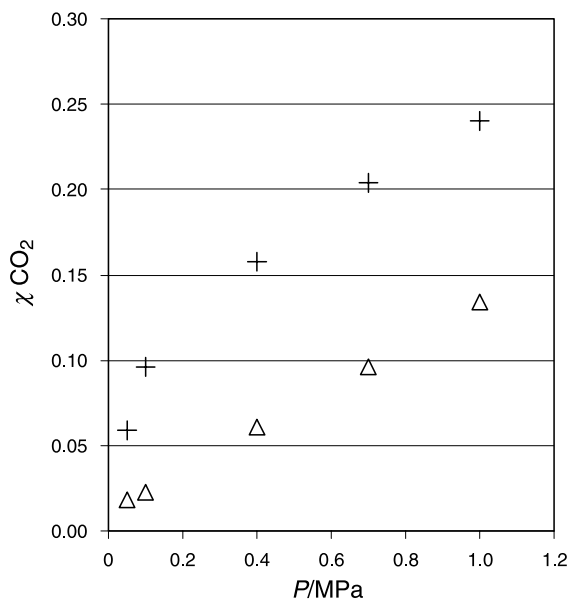

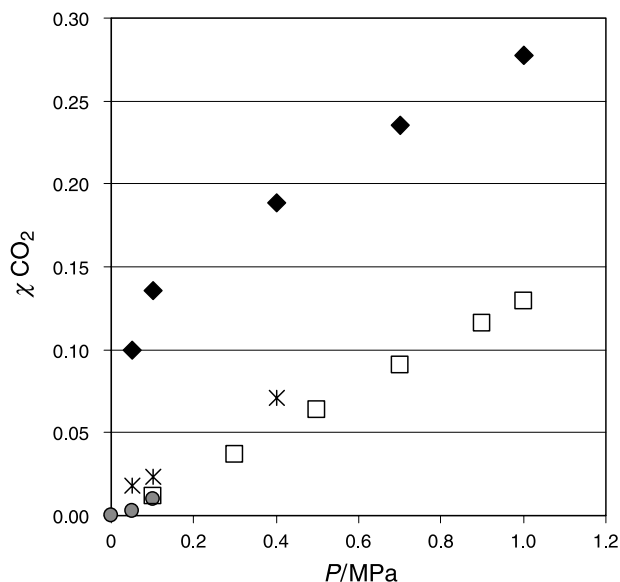**Fig. 15.** CO_2 solubility at 303 K in △ [*bmim*][DCA], + [*Am-im*][DCA]

Fig. 16. CO_2 solubility at 303 K in □ [*bmim*][BF$_4$], ◆ [*Am-im*][BF$_4$], ✳ [*3Am-im*][BF$_4$], and ◉ [*OH-im*][BF$_4$]

which have [*Am-im*]$^+$ as a cation. In this type of cation, the imidazolium alkyl chain contains a primary amine functional group.

The CO_2 absorption in [*Am-im*][DCA] is about 4 times larger than the one achieved into [*bmim*][DCA] at 0.1 MPa and just over a factor of 1.8 larger at 1 MPa.

Compared with molar fraction data for [*bmim*][BF$_4$] at 303 K, the CO_2 absorption was improved by a factor of 13 at 0.1 MPa with [*Am-im*][BF$_4$]. The effect of the functionalized IL on the CO_2 absorption was smaller at 1 MPa and absorption in [*Am-im*][BF$_4$] was around twice the CO_2 molar fraction in the non-functionalized IL.

As can be seen in Fig. 16, the improvement on CO_2 absorption by [*Am-im*][BF$_4$] was significantly higher compared with [*3Am-im*][BF$_4$], with a tertiary amine attached to the imidazolium alkyl chain. The CO_2 solubility into [*3Am-im*][BF$_4$] is around 1.5 times the molar CO_2 solubility into [*bmim*][BF$_4$] at 0.4 MPa and 303 K. The smaller effect of the amine functionalized [*3Am-im*][BF$_4$], in comparison with [*Am-im*][BF$_4$] can probably be explained by the lower reactivity of the tertiary amine in comparison with the primary amines and CO_2. The attached hydroxyl group did not cause a remarkable improvement on the CO_2 absorption behavior in comparison to the ones exhibited by the non-substituted imidazolium tetrafluoroborate ionic liquid.

Concerning the solvent behavior of functionalized ILs and non-functionalized ILs, clear differences can be seen in Figs. 15 and 16. The CO_2 absorption into [*bmim*][BF$_4$] and [*bmim*][DCA] is probably attributed to physical mechanisms, while chemical and physical mechanisms are involved during the CO_2 absorption into the functionalized ILs. At pressures lower than 0.1 MPa, the CO_2 absorption trend exhibited by functionalized ILs indicated that a chemical reaction was taking place and that the CO_2 absorption was enhanced as a result of that. This fact is remarkably evident for CO_2 absorption into [*Am-im*][DCA] and [*Am-im*][BF$_4$]. Whereas the physical mechanisms contribute to the CO_2 absorption into [*bmim*][BF$_4$] and [*bmim*][DCA] through the whole interval of measured pressures. Moreover, physical absorption is the main mechanism for the CO_2 absorption into functionalized ILs at pressures above 0.1 MPa.

A comparison of the solvent volumetric gas load between measured data of ionic liquids at 303 K and reported equilibrium CO_2 loads for primary, secondary, and tertiary amines is found in Fig. 17.

The CO_2 load for the primary amine substituted ionic liquids was the highest and decreased in the following order: [*Am-im*][BF$_4$] > [*Am-im*][DCA] > [*3Am-im*][BF$_4$] ≈ [*OH-im*][BF$_4$] ≈ [*bmim*][DCA] ≥ [*bmim*][BF$_4$]. The solvent CO_2 load behavior of [*Am-im*][BF$_4$] and [*Am-im*][DCA] is comparable to the ones exhibited by aqueous *DEA* and *MDEA* solutions, see Fig. 17. It can be seen in Fig. 17 that at pressures around 0.5 MPa, the CO_2 loads for [*Am-*
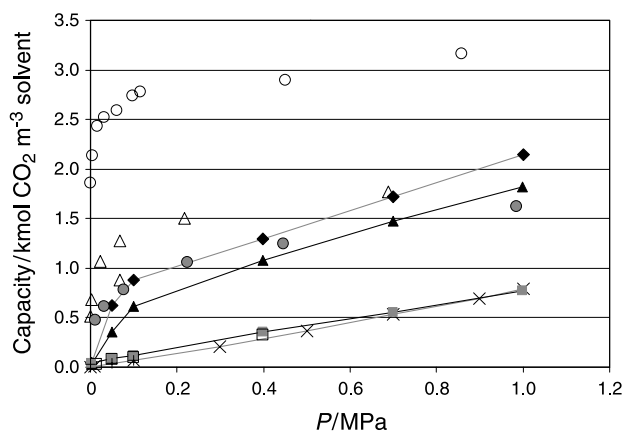
Fig. 17. Volumetric solvent CO_2 loads. Data for all RTILs at 303 K: ✕ [*bmim*][BF$_4$], □ [*3Am-im*][BF$_4$], ■ [*bmim*][DCA], ▲ [*Am-im*][DCA], ◆ [*Am-im*][BF$_4$], + [*OH-im*][BF$_4$]. △ 20% *DEA* at 323 K, taken from *Lee et al.* [38]. ○ 30% *MEA* at 333 K and ◉ 30% MDEA at 333 K, taken from *Shen* and *Li* [39]. Dotted lines plotted for view aid purposes

im][BF$_4$] and [*Am-im*][*DCA*] at 303 K are comparable to CO$_2$ loads from 20% *DEA* at 323 K and 30% *MDEA* at 333 K. At higher pressures, the CO$_2$ load of ionic liquids continued increasing while for the aqueous amine solvent remained constant.

Ionic Liquids for CO$_2$ Absorption

The CO$_2$ absorption behavior of [*bmim*][BF$_4$], [*bmim*][*DCA*], and four functionalized ILs is similar to that of the usual solvents for CO$_2$ absorption. It increased with a rise in pressure and decreased with an increase in temperature. The CO$_2$ absorption behavior of the ILs changed when functionalized chains were attached to the cation of the IL.

Primary amine groups incorporated into the cation structure improved the CO$_2$ absorption performance of [*bmim*][BF$_4$] and [*bmim*][*DCA*]. In terms of molar fraction, [*Am-im*][BF$_4$] and [*Am-im*][*DCA*] improved the CO$_2$ absorption of the non-functionalized ILs by a factor of 13 and 4 at 0.1 MPa and by a factor of 1.8 and 2 at 1 MPa.

At low pressures ($\leq$0.1 MPa), the removal of CO$_2$ with [*Am-im*][BF$_4$] and [*Am-im*][*DCA*] followed a similar pattern as the chemical absorption of CO$_2$ into aqueous amine solutions. In contrast, at higher pressures ($\geq$0.2 MPa), the aqueous amine solutions reached the maximum capacity and any further increment is not possible. On the other hand, the CO$_2$ load of the functionalized ILs continued rising steadily with an increment in pressure.

Conclusions

Several ionic liquids are suitable for the separation of aromatic and aliphatic hydrocarbons. The main conclusion of the process evaluation is that ILs which show a high aromatic distribution coefficient with a reasonable aromatic/aliphatic selectivity could reduce the investment costs of the aromatic/aliphatic separation.

COSMO-RS is a suitable simulation tool for predicting the performance of ionic liquids as extraction solvents. Promising combinations of cations and anions can be designed.

CO$_2$ absorption behavior was influenced by the functionalized chains appended to the RTIL cation. A chemical enhancement of the CO$_2$ absorption was observed when functionalized RTILs were used as absorption solvents.

Ionic liquids seem able to combine the chemical features of amine solutions with the characteristic advantages of the physical solvents used for CO$_2$ absorption.

Ionic liquids offer tremendous opportunities to intensify reactions and separations in process technologies by tuning their physical and chemical properties.

Experimental

Liquid–Liquid Extractions
Before each experiment, the ionic liquids were dried at 75°C under reduced pressure in a rotary evaporator. Liquid–liquid extraction experiments were carried out in jacketed vessels with a volume of approximately 70 cm^3. The top of a vessel was closed using a *PVC* cover, through which the stirrer shaft passed. Two stainless steel propellers were used with an electronic stirrer. The vessels were jacketed to circulate water from a water bath, maintaining the temperature inside the vessels at either 40 or 75°C.

For each experiment, 20 cm^3 of the ionic liquid and 10 cm^3 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 min and analysing them. In order to avoid this procedure for the other ternary mixtures, all extraction experiments were continued for 20 minutes. After stirring, the two phases were allowed to settle for about one hour. The concentrations of the aromatic and aliphatic hydrocarbons in the samples were analysed by gas chromatography. Because the ionic liquid has no vapor pressure, it could not be analyzed by GC. Therefore, the concentrations of the ionic liquid in both phases were calculated by using a mass balance [16, 17].

CO$_2$-Absorption
The density was measured with a density-meter Anton Paar DMA 5000, repeatability 1×10^{-6} g·cm^{-3} and 0.001°C at atmospheric pressure and a standard deviation (*STD*) of 1.4×10^{-6} g·cm^{-3}. The determination of the viscosity was carried out in an *Ubbelohde* viscosimeter, *STD* 6 mPa·s, placed in a heated water bath and the set up gas was previously flushed with argon gas. The surface tension values were obtained using the ring method with a tensiometer Kruss K11, *STD* 0.4 mN·m^{-2}.

The CO$_2$ solubility measurements were carried out in an Intelligent Gravimetric Analyzer (IGA 003, Hiden Analytical) at temperatures ranging from 298 to 363 K and pressures up to about 1.2 MPa. The balance has a weight range of 0–100 mg with a resolution of 0.1 μg. A more detailed description of the set up can be found in Ref. [40]. When the experimental temperature and the sample mass were constant, CO$_2$ was introduced up to the set pressure and the increment in weight was monitored. The ionic liquid and the gas seemed to have reached equilibrium, when at constant pressure no further weight change was observed throughout time, weight change

rate $<0.001\,\mathrm{mg\cdot h^{-1}}$. The time required for reaching equilibrium at each pressure level strongly depended of the nature of the ionic liquid. Intervals between 8 and more than 48 hours were observed. In the solubility calculations the buoyancy effects were accounted for.

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