Ionic Liquids in Chemical Engineering

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ionic liquids, molten salts, catalysis, separation technologies, process machinery

Abstract

The development of engineering applications with ionic liquids stretches back to the mid-1990s when the first examples of continuous catalytic processes using ionic liquids and the first studies of ionic liquid–based extractions were published. Ever since, the use of ionic liquids has seen tremendous progress in many fields of chemistry and engineering, and the first commercial applications have been reported. The main driver for ionic liquid engineering applications is to make practical use of their unique property profiles, which are the result of a complex interplay of coulombic, hydrogen bonding and van der Waals interactions. Remarkably, many ionic liquid properties can be tuned in a wide range by structural modifications at their cation and anion. This review highlights specific examples of ionic liquid applications in catalysis and in separation technologies. Additionally, the application of ionic liquids as working fluids in process machines is introduced.

INTRODUCTION TO IONIC LIQUIDS

Ionic liquids are salts that are characterized by the following three criteria:

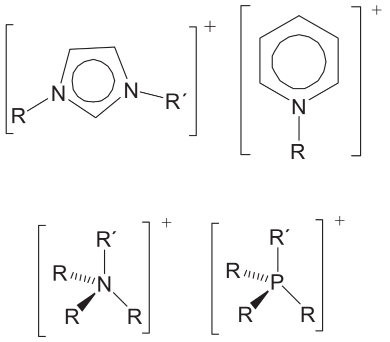
1. They consist entirely of ions;
2. They have melting points below 100°C;
3. They exhibit extremely low vapor pressures below their temperatures of thermal decomposition.

Ionic liquids represent a new class of fascinating liquid materials with unique property profiles. For example, negligible vapor pressure is combined in many ionic liquids with unusual solubility and miscibility properties, attractive electric conductivity, quite interesting polarity/nucleophilicity for catalysis, and remarkable tribologic properties. Such unique property profiles originate from a complex interplay of coulombic, hydrogen bonding, and van der Waals interactions among the ions of the ionic liquid and between the ionic liquid and dissolved substances and surfaces. Attempts to understand and utilize these complex interactions are the heart of ionic liquid science and lead to the optimization of ionic liquid structures for specific applications (1). **Figure 1** provides a list of typical cations and anions used in the formation of ionic liquids.

As the substituents R and R′ can vary independently and include linear alkyl chains as well as highly functionalized, branched, aromatic, or cyclic moieties, the structural variability of ionic liquids is enormous. Consequently, the class of ionic liquids covers a wide range of chemically different, low-melting salts with a huge diversity of properties. Some combinations of ionic liquids have even been found that differ so much in their physicochemical nature that they are not miscible with each other (2). Owing to their diversity and the opportunity to modify their physicochemical properties gradually by tailoring cation and anion, the term "designer solvents" has been coined for ionic liquids (3).

Despite this great variability, some properties of ionic liquids are more or less intrinsic to the approach. For example, it would be difficult to design highly volatile, nonconductive, or totally apolar ionic liquids. **Table 1** provides an overview of the typical ranges of ionic liquid properties. It gives typical values for selected properties as well as known upper and lower limits. Much more detailed information about the specific properties of ionic liquids can be found elsewhere (1).

Structural characteristics determine which type of ionic liquid is used for which type of application. For example, whereas ionic liquids with "cheap" anions, such as toluenesulfonates (4), octylsulfates (5), and hydrogensulfates (6), have been developed for potential bulk applications (e.g., in synthesis, catalysis, separation technologies, lubrication, formulation, and antistatics),



Cl^-, Br^-, I^-
$[AlCl_4]^-$, $[Al_2Cl_7]^-$, $[Al_3Cl_{10}]^-$

$[PF_6]^-$, $[PF_3(C_2F_5)_3]^-$, $[BF_4]^-$

$[CF_3CO_2]^-$, $[CF_3SO_3]^-$
$[(CF_3SO_2)_2N]^-$

$[HSO_4]^-$, $[RSO_4]^-$, $[RSO_3]^-$

$[H_2PO_4]^-$, $[R_2PO_4]^-$

$[CH_3CO_2]^-$,
$[N(CN)_2]^-$, $[C(CN)_3]^-$, $[B(CN)_4]^-$

Figure 1

Typical cations and anions used to form ionic liquids.

Table 1 Typical property ranges of ionic liquids

Property	Lower limit example	Typical range of most ionic liquids	Upper limit example
Melting point/glass transition	[EMIM]Cl/AlCl$_3$ = (1:2) = −96°C (glass transition)	0°C–60°C	100°C by definition
Density	[HMpyr][N(CN)$_2$] = 0.92 g L^{-1}	1.1–1.6 g/L^{c}	[EMIM]Br-AlBr$_3$:1/2 = 2.2 g L^{-1}
Viscosity	[EMIM]Cl-AlCl$_3$:1/2 = 14 mPa s^{a}	40–800 mPa s^{c}	[BMIM]Cl (supercooled) = 40.89 Pa s^{a}
Thermal stability	[EMIM][OAc] = ∼200°C^{b}	230°C–300°C^{b}	[EMIM][NTf$_2$] = 400°C^{b}
Surface tension	[C$_{12}$MIM][PF$_6$] = 23.6 mN m^{-1}	30–50 mN m^{-1}	[MMIM[MeSO$_4$] = 59.8 mN m^{-1}
Heat capacity	[BMIM][MeSO$_4$] 247 J mol^{-1} K^{-1}	300 to 400 J mol^{-1} K^{-1}	[OMIM][NTf$_2$] = 654 J mol^{-1} K^{-1}
Water miscibility	[NTf$_2$]$^{-}$, [P(C$_2$F$_5$)$_3$F$_3$]$^{-}$	many ILs do mix with water but also can be extracted from water	[RSO$_3$]$^{-}$, [RSO$_4$]$^{-}$, [R$_2$PO$_4$]$^{-}$
Hydrolytic stability	[BF$_4$]$^{-}$, [PF$_6$]$^{-}$	heterocyclic cations can hydrolyze under extreme conditions	[NTf$_2$]$^{-}$, [OTf]$^{-}$, [CH$_3$SO$_3$]$^{-}$
Base stability	[Al$_2$Cl$_7$]$^{-}$, [HSO$_4$]$^{-}$	all 1,3-dialkylimidazolium ILs are subject to deprotonation	[PR$_4$]$^{+}$, [OAc]$^{-}$
Corrosion	[NTf$_2$]$^{-}$, [OTf]$^{-}$	most ILs are corrosive versus Cu; additives available	Cl^{-}, HF formed from [MF$_x$]$^{-}$ hydrolysis
Toxicity	[cholinium][OAc]	often increasing toxicity for aquatic systems with increasing lipophilicity	[EMIM][CN]
Price	[HNR$_3$][HSO$_4$] = ∼3 € kg^{-1c}	25–250 € kg^{-1}	[BMMIM][NTf$_2$] = ∼1.000 € kg^{-1}

Data taken from (1, 149) and references cited therein. [EMIM]: 1-ethyl-3-methylimidazolium, [HMpyr]: 1-hexyl-1-methylpyrrolidinium, [BMIM]: 1-butyl-3-methylimidazolium, [C$_n$MIM]: 1-alkyl-3-methylimidazolium, [NTf$_2$]: [(CF$_3$SO$_2$)$_2$N], [BMMIM]: 1-butyl-2,3 dimethylimidazolium.

[a] At room temperature.

[b] TGA experiments at 10 K min^{-1}.

[c] Estimation made for a production scale of 1000 kg and for a purity >98%.

ionic liquids containing “expensive” functionalized (7), fluorinated (8), deuterated (9), or chiral ions (10) have been designed to be used in small amounts in applications with very high added value (e.g., in analytical applications, sensors, electrolytes, and coatings).

How does one identify and design the best ionic liquid structure for a given application? As an illustrative example, we describe the optimization of the solubility of molecular organic compounds in ionic liquids, a property of utmost importance for almost all ionic liquid engineering applications. Although in recent years a steeply growing amount of experimental solubility data has been published (11), the first theoretical predictions have also been described using the conductor-like screening model for realistic solvation (COSMO-RS) approach (12, 13, 14). The COSMO-RS method can be applied to predict the solubility of a compound in an ionic liquid in thermodynamic equilibrium. It starts from separate density functional theory (DFT) calculations of the ionic liquid ions and the solute molecules. These calculations must take into consideration different conformers (12). Interestingly, data files can be combined so that, for example, a file generated for the 1-ethyl-3-methylimidazolium [EMIM]$^{+}$ ion can be used in combination with different anion files and substrate files to calculate solubilities in different systems. This makes the method particularly efficient for ionic liquids. The DFT results for each moiety are converted into a statistics of surface elements of the same charge density. This distribution—the so-called σ-profile—is used to calculate the activity coefficient of each component by pair-wise interacting the surface elements of the different components and minimizing the system energy in this process. As one result of this exercise, the activity coefficient of the solute in the cation/anion mixture forming the ionic liquid is obtained, which allows the calculation of the properties, such as solubility data, distribution coefficients, or vapor pressures, of volatile substances in the ionic liquid.

In many engineering applications (e.g., multiphase catalysis, extraction, absorption) fast mass transport between the ionic liquid and its neighboring phases is an additional important requirement to make the processes efficient. Sufficiently fast mass transport of molecules into an ionic liquid phase is not a trivial prerequisite because of the relatively high viscosity of ionic liquids compared with classical organic solvents (15). Other important aspects of practical relevance for ionic liquid–based, multiphase engineering applications concern the ease of phase separation and the accumulation of high-boiling impurities in the ionic liquid.

The development of engineering applications of ionic liquids dates back to the mid-1990s when the first examples of continuous catalytic processes using ionic liquids (16) and the first studies of ionic liquid–based extractions (17) were published. Quickly researchers found that some characteristics of ionic liquids enable more efficient and greener processes. Indeed, the negligible vapor pressure of ionic liquids at ambient conditions is a strong green asset in comparison with volatile organic solvents. Atmospheric pollution by ionic liquids is highly unlikely even if the liquids are handled in open containers. Moreover, the vapor pressure of organic reactants and products is reduced when dissolved in ionic liquids, which decreases their potential for atmospheric pollution as well. In addition, a reduced volatility of solvents and reactants adds to the operational safety of a given process, as mixtures of volatile organics and air are always linked with explosion hazards. Finally, the use of ionic liquids often leads to clever multiphase engineering with opportunities to recycle the ionic liquid working fluid within the process.

Despite these clear advantages, most ionic liquids are more difficult and more costly to prepare than molecular solvents. Moreover, some ionic liquid structures can exhibit problematic toxicity and ecotoxicity properties. Compared with methanol, ionic liquids always will be more expensive and more difficult to produce and to dispose of. Thus, ionic liquids are not intrinsically green. They are, however, new liquid materials providing unique combinations of properties. By making use of these unique properties, more efficient and greener processes can be realized. The following sections aim to illustrate this statement by discussing specific applications of ionic liquids in catalysis, separation technologies, and process machinery.

IONIC LIQUIDS IN CATALYTIC PROCESSES

Similar to molecular solvents, ionic liquids dissolve many transition metal complexes in quantities sufficient enough for catalysis (18). The ability to form ionic catalyst solutions is an obvious, but not a trivial, prerequisite for applying ionic liquids in homogeneous catalysis. In addition, many ligands from the vast library developed for biphasic catalysis in aqueous media are highly soluble in ionic liquids. Loss of the expensive ligand can affect the process economics in a way similar to metal leaching; fortunately, ligand leaching from the ionic liquid phase can be avoided in most cases owing to the low cross-solubility of polar ligands in the organic phase (19).

The reactivity of a transition metal complex dissolved in an ionic liquid is a result of its interaction with the ionic liquid's ions. Thus, for efficient catalytic processes, it is important to understand which ionic liquid provides the ideal environment for the catalytic center to perform the reaction in the most selective and most active way and with an extremely long lifetime. Depending on the type of metal complex dissolved in the ionic liquid, two general cases can be distinguished:

1. The catalyst in the ionic liquid is catalytically active by itself or after self-activation (e.g., by thermal abstraction of a protecting group);
2. A chemical reaction between the ionic liquid and the catalyst precursor forms the active catalyst in situ.

In the first case, ionic liquids with weakly coordinating, inert anions (e.g., $[NTf_2]^-$, where $Tf = (CF_3SO_2)_2$; $[BF_4]^-$; $[SbF_6]^-$; or $[PF_3(C_2F_5)_3]^-$) and inert cations are preferred. Here the role of the ionic liquid is to provide a moderately polar medium that does not compete with the substrate for free coordination sites. Moreover, the ionic liquid should be selected to provide sufficient feedstock solubility and efficient options for product isolation. Many ionic liquids offer a special combination of polarity and nucleophilicity that, compared with classical organic solvents, provides a superior reaction environment for many electrophilic and cationic transition metal complexes (20).

In the second case it is essential to understand and control exactly the reaction that forms the active catalyst in the ionic liquid to make sure that 100% of the precious catalyst precursor ends up in the most active, most selective, and most stable catalyst complex. Activation of transition metal complexes by Lewis-acidic ionic liquids and in-situ formation of metal carbene complexes are two of the most common reactions to form active catalysts in ionic liquids through ionic liquid-precursor reactions (21).

Among the options for applying ionic liquids in catalysis, liquid–liquid biphasic catalysis is a particularly attractive reaction mode for two reasons:

- The reaction products easily can be separated from the reactive ionic catalyst phase, thus circumventing a major drawback of classical homogeneous catalysis, and recycling of the dissolved catalyst and the ionic liquid is readily achieved without applying any thermal stress to the ionic catalyst solution. Because the transition metal complexes and the elaborate ligands used in homogeneous catalysis are usually quite expensive, complete recovery of both metal and ligand is crucial in a commercial situation.
- The immiscible ionic catalyst phase maintains the beneficial ionic environment for the dissolved catalyst even in cases in which the ionic liquid is applied in tiny amounts compared with the organic reaction mixture.

The principle behind a continuous, liquid–liquid biphasic catalytic process is schematically shown in **Figure 2**.

Over the past decade, many successful examples of ionic liquid–based liquid–liquid biphasic catalysis have been reported, far too numerous to mention here. The reader interested in a more complete picture of these research activities is referred to the many excellent reviews on the topic, most recently Wu et al. (22), Geldbach (23), Parvulescu & Hardacre (24), and Haumann & Riisager (25).

In the following, some important principles of liquid–liquid biphasic catalysis with ionic liquids will be introduced; selected publications on catalytic hydrogenations, dimerization, and hydroformylations are used as examples.

Ionic Liquid/Organic Biphasic Hydrogenation Reactions

Hydrogenation, in principle, is very well suited for a biphasic reaction mode using ionic liquids. Many ionic hydrogenation catalysts are known, and the formation of heavy, polar side products that would accumulate in the ionic liquid during recycling is unlikely. The de Souza and Chauvin

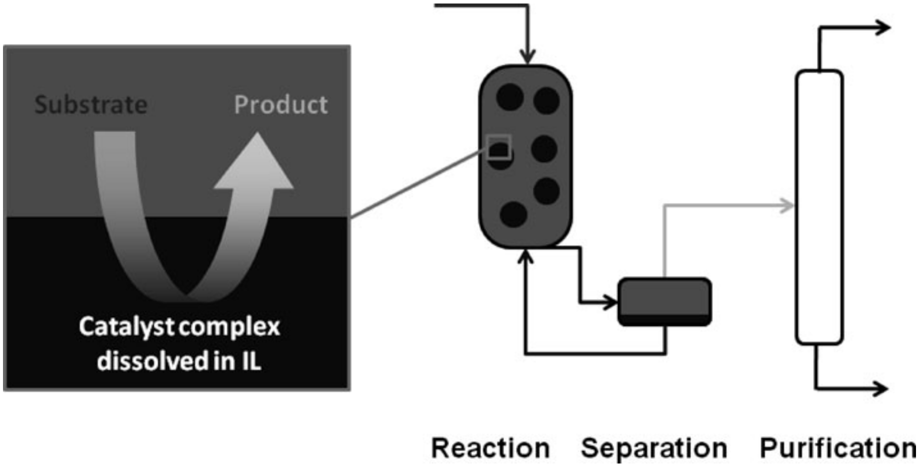
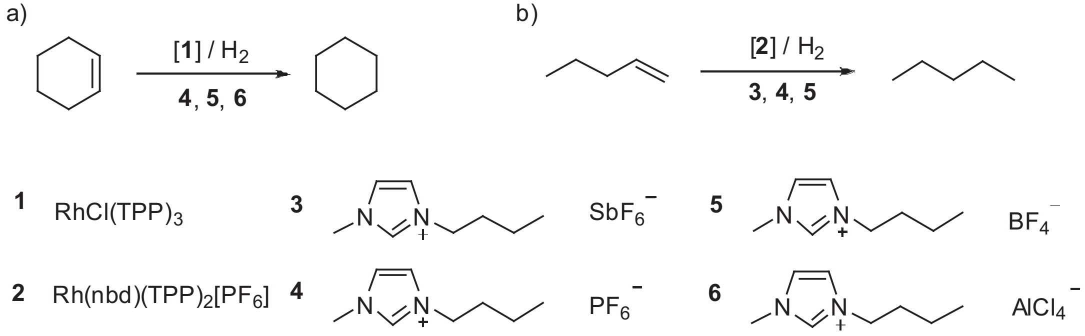


Figure 2

Organic-ionic liquid biphasic catalysis. (*left*) General principle. (*right*) Possible process flow scheme. IL: ionic liquid.

groups reported the first transition metal–catalyzed hydrogenation reactions in ionic liquids in 1995 (**Scheme 1**) (26, 27).



Scheme 1. Hydrogenation of (*a*) cyclohexene and (*b*) 1-pentene. TPP: triphenylphosphine ligand, nbd: norbornadiene ligand.

De Souza et al. investigated the hydrogenation of cyclohexene catalyzed by Wilkinson's catalyst $RhCl(TPP)_3$ **1** (where TPP = triphenylphosphine) in [BMIM][PF_6] **4**, [BMIM][BF_4] **5**, and [BMIM][$AlCl_4$] **6** (where BMIM = 1-butyl-3-methylimidazolium). For the biphasic hydrogenation of 1-pentene, Chauvin et al. dissolved the cationic [Rh(nbd)$(TPP)_2$][PF_6] **2** (Osborn's catalyst) in the ionic liquids **3**, **4** and **5**, which all contain weakly coordinating anions. **Table 2** summarizes the most relevant results of this early study.

Although the reactants exhibit only limited solubility in the catalyst phase, the rates of hydrogenation in [BMIM][SbF_6] **3** are almost five times faster than for the comparable reaction in acetone. However, the reaction was found to be much slower using the hexafluorophosphate ionic liquid **4**. This effect was attributed to the better solubility of pentene in the hexafluoroantimonate ionic liquid **3**. The very poor yield in [BMIM][BF_4] **5**, however, was due to a high amount of residual Cl^- ions in the ionic liquid, which led to catalyst deactivation. All ionic catalyst solutions could be reused repeatedly. The loss of rhodium through leaching into the organic phase

Table 2 Hydrogenation of 1-pentene

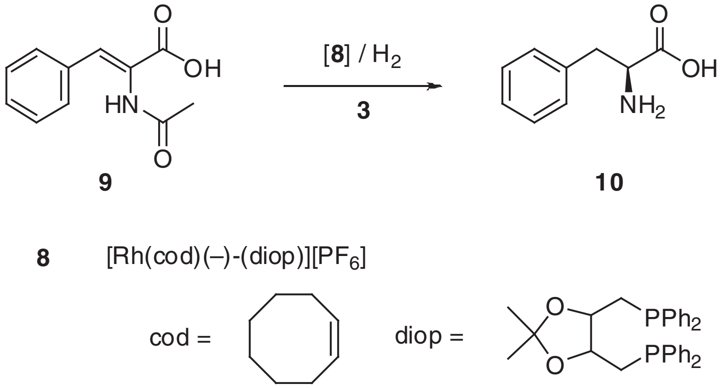
Solvent	$X_{1\text{-pentene}}$ (%)	Y_{pentane} (%)	$Y_{2\text{-pentene}}$ (%)	TOF[a] (h^{-1})
Acetone[b]	99	38	61	33.0
[BMIM][SbF_6] **4**	96	83	13	152.4
[BMIM][PF_6] **5**	97	56	41	103.2
[BMIM][BF_4] **6**	10	5	5	9.0

Reaction conditions: 0.05 mmol catalyst, 8.4 mmol 1-pentene, 4 ml solvent, T = 30°C, p(H_2) = 0.1 MPa, t_{reaction} = 2 h.
[a] Turnover frequency (TOF) = $\text{mol}_{\text{pentane}}\ \text{mol}_{\text{rhodium}}^{-1}\ h^{-1}$
[b] 10 ml acetone, 9.2 mmol 1-pentene.

was below the detection limit of 0.02%. These results are of general importance for the field of biphasic catalysis because this was the first time that a rhodium catalyst was immobilized in a polar solvent without the use of specially designed ligands. Several other papers dealing with nonstereoselective hydrogenations of alkenes in ionic liquids using liquid–liquid biphasic systems have been published since (28, 29).

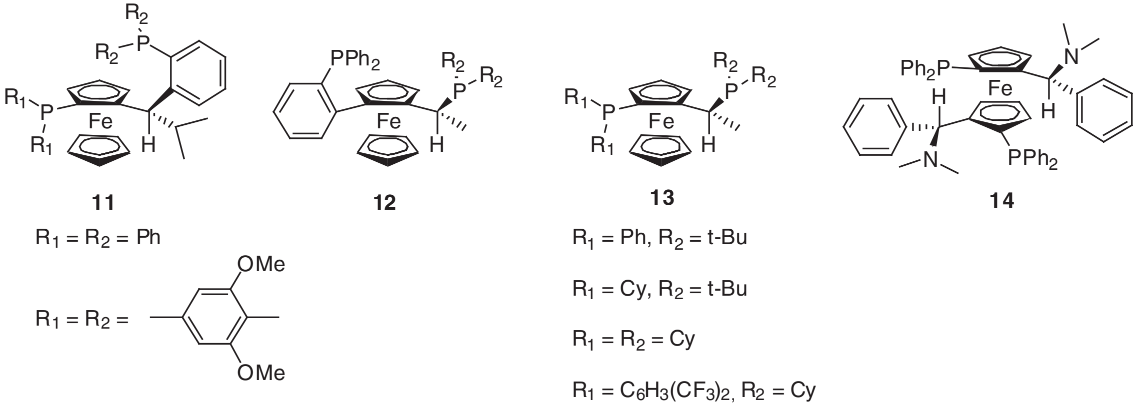
The hydrogenation of arenes is industrially important but thus far has been dominated by the use of heterogeneous catalysts. Dyson et al. used ruthenium clusters obtained from the ionic [$H_4Ru_4(\eta^6\text{-}C_6H_6)_4$][$BF_4$]$_2$ **7** precursor as a catalyst for the hydrogenation of benzene, toluene, cumene, ethylbenzene, and chlorobenzene (30, 31). A direct comparison of the two biphasic systems, water/organic solvent and ionic liquid/organic solvent, showed that the turnover frequencies obtained in the ionic liquid and the aqueous media are similar. Again the advantage of the ionic liquid-containing biphasic system was the easy separation of products and the potential to reuse the catalytic active phase.

Since 1995 several enantioselective hydrogenation reactions have been described using ionic liquids as the catalyst immobilization phase. Chauvin et al. pioneered the field by using [Rh(cod)(–)-(diop)][PF_6] **8** [where cod = cyclooctadiene ligand, diop = isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane ligand] as a catalyst to hydrogenate α-acetamido cinnamic acid **9** in [BMIM][SbF_6] **3** to create (S)-phenylalanine **10** with 64% enantiomeric excess (ee) (26). The reaction is depicted in **Scheme 2**.



Scheme 2. Hydrogenation of α-acetamido cinnamic acid in [BMIM][SbF_6] as described by Chauvin et al. (26). cod: cyclooctadiene ligand, diop: isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane ligand.

The product was easily and quantitatively separated, and the ionic liquid could be recovered. The loss of rhodium was less than 0.02% per run. Based on these promising first results, several research groups pursued asymmetric hydrogenation in ionic liquids. Pugin et al. carried out a broad screening of ligands and ionic liquids for the Rh-catalyzed hydrogenation of enamides (32). Rhodium-ferrocenyldiphosphine ligands with taniaphos **11**, walphos **12**, josiphos **13,** and mandyphos **14** ligands, depicted in **Scheme 3**, were identified in this study as the most effective catalyst ligand systems.



Scheme 3. Ligands applied to the asymmetric hydrogenation of enamides in ionic liquids.

The screening of the different reaction media proved that the application of an ionic liquid/water mixture—a wet ionic liquid—led to improved catalyst recycling compared with the reaction in an ionic liquid without cosolvent. This comparative study yielded good results for the hydrogenation of various enamides in wet ionic liquids with respect to conversion, enantioselectivity, and catalyst separation. More details on the asymmetric hydrogenation in ionic liquids can be found in Reference 21.

Ionic Liquid/Organic Biphasic Dimerization Reactions

A technically important oligomerization reaction that could not be carried out in a liquid–liquid biphasic mode prior to the invention of chloroaluminate ionic liquids is the Ni-catalyzed dimerization of propenes and/or butenes. The homogeneous monophasic version of the reaction was intensively studied in the 1960s and commercialized later as the Dimersol Process by the Institut Français du Pétrole (IFP). The Dimersol Process benefits from a catalytic species that forms in situ by reaction of a Ni(II) source and an aluminum alkyl cocatalyst. Remarkably, all polar molecular solvents that are able to establish a liquid–liquid biphasic system with the olefinic products were found to deactivate this highly electrophilic Ni center in a complete manner.

As early as 1990, Chauvin and coworkers from IFP published the first results on a successful, biphasic, Ni-catalyzed dimerization of propene using ionic liquids of the type [BMIM]Cl/$AlCl_3$/$AlEtCl_2$ (Et = ethyl) as a new type of catalyst phase (33). A significant advantage of the biphasic ionic liquid system is the low solubility of higher alkenes, which are formed during the dimerization reaction, in the ionic liquid catalyst phase. Thus, in the liquid–liquid biphasic dimerization of the alkene A, the dimer products A–A are immediately extracted from the ionic liquid into the organic phase. By this in-situ extraction, the selectivity of A–A in the catalyst phase remains low even at high conversions of A, and the undesired consecutive reaction to form

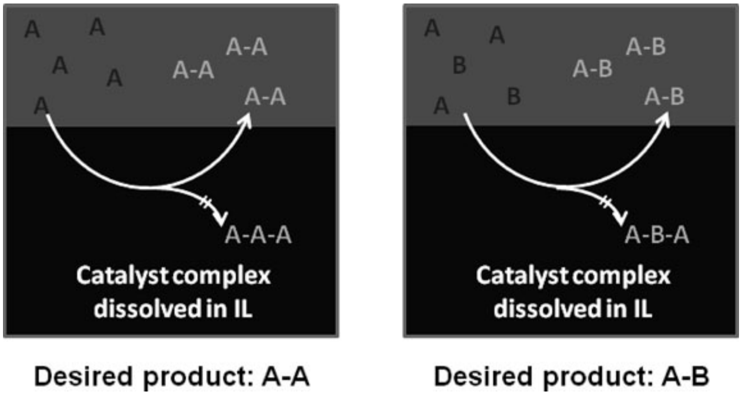


Figure 3

Improvement of selectivity through in-situ extraction of the desired products from the catalytic phase. (*left*) Dimerization of A to A–A. (*right*) Addition reaction of B to A forming A–B.

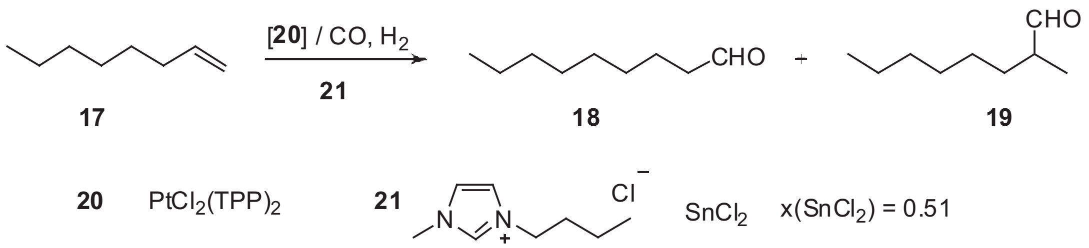
A–A–A is effectively suppressed. The same principle also works for addition reactions in which the desired product A–B is prone to a consecutive reaction to undesired A–B–A if the ionic liquid favors a rapid extraction of A–B from the catalytic phase (see **Figure 3**).

Based on these results, IFP has developed a biphasic version of their established monophasic Dimersol Process, which is offered for licensing under the name Difasol Process (34). The Difasol Process uses slightly acidic chloroaluminate ionic liquids with small amounts of aluminum alkyls as the solvent for the catalytic Ni center. In comparison with the established Dimersol Process, the new biphasic ionic liquid process drastically reduces the consumption of the Ni catalyst and aluminum alkyls. Additional advantages arise from the good performance obtained with highly diluted feedstock and the significantly improved dimer selectivity of the Difasol Process. **Figure 4** displays a flow scheme of the combined Dimersol-Difasol Process that is offered by IFP to improve the performance of existing Dimersol plants.

Ionic Liquid/Organic Biphasic Hydroformylation Reactions

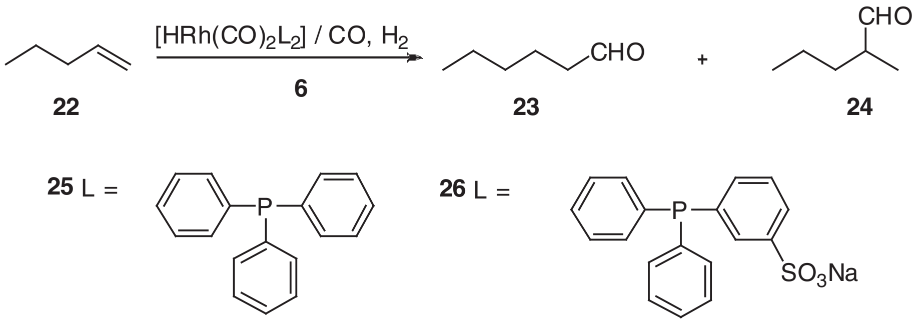
In hydroformylation, biphasic catalysis is a well-established method for effective catalyst separation and recycling. In the case of Rh-catalyzed hydroformylation reactions, this principle is technically realized in the Ruhrchemie-Rhône-Poulenc process in which water is used as the catalyst phase. Catalyst recycling and product separation is achieved according to the flow scheme in **Figure 2**. Unfortunately, this process is limited to C2–C5 alkenes due to the low water solubility of higher alkenes (35).

In 1972 Parshall described the platinum-catalyzed hydroformylation of ethene in tetraethylammonium trichlorostannate melts, $[NEt_4][SnCl_3]$ **15** (36). The ionic liquid used for these investigations has a melting point of 78°C. Later, the platinum-catalyzed hydroformylation was expanded to ionic liquids with imidazolium cations using the system $[BMIM]Cl/SnCl_2$ **16** and 1-octene **17** as the substrate (**Scheme 4**) (37). The high *n*/iso selectivity (95% **18** versus 5% **19**) is a remarkable feature of this catalytic system given that simple TPP is used as ligand for the applied catalyst **20**. Furthermore, a remarkable activity of the platinum catalyst was achieved with a turnover frequency (TOF) of 126 $mol_{aldehyde}\ mol_{Pt}^{-1}\ h^{-1}$ despite the limited solubility of 1-octene in the ionic catalyst phase.



Scheme 4. Pt-catalyzed hydroformylation of 1-octene in chlorostannate ionic liquids.

Initial investigations of rhodium-catalyzed hydroformylation in room temperature ionic liquids were published by Chauvin et al. in 1996 (26). The hydroformylation of 1-pentene **22** with the neutral catalyst system $HRh(CO)_2L_2$ (L = triarylphosphine) (see **Scheme 5**) was carried out in a biphasic reaction using $[BMIM][PF_6]$ **6** as the ionic liquid.



Scheme 5. Rh-catalyzed hydroformylation of 1-pentene in a hexafluorophosphate ionic liquid.

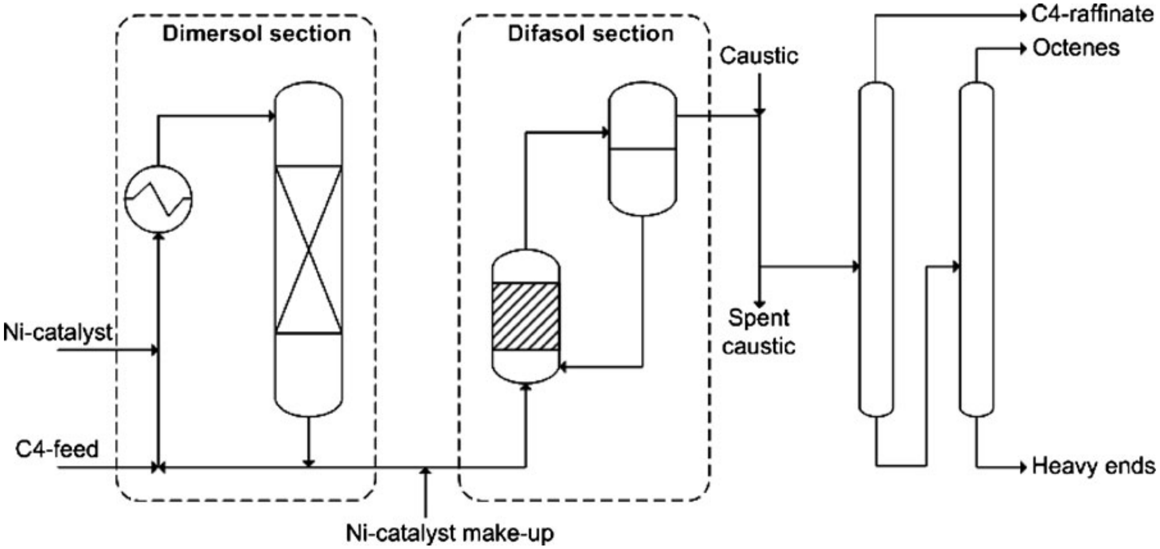
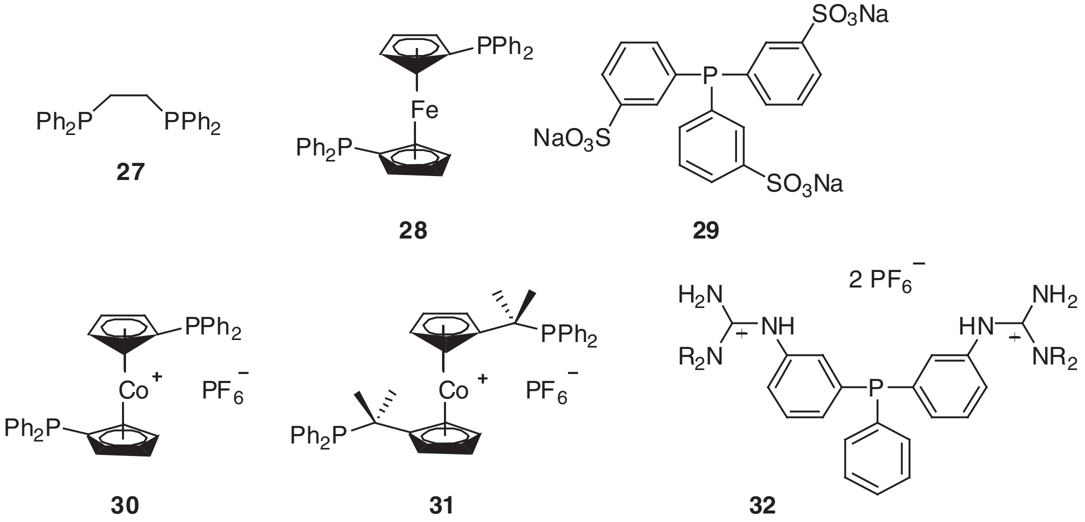


Figure 4

Flow scheme of the combined Dimersol-Difasol Process at the Institut Français du Pétrole (IFP). The C4 feed can consist of either pure butenes (1- and 2-butenes) or a mixture of butenes and butanes.

However, in this early study with none of the ligands tested was it possible to combine high activity, complete immobilization of the catalyst in the ionic liquid, and high selectivity for the desired linear hydroformylation product. High metal leaching from the ionic liquid into the organic phase was observed for ligand **25**, whereas ligand **26** resulted in poor activity.

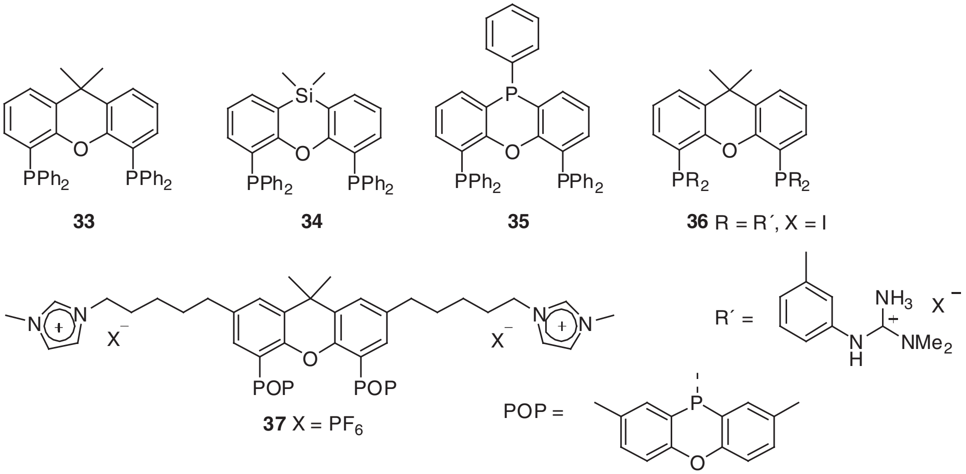
Based on this proof of principle, a systematic ligand optimization was carried out in academia during the following years. A first immobilization concept reported by Brasse and coworkers utilized ligands with a cobaltocenium backbone that were especially designed for use in ionic liquids (38). The two cobaltocenium-based, cationic ligands **30** and **31** are compared with several neutral and ionic ligands (see **Scheme 6**) with regard to their suitability in the biphasic, Rh-catalyzed hydroformylation of 1-octene.



Scheme 6. Ligand systems for biphasic hydroformylation in [BMIM][PF_6] as applied by Brasse et al. (38).

Whereas the use of the neutral ligands **27** and **28** went hand in hand with significant catalyst leaching, all charged ligands gave good to excellent immobilization. Interestingly, **29** and **31** were much less active and selective than **30**, which combined an *n*/iso ratio of 16.2 with a TOF of 810 h^{-1}. The modification of neutral phosphine ligands with cationic phenylguanidinium groups (**32** in **Scheme 6**) proved to retain the catalyst activity better than the use of the sulfonated triphenylphosphine derivative. Moreover, **32** provides excellent Rh immobilization in the ionic liquid, and ten consecutive recycling runs could be performed with this ligand system without a drop in activity (39).

Further development aimed at adapting charged groups to ligand structures that promised even better regioselectivity in the hydroformylation reaction. It is well known that bidentate phosphine ligands with large P–metal–P bite angles form highly regioselective hydroformylation catalysts (40). Here, the xanthene-based ligands (P–metal–P ~ 110°) depicted in **Scheme 7** and developed by van Leeuwen's group proved to be especially suitable (41).



Scheme 7. Xanthene-based ligands and their specially developed derivatives (**36** and **37**) for catalysis in ionic liquids.

Van Leeuwen et al. applied the imidazolium-based dicationic phenoxaphosphino-modified xantphos-type ligand **37** to the hydroformylation of 1-octene in [BMIM][PF_6] (42). The ligand provided excellent immobilization of the catalyst system with no Rh or P leaching detectable in the organic product phase and no loss in catalyst activity or selectivity observable in seven recycling experiments. Moreover, this ligand system provided a *n*/iso ratio of up to 65.

Supported Ionic Liquid Phase Catalysis

The extremely low vapor pressure of ionic liquids enables efficient product isolation by distillative processes. During product distillation the ionic liquid is able to stabilize the homogeneous catalyst by providing a nonvolatile and mildly coordinating solvent environment (43). Recently, a new concept for catalytic processes with ionic liquids has been introduced that makes explicit use of the above described effects but tries at the same time to reduce the amount of ionic liquid to an absolute minimum—the supported ionic liquid phase (SILP) concept. The ionic catalyst solution is confined on the surface of a highly porous solid by various methods such as physisorption, tethering, or covalent anchoring of ionic liquid fragments (44). This preparation results in a solid that appears macroscopically as a heterogeneous catalyst but acts chemically like a homogeneous catalyst owing to the molecularly defined, uniform ionic liquid environment provided to the dissolved metal complex by the supported ionic liquid film.

During a catalytic reaction using a SILP catalyst, the feedstock molecules diffuse through the residual pores of the catalyst, dissolve in the ionic liquid catalyst phase, and react at the dissolved transition metal complex within the thin liquid catalyst film that is dispersed on the walls of the support material. The products diffuse back into the void pore space and then further out of the catalyst particle (see **Figure 5**).

In general, the catalytic performance of a SILP-type catalyst depends considerably on the amount of ionic liquid loading (defined as the ratio between the liquid volume and support pore volume). This amount must be large enough to cover completely the solid surface, but pore plugging caused by an excess of ionic liquid must be avoided. As a consequence, the ionic liquid layer of SILP catalysts is usually a few nanometers thick. This makes diffusion problems during the catalytic reaction very unlikely.

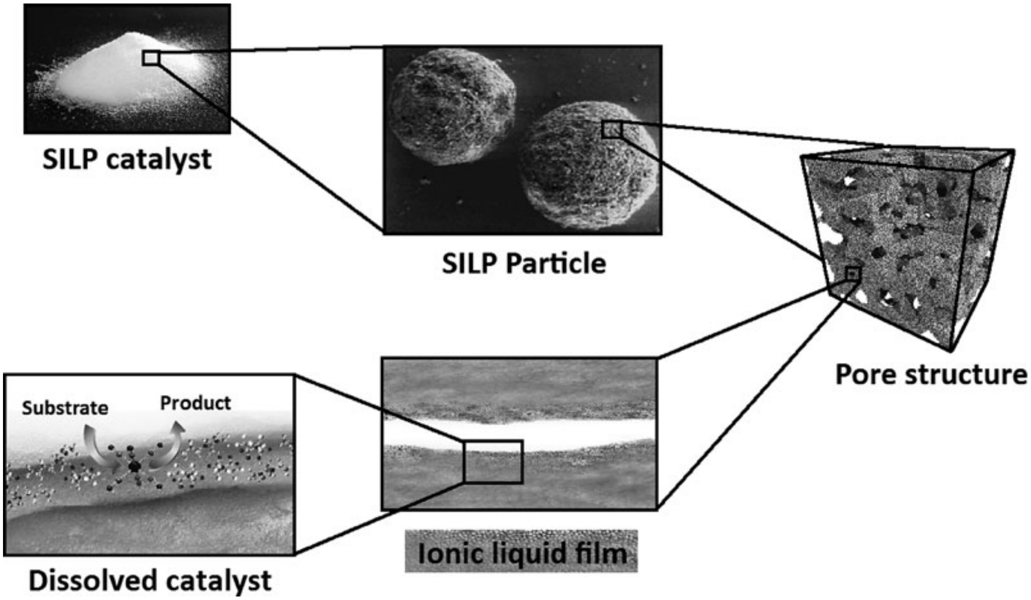


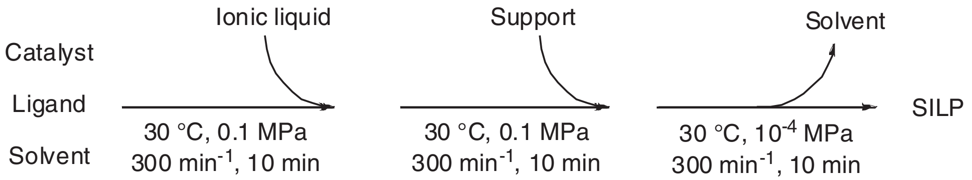
Figure 5

Schematic representation of a supported ionic liquid phase (SILP) catalyst.

SILP catalysis is a particularly efficient way to perform transition metal catalysis with ionic liquids if all of the reactants are contacted with the SILP material in gaseous form. In this case no specific ligand design is necessary to immobilize the transition metal complex in the ionic liquid as long as the metal complex does not evaporate or sublime from the ionic liquid during gas-phase contact.

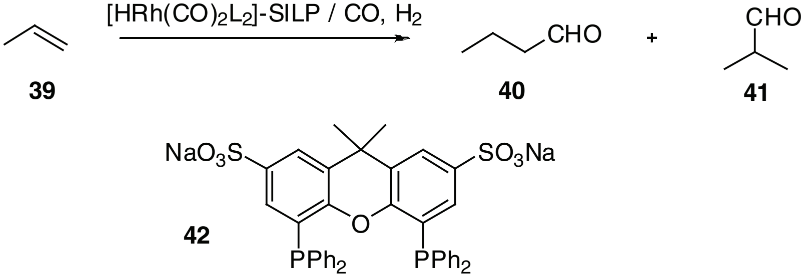
In contrast, the application of SILP catalysts in liquid slurry-phase reactions is often restricted by cross-solubility problems, mechanical removal of the ionic liquid film, or catalyst leaching from the SILP film into the product mixture (45). Recently, Gu & Li published an excellent and quite comprehensive review on the actual development of SILP catalysis (46). Here, the Rh-SILP-catalyzed hydroformylation of propene and 1-butene in continuous gas-phase contact will be used to illustrate the SILP concept in more detail.

A typical SILP material for gas-phase hydroformylation is prepared, for example, by immobilizing $[Rh(CO)_2L_2]$ and the applied phosphine ligands in a film of $[BMIM][n\text{-}C_8H_{17}OSO_3]$ **38** ionic liquid on silica gel, using impregnation with degassed solutions of methanol (see **Scheme 8**) (47).



Scheme 8. Preparation of a catalytic supported ionic liquid phase (SILP) material by physisorptive fixation of the ionic catalyst solution on a support.

A SILP material obtained in this way with an ionic liquid loading of 10 vol%, a rhodium content of 0.2 wt%, and the ligand sulfoxantphos **42** (L/Rh = 10) proved particularly interesting in the continuous hydroformylation of propene (**Scheme 9**) (44).



Scheme 9. Rh-SILP-catalyzed propene hydroformylation using the sulfoxantphos ligand (42).

In the gas-phase hydroformylation of propene, these SILP catalysts exhibited activities of more than 400 h^{-1} combined with the high selectivity of 95% n-butanal **40**. At 120°C and 10 bar syngas pressure, the stability of the catalyst exceeded 700 h time-on-stream without loss in activity or selectivity. A space-time yield of 0.11 $t\ m^{-3}\ h^{-1}$ was determined for this example, which can be significantly improved under optimized reaction conditions (e.g., higher catalyst loading). Remarkably, these SILP materials have been stored on the bench for more than six months, after which they still exhibit their initial performance (48).

SILP systems have proved to be especially suitable for kinetic studies of hydroformylation catalysis under steady-state conditions. For example, the kinetic parameters have been determined for the Rh-**42**-SILP catalyst (47). A first order dependency of the reaction rate on propene partial pressure was found, whereas syngas variation studies yielded a slightly positive order for hydrogen and a negative order for carbon monoxide partial pressures. The activation energy for propene hydroformylation was determined from an Arrhenius plot to be 64 kJ mol^{-1}. All these data are in good agreement with the established Wilkinson catalytic cycle for ligand-modified rhodium catalysis. Thus, it was concluded that the Rh-sulfoxantphos catalyst is indeed homogeneous in the ionic liquid thin film and does not interfere with the surface. The homogeneous nature was further verified by Fourier transform-infrared (FT-IR) spectroscopy under reaction conditions and by solid-state NMR experiments (47). When the substrate was changed from propene to 1-butene, similar kinetic parameters were obtained (see **Figure 6**) (49). However, owing to the 2.4 times higher solubility of 1-butene in the ionic liquid, the observed TOF was higher for 1-butene hydroformylation by a factor of 2.5, clearly demonstrating that the substrate solubility in the ionic liquid film determines the catalyst performance. Additionally, by variation of the rhodium loading in the SILP catalyst, the reaction order of rhodium has been determined to be 0.9, which indicates that the overall reaction rate is not limited by mass transport effects and the entire metal inventory is utilized.

In addition to homogeneous catalysis in ionic liquids—which occupies by far the most space in the literature—examples of nanoparticle catalysis, biocatalysis, and heterogeneous catalysis in and with ionic liquids have been published in increasing number over the past couple of years. These reactions possess very attractive features from an engineering point of view.

The interest in nanoparticle catalysis in ionic liquids was triggered because many ionic liquids have been shown to be suitable media for the generation and stabilization of metallic nanoparticles (50) suitable for catalytic applications, such as hydrogenations (51) and Heck coupling (52). Ionic

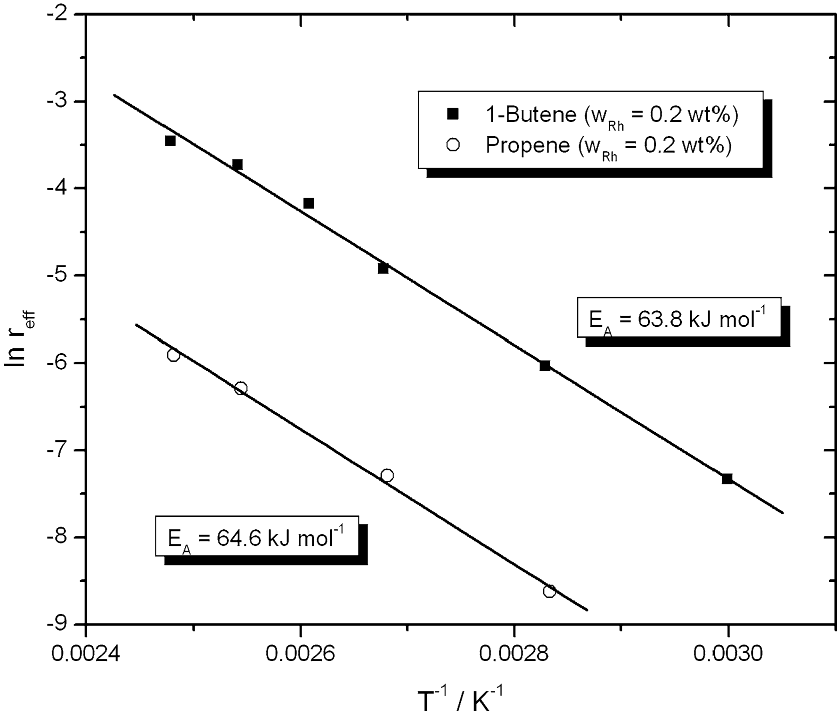


Figure 6

Arrhenius plot for propene and 1-butene hydroformylation catalyzed by Rh-42-SILP. r_{eff}: effective rate of reaction (bar s^{-1}), w_{Rh}: rhodium content (wt%), E_A: apparent activation energy (kJ mol^{-1}).

liquids are of interest as solvents or cosolvents in biocatalytic processes if the reaction mixture includes hydrolysis-labile substrates or products. Moreover, enzymatic condensation reactions in ionic liquids have proven to be possible and synthetically highly interesting. In the reported examples the greatly reduced water activity in the ionic liquid-containing systems strongly influences the reaction equilibria (53).

Finally, heterogeneous catalysis in the presence of ionic liquids can be attractive if the ionic liquid has a distinct positive effect compared with the application of the heterogeneous catalyst alone. The modification of a catalytic solid by contacting it with an ionic liquid is straightforward, as it does not require any additional synthetic steps. The coating of a heterogeneous catalyst with an ionic liquid, a technology for which the term solid catalyst with ionic liquid layer (SCILL) was coined (54), can lead to a modified reactant concentration at the active site (owing to the ionic liquid's differential solubility) and/or to chemical modification of the catalytic sites (owing to the ionic liquid's reactivity with the active surface site).

Obert et al. recently added a new aspect to the concept of heterogeneous catalysis in ionic liquids (55). These authors demonstrated that ionic liquid-organic biphasic systems can efficiently separate highly dispersed heterogeneous catalysts from liquid reaction products, thus avoiding tedious filtration processes. For example, a Ru on C catalyst remains selectively attached to the ionic liquid phase even when the latter is the less dense phase (e.g., versus trichlorobenzene, as shown in **Figure 7**). The observed effect was used to recycle the ionic catalyst suspension after a catalytic hydrogenation by a simple decantation process.

IONIC LIQUIDS IN SEPARATION PROCESSES

In the chemical industry, separation processes play an important role. In a typical plant, 60–80% of the total cost is attributed to the separation steps because the upstream chemical reaction is neither 100% selective nor operated at full conversion (56). In separation processes such as extraction, distillation, absorption, membrane processes, or adsorption, the rules of chemical thermodynamics are applied to separate the different components of the reaction mixture and to obtain the product in the desired purity.

By far the most common separation process in industry is distillation/rectification, in which a difference in the vapor pressure/fugacity of the components is the driving force for separation. Absorption processes are employed to remove compounds from a gas stream. In contrast, extraction uses the relative difference in activity coefficients to separate components in a liquid–liquid biphasic system. Extractive distillation, extraction, and absorption processes gain importance if distillation proves unfeasible, e.g., because of azeotropic points or separation factors that are very close to one. All three processes require the utilization of special solvents that are able to alter the partition coefficients in a favorable way. Ionic liquids with their unique and tunable miscibility and solubility properties have been successfully tested in these separation processes both in academia and industry. The following sections aim to introduce the reader to the state-of-the-art in these ionic liquid–based separation technologies.

Extraction

Due to their polar nature, almost all ionic liquids show a pronounced miscibility gap with apolar organic solvents. In addition, liquid–liquid biphasic systems with aqueous phases can be realized with hydrophobic ionic liquids such as [BMIM][$(CF_3SO_2)_2N$]. For all extractions with ionic liquids, the knowledge of the distribution coefficients and the ionic liquid selectivity is crucial. From the engineering point of view, it is important that the higher viscosity of ionic liquids compared with organic solvents changes the hydrodynamic design of extraction columns drastically (57). Little is still known about coalescence phenomena in biphasic mixtures containing ionic liquids.

Removal of heavy metal traces. In conventional processes the extractive recovery of metal oxides usually is composed of a first process step in which the metal compound is dissolved in an aqueous medium with the aid of a strong acid or base, followed by an extraction step with organic solvents. To make this extraction efficient, complexing agents are added to the mixture, which leads to improved partitioning of the metal compound into the organic phase (58). Aliphatic amines, crown ethers (cyclic polyethers), and ammonium salts are used as complexing agents.

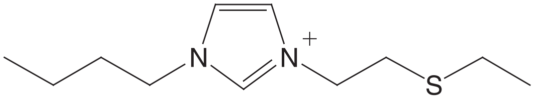
The extraction of hydrophobic compounds from water is possible with the use of a hydrophobic ionic liquid. To create metal ions of sufficient hydrophobicity for extraction into a hydrophobic ionic liquid, extraction agents are again required (59–61). Recently, task-specific ionic liquids carrying the complexing group in one ion have been successfully applied in metal ion extraction. These systems work both as extractants and as solvents (62, 63).

One advantage ionic liquids can offer in contrast to conventional solvents is that their ionic nature can help in the separation of ionic metal complexes (59). However, to achieve good efficiency in the extraction process, the hydrophobicity of the ionic liquid, the type of extractant, and the pH value of the system have to work together in a suitable manner.

Successful examples of metal extraction from water using hydrophobic nonfunctionalized ionic liquids include the removal of radioactive metal traces from aqueous solutions (61) and the selective extraction of yttrium. The latter has been achieved with the ionic liquid

1-octyl-3-methylimidazolium hexafluorophosphate [OMIM][PF_6] with addition of ethylenediaminetetraacetic acid (EDTA) as the complexing agent (64).

Visser and coworkers have reported the use of functionalized ionic liquids in extraction (65). These authors used ionic liquids carrying urea, thioether, and thiourea functionalities (see **Scheme 10**) to remove mercury (Hg^{2+}) and cadmium (Cd^{2+}) from water. Although good distribution coefficients could be achieved, the recovery of the ionic liquid has not been addressed in detail.



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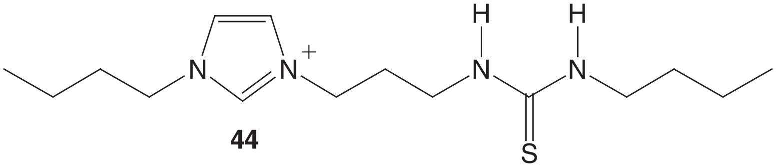

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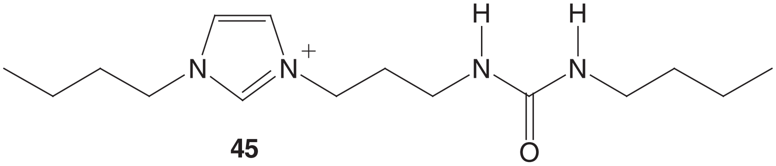

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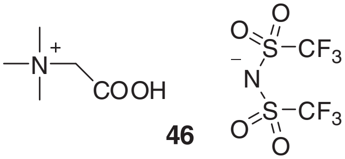
Scheme 10. Structures of the cations of task-specific ionic liquids for the extraction of Hg^{2+} and Cd^{2+} ions from water (65).

Nockemann et al. applied a protonated betaine [NTf_2] system **46** to dissolve a wide range of metal oxides including oxides of the trivalent rare earths, such as uranium(VI) oxide, zinc(II) oxide, cadmium(II) oxide, mercury(II) oxide, nickel(II) oxide, copper(II) oxide, palladium(II) oxide, lead(II) oxide, manganese(II) oxide, and silver(I) oxide (see **Scheme 11**) (66). After dissolution, the metals could be stripped from the ionic liquid by treatment with an acidic solution. After transfer of the metal ions to the aqueous phase, the ionic liquid can be reused.



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Scheme 11. Protonated betaine [NTf_2] system used by Nockemann et al. for the extraction of metal oxides from aqueous solutions (66).

In summary, the removal of heavy metal ions from water by extraction with ionic liquids is a field of intense research and some promise. However, important practical questions, such as the complete recovery of the ionic liquid and the full isolation of the extracted metal from the ionic liquid, still need more attention (67, 68).

Aromatic hydrocarbon removal. The separation of aromatic hydrocarbons, such as benzene, toluene, or xylenes, from their aliphatic hydrocarbon counterparts is challenging because of the small difference in boiling points and the existence of azeotropes (69). Depending on the amount of aromatic compounds in the mixture, different processes are suitable. Liquid extraction is favored for an aromatic content of less than 65%, whereas extractive distillation is the most suitable option between 65% and 90% aromatic content (70). In the case of a very high aromatic content, azeotropic distillation is used. The polar solvents applied in conventional processes, such as *N*-methyl pyrrolidone (NMP), sulfolane, or ethylene glycol, suffer from a significant cost of regeneration that is linked to the high energy cost for distillation or back-extraction (71).

The extremely low vapor pressure of ionic liquids enables easier recovery by simple flash distillation or stripping, which could result in lower energy consumption. Moreover, many ionic liquids show very favorable selectivities in the extraction of aromatics from hydrocarbons.

As early as 1998, the Rogers group published a communication on the use of [BMIM][PF_6] in the extraction of several aromatic compounds (17). Since then several papers have reported on the distribution coefficients and selectivities found in ionic liquid/aromatic biphasic systems (72, 73).

Meindersma et al. performed the first economic evaluations of the liquid–liquid extraction of aromatics with ionic liquids (74–76). These authors compared the extraction of a naphtha cracker feed with ionic liquids (e.g., [EMIM][$EtSO_4$], 1-butyl-4-methylpyridinium [PF_6], 1-butyl-4-methylpyridinium dicyanamide) with the technical standard sulfolane and calculated an annual savings of approximately 50% for the ionic liquid–based extraction concept. Recently, the Seddon group also investigated the ternary hexane/benzene/[EMIM][NTf_2] system and claimed a superior performance for the ionic liquid–based extraction in comparison with current process technologies (77).

In summarizing the current state-of-the-art, it can be stated that the technical potential of ionic liquids in the extraction of aromatic or unsaturated hydrocarbons from aliphatic hydrocarbons is high. Further improvements can be expected in the near future from model-based structural modifications of the applied ionic liquids, which will lead to even higher selectivities and capacities.

Fuel desulfurization. In today's refineries desulfurization is carried out by a catalytic hydrodesulfurization. Stricter environmental legislation and less favorable crude oil qualities have led to the situation that S-compounds that are extremely difficult to hydrogenate, e.g., alkyl-substituted dibenzothiophenes, also need to be removed from fuel. For these extremely unreactive structures, hydrodesulfurization is combined with extreme reaction conditions, long residence times, and a huge hydrogen recycling effort that has stimulated interest in alternative desulfurization concepts (78, 79).

In 2001 Bösmann et al. published a first paper describing deep desulfurization of real diesel fuel by extraction with chloroaluminate ionic liquids (80). Although 80% of the sulfur components could be removed successfully in a five-stage extraction at 60°C, this system has inherent hydrolytic instability, which makes its use in a technical context difficult. Later, extractive removal from diesel fuels was successfully demonstrated for hydrolytically stable ionic liquids; however, ionic liquid regeneration by distillation or stripping proved inappropriate because of the very low vapor pressure of the extracted S-compounds in the ionic liquid (78, 81). Re-extraction procedures were successfully tested to regenerate the ionic liquid, but this methodology requires a significant amount of additional re-extraction solvent. Therefore, extractive desulfurization with ionic liquids is much more promising and straightforward if relatively low-boiling S-compounds are to be removed, a scenario that still allows the use of distillative ionic liquid regeneration.

In this context several groups reported the extraction of thiophenes (82, 83) and thiols from model oils, and for the case of butylmercaptan extraction, ionic liquid recovery and reuse over six cycles was successfully demonstrated (81). Several groups are also active in developing ionic liquids with task-specific, often mildly Lewis acidic functionalities to support the physisorptive interactions by a reversible chemisorption contribution (81, 84, 85). This concept promises better selectivities and capacities but will also be restricted to lower-boiling S-compounds, as a stronger chemical interaction of the S-compound with the ionic liquid will lead to an additional decrease in the vapor pressure of the S-compound.

Protein extraction. Modern biotechnology requires efficient bioseparation because purification costs can be a major portion of the total process cost (86). Currently, extraction via aqueous two-phase systems, adsorption, and membrane separation are applied in this field. The aqueous two-phase systems typically utilize the highly viscous polyethylene glycol (PEG) as the extractant (87). However, one can successfully employ ionic liquids in protein extraction because of their generally lower viscosity in comparison with PEG, their smaller emulsion formation, and their better recyclability (88–90).

In the literature, the extraction of myoglobin, human serum albumin, and immunoglobulin G with alkyl substituted phosphonium-[NTf_2] ionic liquids has been reported. Furthermore, the use of [RMIM]Br, (R = butyl, hexyl, octyl) for trypsin, cytochrome c, and globulins extraction has been tested, and yields between 75% and 100% obtained (91, 92).

Recently, an almost quantitative recovery of lysozyme by extraction with [BMIM][PF_6] was reported. Obviously the known hydrolytic instability of the ionic liquid caused no major problems when operating in a pH range of 9–11 (93).

Extractive Distillation

When close-boiling mixtures or even azeotropes are to be separated, classical distillation is impossible. By adding a solvent that selectively interacts with one component of the mixture, one can use the nonideality of mixtures to enable effective separation. In the case of the addition of a volatile entrainer, an azeotropic distillation process can be established, whereas the addition of a nonvolatile entrainer results in extractive distillation (94). The recovery and reuse of the selective solvent after separation is crucial for the process economics. The addition of mostly corrosive salts to an extractive distillation mixture has been suggested as a way to increase the volatility of the light components by salting out the heavy components. A reduction of the solvent-to-feed ratio thus could be realized (95).

The use of ionic liquids as selective entrainers is interesting for many reasons. For example, the tunable solvent nature of ionic liquids allows the design of an ionic entrainer for specific interaction with one of the components. The usually less corrosive nature of ionic liquids is an important advantage when compared with earlier tested salt additions (96). The ionic liquid entrainer technology is covered by a patent by Arlt and BASF SE (97). Ionic liquid entrainers are usually applied in amounts of 30 to 50 wt% (98). This amount seems large but is smaller than typical additions of classic entrainers such as dimethylformamide (DMF). The advantage of an ionic liquid entrainer over a classic entrainer is that the extremely low vapor pressure of the ionic liquid entrainer saves the solvent regeneration column and thus a lot of energy. A benchmark calculation carried out at BASF SE for a technically relevant example has revealed potential savings of approximately 37% for energy costs and 22% for investment costs (99). BASF SE ran an extractive distillation process with an ionic liquid entrainer in a pilot plant continuously for 3 months. The applied ionic liquid faced a severe thermal stress in this process (250°C in the recycling step) but maintained its full performance over this testing time.

Hydrocarbon/water separation. The separation of hydrocarbons from water often results in the formation of azeotropes. For these cases (e.g., THF/water, ethanol/water) the use of an ionic liquid entrainer has proven particularly effective, and very high separation factors have been achieved. These results are understandable considering that most ionic liquids are hygroscopic materials with a strong affinity for water.

In the case of THF/water, the azeotrope can be broken by using, for example, [BMIM]Cl as entrainer (100). For the separation of ethanol from water, the addition of [EMIM][BF_4] has been successfully applied and resulted in a 25% energy reduction in comparison with the classical process employing ethanediol as the entrainer (96). The Gmehling group has investigated systematically the influence of various ionic liquids on the phase behavior of hydrocarbon/water/ionic liquid systems (101–103). Arlt and coworkers have explored the possibility of using a model-based approach to design ionic liquids that will be most effective in this kind of extractive distillation (13).

Alkene/paraffin separation. The system 1-hexene/n-hexane is a typical example of an alkene/paraffin separation problem. Arlt and coworkers studied this problem intensively by performing a COSMO-RS-based ionic liquid structure optimization as well as experimental measurements via headspace GC (104). The obtained results were compared with the technical benchmark NMP. The best ionic liquid in this study in terms of selectivity and capacity was the $[NTf_2]^-$ salt of $[OMIM]^+$, but the conventional solvent NMP still exhibited better results. The authors concluded that in this particular case the application of [OMIM][NTf_2] might be favorable only if the thermal or chemical stability of NMP is in question (104, 105). Recently the Gmehling group published an approach for the calculation of the required vapor-liquid-equilibrium (VLE) data and verified their conclusions experimentally for 1-hexene/n-hexane in contact with different $[NTf_2]^-$-based ionic liquids (106).

Aromatic/aliphatic hydrocarbon separation. The situation for ionic liquid–based extractive distillation is more favorable for separations of aromatic and aliphatic hydrocarbons (107). Hydrophobic ionic liquids with the $[NTf_2]^-$ anion such as [OMIM][NTf_2] show selectivities in the range of conventional entrainer solvents (e.g., sulfolane, NMP, or DMF) but have been found to exhibit significantly higher capacities (13). Therefore, the application of ionic liquid entrainers for these separations appears favorable.

Absorption

The solubility of different gases in ionic liquids has been intensively studied by many groups in the past couple of years (108–113). In general, ionic liquids exhibit low gas solubilities for hydrogen, oxygen, nitrogen, argon, and CO, whereas carbon dioxide, ammonia, and sulfur dioxide exhibit generally high solubilities in ionic liquids (114). But the selective solubility of a gaseous component is not the only prerequisite for a feasible absorbent. The main cost of the absorption process usually arises from the recovery of the absorbent, and in this context it is decisive whether the gas dissolves via pure physisorption or by means of a chemical reaction (115).

In the case of ionic liquids, the regeneration of the ionic absorbent is particularly straightforward, as flash distillation or stripping can be performed without the need to recondense the absorbent. Besides the ease of recovery, the capacity of the absorbent is a crucial point as this quantity determines the amount of absorbent needed and thus the size of the absorber.

Currently the absorption of CO_2 from power plant exhaust streams is of great interest in industry. Promising candidates for that process are the application of aqueous monoethanolamine

(MEA) or methyldiethanolamine (MDEA) solutions. But again, the loss of absorbents due to vapor pressure and the ease of recovery remains a problem.

Ionic liquids appear to reach the highest capacities when fluoroalkyl anions such as $[CTf_3]^-$ or $[NTf_2]^-$ are used (109, 110, 116). Promising results in this field have been found mainly for functionalized ionic liquids. In the Meindersma and de Haan group, amino-functionalized imidazolium ionic liquids were found to perform the same as a 30% MEA-water solution (117). Other groups have intensively studied similar approaches, including theoretical approaches to the structural optimization of the applied ionic liquid (118–121). Also, the application of polymeric ionic liquids has been suggested to enhance the CO_2 capture efficiency (122–124).

From today's knowledge one can conclude that CO_2 capture with ionic liquids provides several interesting features that clearly justify more research efforts in this direction. Given the very specific requirements of the application of these ionic liquids in the exhaust gas stream of a commercial power plant, more attention must be given to the robustness and to the economic aspects (price, lifetime, exchange rate) of this approach.

Membrane Processes

The application of ionic liquids in separation processes can also be combined with membrane technology. Two general approaches can be distinguished: the use of ionic liquids as bulk liquid membranes (BILMs) (125, 126) or supported ionic liquid membranes (SILMs) (127, 128) for the separation of fluid mixtures, and the application of membranes to isolate nonvolatile, polar substances from the ionic liquid (129–131). In the first case the ionic liquid acts as a selective separation layer, whereas in the second case the membrane solves a product isolation problem that often occurs if the isolation of products or by-products from the ionic liquid cannot be achieved by distillation or extraction.

Reported examples for SILMs include reactions with in-situ product removal (132), extraction of bioorganic substances (133–135), and removal of CO_2 and SO_2 from gas streams (136–140). SILMs have also been successfully tested in the separation of alkenes and paraffins (141) and in the removal of aromatic hydrocarbons (142, 143).

CONCLUSIONS

The development of engineering applications of ionic liquids requires a profound knowledge of the nature of these liquids and of all relevant aspects of the intended application. The examples presented in previous sections clearly show that many of the discussed concepts are still at an early stage of development. This is mainly because ionic liquids is a young field of research that the engineering community has only recently discovered.

There is absolutely no doubt that the unique properties of ionic liquids offer great potential to improve existing engineering applications or to develop attractive new ones. However, most of the reported examples in the literature still represent proof-of-concept research. Consequently, often not enough data are available to predict conclusively whether a certain application will truly profit in its efficiency on a commercial level from the use of an ionic liquid. Indeed, much of the information that is necessary to evaluate the efficiency of an ionic liquid in a given engineering application is generated only in a more advanced state of development in which more attention can be given to aspects such as recycling efficiency, ionic liquid recovery, or the degree of ionic liquid degradation over time. In this more advanced state of development, a detailed benchmarking with existing process alternatives can also be expected.

This review has strongly focused on the application of ionic liquids in catalytic applications and separation technologies. For advances in these two application areas, the understanding of many chemical and physicochemical phenomena in complex, dynamic mixtures is required, which slows the development process down. To demonstrate that this degree of complexity is responsible for the still relatively low number of industrial ionic liquid applications in catalysis and separation, a closer look at another young area of ionic liquid engineering applications is instructive.

Following the first pioneering studies in 2001 (144), the application of ionic liquids as lubricants and working fluids in process machines has been developed. A first commercial application of this approach has already been realized, the Linde ionic compressor (145), in which an ionic liquid substitutes the metallic piston that compresses the gas. The concept builds on the extremely low vapor pressure of the ionic liquid but also on its excellent tribologic behavior and its very low solubility for the gases to be compressed (e.g., methane, hydrogen). Advantages of this concept versus the traditional metallic piston compressor are a drastic reduction of movable parts, a very high volumetric efficiency, and a quasi-isothermal compression (the ionic liquid piston can be cooled using a classical heat exchanger). Recently, the same concept was applied to the compression of pure oxygen, a gas that would undergo heavy oxidation reaction with normal organic lubricants (146). Due to the high oxidation stability and strong flame resistance of the applied ionic liquid, even highly pure oxygen (quality 6.0) could be compressed with the ionic compressor to 16 bar for 3000 hours service time without any technical problems.

In addition to the ionic compressor concept, ionic liquids have been proposed as lubricants in combustion engines, as hydraulic fluids, as working fluids in liquid ring pumps, and as hydraulic oil in hydraulically driven diaphragm pumps (147). Besides the negligible vapor pressure, all these applications profit from the excellent lubricating properties of most ionic liquids as well as their high thermal stability (compared with mineral oils), good flame resistance, very low compressibility, moderate corrosion potential, and excellent wettability for metallic surfaces (148).

In the light of these recent success stories, we are convinced that ionic liquids offer a huge potential for better, more efficient, safer, or completely new engineering applications, but much remains to be achieved and developed to realize all promising opportunities. Optimized ionic liquid structures, more physicochemical and engineering data, improved theoretical prediction tools, and the development of dedicated process units and devices are needed. We hope that this contribution will help attract more engineers to this highly exciting field of research.

DISCLOSURE STATEMENT

The authors are not aware of any affiliations, memberships, funding, or financial holdings that might be perceived as affecting the objectivity of this review.

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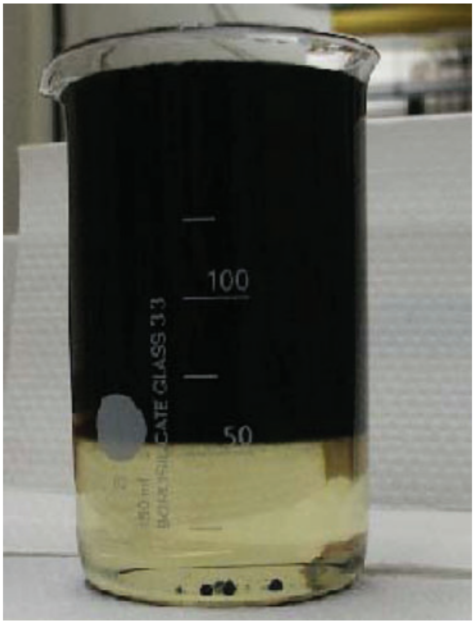

Figure 7

Ru on C catalyst suspended in dimethylcyclohexylammonium hydrogensulfate (*top phase*) in the presence of 1,2,4-trichlorobenzene (*bottom phase*).

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Contents

Errata

An online log of corrections to *Annual Review of Chemical and Biomolecular Engineering* articles may be found at http://chembioeng.annualreviews.org/errata.shtml