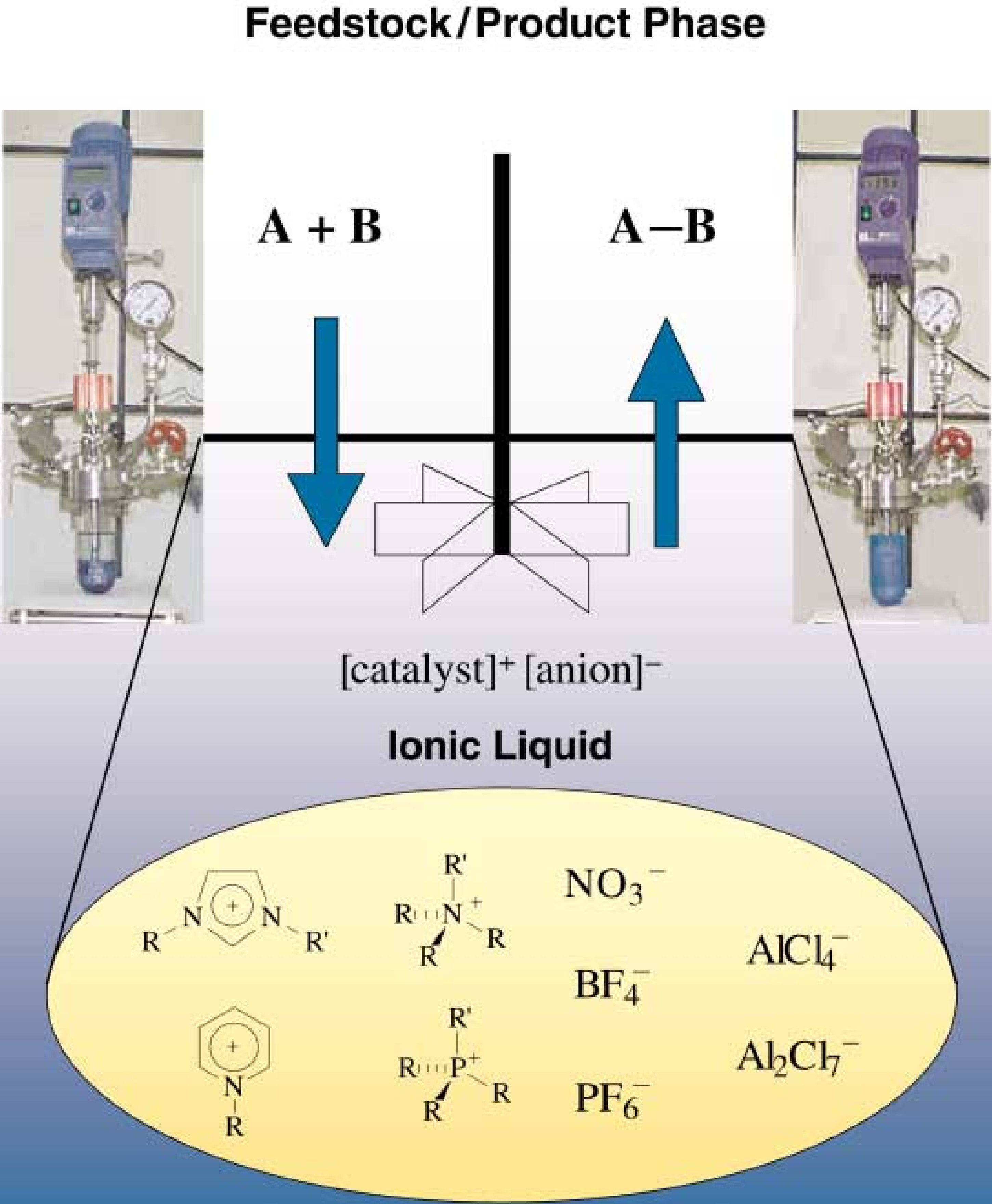

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Ionic Liquids—New “Solutions” for Transition Metal Catalysis

Peter Wasserscheid* and Wilhelm Keim

Ionic liquids are salts that are liquid at low temperature ($< 100\,^{\circ}C$) which represent a new class of solvents with nonmolecular, ionic character. Even though the first representative has been known since 1914, ionic liquids have only been investigated as solvents for transition metal catalysis in the past ten years. Publications to date show that replacing an organic solvent by an ionic liquid can lead to remarkable improvements in well-known processes. Ionic liquids form biphasic systems with many organic product mixtures. This gives rise to the possibility of a multiphase reaction procedure with easy isolation and recovery of homogeneous catalysts. In addition, ionic liquids have practically no vapor pressure which facilitates product separation by distillation. There are also indications that switching from a normal organic solvent to an ionic liquid can lead to novel and unusual chemical reactivity. This opens up a wide field for future investigations into this new class of solvents in catalytic applications.

Keywords: biphasic catalysis · homogeneous catalysis · ionic liquids · solvent effects

1. Introduction

In general, an ionic liquid is a liquid that consists only of ions. However, this term includes an additional special definition to distinguish it from the classical definition of a molten salt.[1] While a molten salt is generally thought to refer to a high-melting, highly viscous and very corrosive medium, ionic liquids are already liquid at low temperatures ($< 100\,^{\circ}C$) and have relatively low viscosity. The apparently somewhat arbitrary line drawn between molten salts and ionic liquids at a melt temperature of 100°C can be justified by the abrupt improvement in the range of applications for liquid salts below this temperature. Even though some examples are known in which high-temperature salt melts have been successfully used as reaction media for synthetic applications,[2] only a liquid range below 100°C can enable the versatile substitution of conventional, organic solvents by ionic liquids.

The development of ionic liquids goes back to 1914. First research efforts dealt with the synthesis of ethylammonium nitrate.[3] This salt is liquid at room temperature but usually contains a small amount of water (200–600 ppm).[4]

The first ionic liquids with chloroaluminate ions were developed in 1948 by Hurley and Wier at the Rice Institute in Texas as bath solutions for electroplating aluminum.[5] However, these systems were not studied further until the late 1970s when the groups of Osteryoung and Wilkes rediscovered them. For the first time, they succeeded in preparing room–temperature liquid chloroaluminate melts.[6] Research and development concentrated mainly on electrochemical applications at this time.

As early as 1967, a publication by Swain et al described the use of tetra-*n*-hexylammonium benzoate as a solvent for kinetic and electrochemical investigations.[7] Even though the liquid salt was a hemihydrate at room temperature, this research work had a pioneering significance because it already contained a quantitative determination of the ionization strength of the ionic medium.

In the early 1980s the groups of Seddon and Hussey began to use chloroaluminate melts as nonaqueous, polar solvents for the investigation of transition metal complexes. The investigations generally started with the electrochemical aspects of the relevant transition metal complexes;[8] spectroscopic and complex chemistry experiments followed.[9] It is specially thanks to Seddon's work that ionic liquids became more familiar to a broad public.

The first publications in which ionic liquids were described as new reaction media and catalysts for organic synthesis appeared at the end of the 1980s. Acidic ionic liquids with chloroaluminate ions proved to be effective Friedel–Crafts catalysts;[10] phosphonium halide melts were used successfully in nucleophilic aromatic substitution reactions.[11]

The use of ionic liquids as solvents for homogeneous transition metal catalysts was described for the first time in

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1990 by Chauvin et al. and by Wilkes et al. Chauvin's group dissolved nickel catalysts in weakly acidic chloroaluminate melts and investigated the resulting ionic catalyst solutions for the dimerization of propene.[12] Wilkes et al. used also weekly acidic chloroaluminate melts and studied therein the ethylene polymerization with Ziegler–Natta catalysts.[13]

The concept of ionic liquids received a substantial boost by the work of Wilkes's group when they described in 1992 the synthesis of systems with significantly enhanced stability against hydrolysis, for example low melting tetrafluoroborate melts.[14] In contrast to chloroaluminate ionic liquids, these systems offer high tolerance versus functional groups which opens up a much larger range of applications especially for transition metal catalysis. Ionic liquids with tetrafluoroborate ions have been successfully used, for example, in the rhodium-catalyzed hydroformylation of olefins.[15]

Based on Wilkes's work, it became clearly apparent that ionic liuids were by no means limited to chloroaluminate melts, quite to the contrary, a whole range of cation/anion combinations can form low-melting salts.

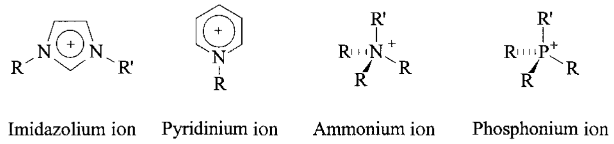
The most recent publications are concerned with the synthesis of new ionic liquids,[16] with the systematic investigation of their physical and chemical properties,[17] and with further applications as solvents and catalysts.[18]

Two excellent reviews by Welton[19] and by Seddon and Holbrey[20] have been already published describing in special detail the use of chloroaluminate ionic liquids in synthetic and catalytic applications. Electrochemical[21] and complex chemistry[22] investigations in ionic liquids have already been reviewed, too.

The aim of our review is to describe the synthesis, properties, and potential of ionic liquids with respect to their application as solvent in transition metal catalysis. In this context, we would like to offer especially to the chemist working in the field of homogeneous catalysis a set of criteria to identify suitable candidates out of the large number of ionic liquids (some authors speak about 10^{18} possible cation/anion combinations[20]). This section will be followed by a selection of examples which demonstrate that ionic liquids can be successful alternative "solutions" for many applications. Hereby, we will focus our attention on recently published work describing transition metal catalysis in "non-chloroaluminate" systems.

2. Ionic Liquid Synthesis

The initial step in the synthesis of ionic liquids is the quaternization, of an amine or phosphane for example, to form the cation.[6c, 22] The most important, reported cation types are shown in Scheme 1. Salts with different anions are obtained by the quaternization reaction depending on the alkylation reagent. Interestingly, melting points under 100 °C can be obtained for a series of cation/anion combinations in this way (Table 1).



Scheme 1. Important types of cations in ionic liquids.

Peter Wasserscheid, born in 1970 in Würzburg, studied chemistry at the RWTH Aachen and received his PhD in 1998 in the group of Professor Keim with a dissertation on Ni-catalyzed C–C linkage reactions in ionic liquids. At present he is carrying out his Habilitation at the Institut für Technische Chemie und Makromolekulare Chemie at the RWTH Aachen and is working on further applications of ionic liquids in synthetic and catalytic reactions. His scientific abilities were recognized at an early stage when he was awarded 1st prize in a German National competition "Jugend Forscht". He received the DECHEMA Student prize for excellent performance in study and diploma work and the Friedrich-Wilhelm prize from the RWTH Aachen.

P. Wasserscheid

W. Keim

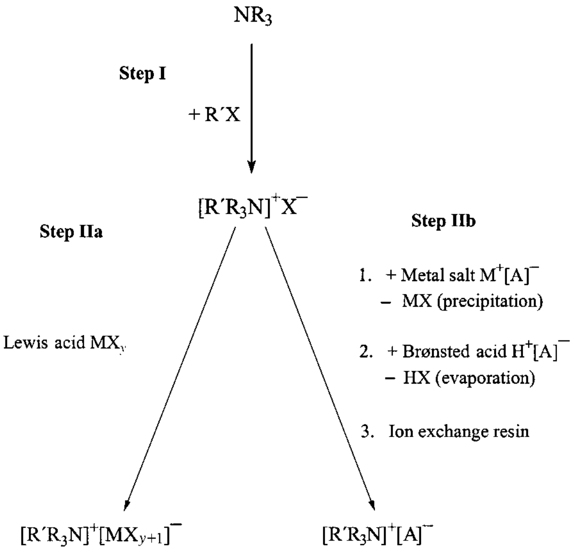
Wilhelm Keim, born in 1934 in Oberhausen, studied chemistry and received his PhD in 1963 under the guidance of Professor G. Wilke at the Max-Planck-Institut für Kohleforschung. After a year as a Postdoc with T. Kalz at Columbia University, New York, he began work at the Shell Development Company in Emeryville, CA. By 1972 he had advanced to Head of Fundamental Research. In 1973 he accepted the position of Professor and Institute Director at the Institut für Technische Chemie und Petrolchemie at the RWTH Aachen. His research activities include homogeneous and heterogeneous catalysis, carbonylation and functionalization of olefins, and selective C–C bonding. In this connection, Professor Keim is investigating aspects of the hetereogenization of homogeneous catalysts and biphasic catalysis. He is the author of around 200 publications and 40 patents. His scientific achievements have recently been recognized with the award of the "Alwin-Mittasch" medal and the "Karl-Engler" medal.

Table 1. Examples of ionic liquids that can be formed by direct quaternization.

Ionic liqiud	Alkylation reagent	M. p. [°C]	Ref.
[EMIM]CF_3SO_3[a]	methyl triflate	−9	[16a]
[BMIM]CF_3SO_3[b]	methyl triflate	16	[16a]
[Ph_3POc]OTs[c]	OcOTs	70–71	[24]
[Bu_3NMe]OTs	MeOTs	62	[25]
[BMIM]Cl	chlorobutane	65–69	[6c]

[a] EMIM = 1-ethyl-3-methylimidazolium; CF_3SO_3 = triflate anion. [b] BMIM = 1-*n*-butyl-3-methylimidazolium. [c] Oc = octyl; Ts = $H_3CC_6H_4$-SO_2 (tosyl).

In cases where it is not possible to form the desired anion directly by the quaternization reaction, a further step follows (synthesis steps IIa or IIb in Scheme 2). For example, starting from an ammonium halide $[R'R_3N]^+X^-$, two different paths to vary the anion are possible. First, the halide $[R'R_3N]^+X^-$ can be treated with a Lewis acid MX_y. This leads to an ionic liquid of the type $[R'R_3N]^+[MX_{y+1}]^-$ (synthesis step IIa, Scheme 2).



Scheme 2. Synthesis paths for the preparation of ionic liquids examplified for an ammonium salt.

Alternatively it is possible to exchange the halide ion X^- for the desired anion. This can be done by the addition of a metal salt $M^+[A]^-$ (with precipitation of M^+X^-) over an ion exchanger or by displacement of the halide ion by a strong acid $H^+[A]^-$ (with the release of H^+X^-) (synthesis step IIb, Scheme 2).

In the first case, several anion species are often present in equilibrium, which depends on the ratio of the two components $[R'R_3N]^+X^-$ and MX_y [Eq. (1)].

$$[R'R_3N]^+\,X^- + MX_y \rightleftharpoons [R'R_3N]^+\,[MX_{y+1}]^- \tag{1}$$

With an excess of the Lewis acid MX_y additional anion species can be formed from further acid–base reactions with the already present anion. Such behavior is displayed by chloroaluminate melts, for example [Eq. (2) and (3)].[26] The formation of different anions occurs as a function of the chloride/$AlCl_3$ ratio. From Figure 1 it can be seen that addition of aluminum trichloride to the chloride initially results in the formation of the $AlCl_4^-$ ion. With an aluminum trichloride mole fraction of exactly 0.5, this is essentially the only anion present. In systems with $x(AlCl_3) > 0.5$ multinuclear chloroaluminate anions are formed which are in equilibrium with each other, the $AlCl_4^-$ ion and, at very high $AlCl_3$ contents, with dimeric aluminum trichloride.[26]

$$[R'R_3N]^+\,AlCl_4^- + AlCl_3 \rightleftharpoons [R'R_3N]^+\,Al_2Cl_7^- \tag{2}$$

$$[R'R_3N]^+\,Al_2Cl_7^- + AlCl_3 \rightleftharpoons [R'R_3N]^+\,Al_3Cl_{10}^- \tag{3}$$

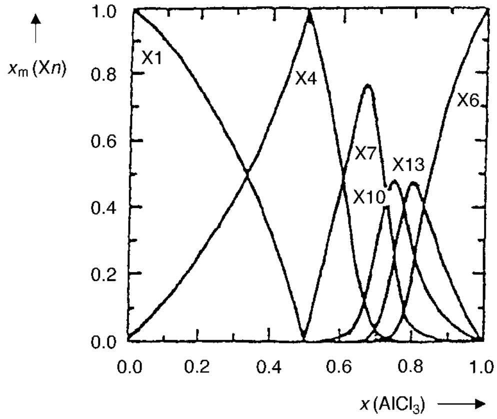


Figure 1. Mole fraction x_m of different anion species *Xn* in chloroaluminate melts (X1 = Cl^-; X4 = $AlCl_4^-$; X7 = $Al_2Cl_7^-$; X10 = $Al_3Cl_{10}^-$; X13 = $Al_4Cl_{13}^-$; X6 = Al_2Cl_6).

Chloroaluminates are the best known but not the only ionic liquids that can be prepared by the reaction of a halide with a Lewis acid. Further examples are shown in Table 2.

Table 2. Examples of ionic liquids that can be generated by the reaction of a halide with a Lewis acid.

Ionic liquid[a]	Established anion	Ref.
[cation]Cl/$AlCl_3$	Cl^-, $AlCl_4^-$, $Al_2Cl_7^-$, $Al_3Cl_{10}^-$	[27]
[cation]Cl/$AlEtCl_2$	$AlEtCl_3^-$, $Al_2Et_2Cl_5^-$	[28]
[cation]Cl/BCl_3	Cl^-, BCl_4^-	[29]
[cation]Cl/CuCl	$CuCl_2^-$, $Cu_2Cl_3^-$, $Cu_3Cl_4^-$	[30]
[cation]Cl/$SnCl_2$	$SnCl_3^-$, $Sn_2Cl_5^-$	[31]

[a] cation = pyridinium, imidazolium ion.

When the anion is varied by anion exchange ionic liquids of the type $[\text{cation}]^+[A]^-$ are formed (synthesis step IIb, Scheme 2), which contain only one anion species when the exchange reaction has proceeded to completion (Table 3).

At this point it should be noted that the synthesis of highly pure, binary ionic liquids places particular demands on the

Table 3. Examples of ionic liquids that can be prepared by anion exchange.

Ionic liquid[a]	Ref.
[cation]BF_4	[14, 32]
[cation]PF_6	[32, 33]
[cation]SbF_6	[30]
[cation]NO_3	[14]
[cation]CH_3CO_2	[14]
[cation]HSO_4	[16f]
[cation]B(Et_3Hex)	[34]

[a] cation = pyridinium, imidazolium, ammonium ion.

preparative work. The purity of the system is essential for many solvent applications and for the characterization of their physical and chemical properties. Whereas organic solvents are usually purified by distillation before use, this method is not suitable to clean up ionic liquids due to their nonvolatile character. For this reason, the highest purity possible must be attained during the synthesis itself. For example, during the exchange of chloride ions for the desired anions, it must be ensured that no halide ions remain in the system. Also traces of the acid used in the synthesis can lead to unwanted chemical reactivity. High purity in the synthesis of binary ionic liquids is usually achieved by anion exchange over an ion exchanger.

The described methods can, of course, also be used to prepare previously unknown combinations of cations and anions which could also result in low-melting salts. In addition there is the possibility to obtain ionic liquids with new properties by the mixture of several different salts.[35]

3. Characteristic Properties of Ionic Liquids

The physical and chemical properties of ionic liquids can be specifically varied over a wide range by the selection of suitable cations and anions. The possibility arises to optimize the ionic reaction medium for a specific application by stepwise tuning the relevant solvent properties. For this reason ionic liquids have been referred to as "designer solvents" in several publications.[36]

In the following section, we attempt to illustrate the relationships between the structural features of an ionic liquid and its important physical and chemical properties, on the basis of a few selected examples.

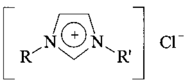
3.1. Melting Point

The key criterion for the evaluation of an ionic liquid is, by definition, its melting point. Of particular significance is therefore the question of the relationship between the structure and chemical composition of an ionic liquid and its melting point.

Comparison of the melting points of different chloride salts illustrates the influence of the cation clearly: High melting points are characteristic for alkali metal chlorides, whereas chlorides with suitable organic cations melt at temperatures below 150 °C (Table 4).[6c, 37]

In the literature, the following features are discussed for cations of low-melting salts: low symmetry,[1] weak intermolecular interactions (such as the avoidance of hydrogen bonding),[16a, 38] and a good distribution of charge in the cation.[39]

Table 4. Melting points of various chlorides.

Salt		M. p. [°C]
NaCl		803
KCl		772
	R = R′ = methyl ([MMIM]Cl)[a]	125
	R = methyl, R′ = ethyl ([EMIM]Cl)	87
	R = methyl, R′ = *n*-butyl ([BMIM]Cl)	65

[a] MMIM = 1,3-dimethylimidazolium.

Besides the cation, the anion influences the melting point, too. Comparison of the melting points of different salts with the 1-ethyl-3-methylimidazolium (EMIM) ion emphasizes that, in most cases, an increasing size of the anion with the same charge leads to a further decrease in the melting point (Table 5).

Table 5. Influence of different anions on the melting point of imidazolium salts.

Imidazolium salt	M. p. [°C]	Ref.
[EMIM]Cl	87	[6c]
[EMIM]NO_2	55	[14]
[EMIM]NO_3	38	[14]
[EMIM]$AlCl_4$	7	[40]
[EMIM]BF_4	6[a]	[17d]
[EMIM]CF_3SO_3	−9	[16a]
[EMIM]CF_3CO_2	−14	[16a]

[a] Glass transition.

For ionic liquids prepared by reaction of a halide $[\text{cation}]^+X^-$ with a Lewis acid MX_y, the molar ratio of the two reactants influences the melting points (Figure 2).[40] As already shown in Figure 1, a quasi-binary system with the $AlCl_4^-$ ion only exists for exact 1:1 mixtures in the system [EMIM]Cl/$AlCl_3$. The fact that a local maximum in melting temperature is observed at exactly this composition indicates that the presence of several anions in the ionic liquid has the effect of decreasing the melting point.

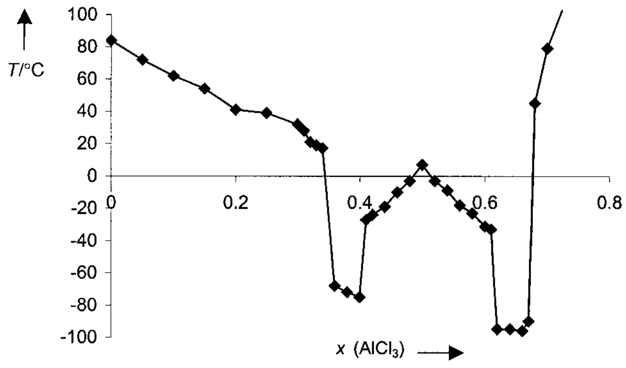


Figure 2. Experimental phase diagram in the system [EMIM]Cl/$AlCl_3$ (EMIM = 1-ethyl-3-methylimidazolium ion).

3.2. Vapor Pressure and Thermal Stability

Ionic liquids have no measurable vapor pressure. This is a great advantage from a process engineering viewpoint, since separation by distillation of a reaction mixture becomes more effective as a method of product isolation. The well-known problem of azeotrope formation between the solvent and the products does not arise.

The thermal stability of ionic liquids is limited by the strength of their heteroatom–carbon and their heteroatom–hydrogen bonds, respectively. Ionic liquids synthesized by direct protonation of an amine or phosphane show, for example, significantly restricted thermal stability. Many melts with trialkylammonium ions already decompose at a temperature below 80 °C in vacuo (depending on the boiling point of the related amine or acid). For ionic liquids obtained by alkylation of an amine or phosphane the tendency to undergo thermally induced transalkylation or dealkylation reactions (retro-quaternization reaction) is strongly related to the nature of their anion. While 150 °C has to be considered as maximum working temperature for most of the quaternary ammonium chloride salts, 1-ethyl-3-methylimidazolium (EMIM) tetrafluoroborate, for example, has been reported to be stable to about 300 °C[41] and [EMIM][$(CF_3SO_2)_2N$] (m.p. −3 °C) is stable up to even more than 400 °C.[16a] Consequently, some ionic liquids have, in contrast to water and most organic solvents, a liquid range of up to more than 400 °C.

3.3. Density

The dependence of the density of an ionic liquid on the type of cation and anion can be illustrated clearly by the example of chloroaluminate and bromoaluminate melts. A comparison of chloroaluminate melts with different cations reveals an almost linear relationship between the density and the length of the *N*-alkyl chain on the imidazolium cation (Figure 3).[40]

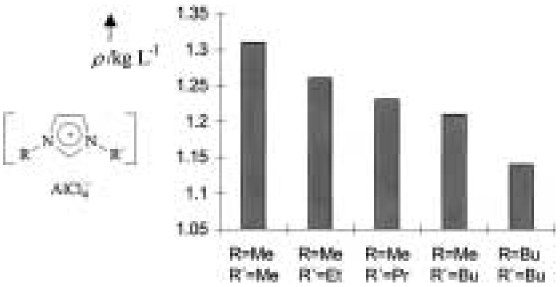


Figure 3. Dependence of the density ρ of 1,3-dialkylimidazolium tetrachloroaluminate melts on the type of both alkyl groups; measurement temperature at 60 °C, $x(AlCl_3) = 0.5$.

More generally, it can be concluded that the density of comparable ionic liquids decreases as the bulkiness of the organic cation increases. Slight structural changes in the cation allow a fine adjustment of the density.

Varying the anion results in more obvious effects in several cases. With bromoaluminate melts for example, it was possible to achieve densities unusual for normal organic solvents (Figure 4).[42] Density measurements of ionic liquids with triflate or trifluoroacetate ions confirmed the more general result that a certain density range is established by the choice of anion, within which a fine adjustment is possible by careful choice of the cation.[16a]

3.4. Viscosity

The viscosity of ionic liquids is essentially determined by their tendency to form hydrogen bonding and by the strength of their van der Waals interactions.[16a]

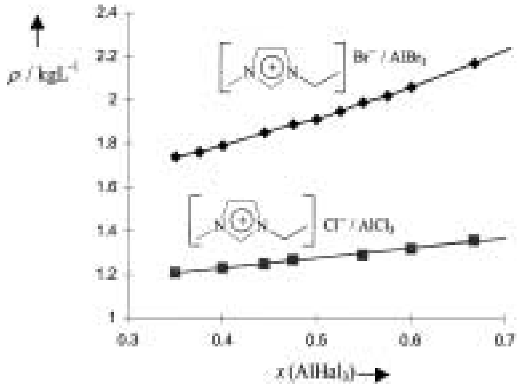


Figure 4. Dependence of the density ρ of two 1-ethyl-3-methylimidazolium tetrahaloaluminate melts on the mole fraction of aluminum trihalide at 60 °C.

The effect of hydrogen bonding becomes clear when, for example, the viscosities of chloroaluminate melts of different compositions are compared (Figure 5).[40] The increase in viscosity of more than a factor of ten in ionic liquids with $x(AlCl_3) < 0.5$ is a result of the formation of hydrogen bonds between the hydrogen atoms of the imidazolium cation and the basic chloride ion. This statement is supported by IR[43] and X-ray spectroscopy,[44] ROESY-NMR, and theoretical calculations.[45] In acidic mixtures, however, the anions $AlCl_4^-$ and $Al_2Cl_7^-$ are present, in which the negative charge is much better distributed. This leads to the formation of weaker hydrogen bonds and a much lower viscosity.

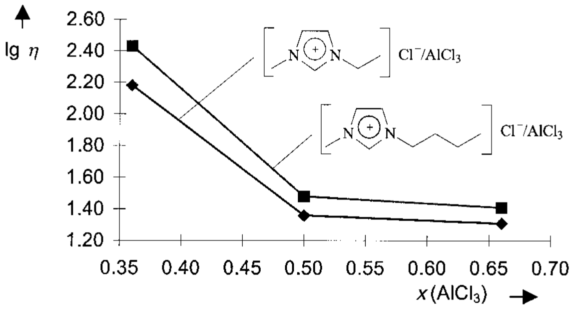
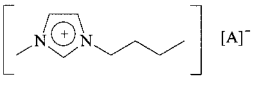


Figure 5. Dependence of the dynamic viscosity η [cP] of two 1,3-dialkylimidazolium tetrachloroaluminate melts on the mole fraction of aluminum trichloride at 25 °C.

Comparison of the viscosity of different, hydrophobic ionic liquids with 1-*n*-butyl-3-methylimidazolium (BMIM) ions emphasizes, in addition, the interplay between van der Waals interactions and hydrogen bonding (Table 6).[16a] The transition from the triflate ion to the $n\text{-}C_4F_9SO_3^-$ ion, and from the trifluoroacetate ion to the $n\text{-}C_3F_7COO^-$ ion reveals an

Table 6. Dynamic viscosities η of various 1-*n*-butyl-3-methylimidazolium (BMIM) salts at 20 °C.

	Anion [A]⁻	η [cP]
	$CF_3SO_3^-$	90
	$n\text{-}C_4F_9SO_3^-$	373
	CF_3COO^-	73
	$n\text{-}C_3F_7COO^-$	182
	$(CF_3SO_2)_2N^-$	52

obvious increase in viscosity. It is apparent that the stronger van der Waals interactions in the case of the n-$C_4F_9SO_3^-$ and n-$C_3F_7COO^-$ ions result in a higher viscosity of the ionic liquid. Comparison of the viscosities of [BMIM]CF_3SO_3 with [BMIM]$(CF_3SO_2)_2N$, reveals a lower viscosity despite stronger van der Waals interactions for ionic liquids with the $(CF_3SO_2)_2N^-$ ion. In this case, the almost complete suppression of hydrogen bonding overcompensates for the expected increase in viscosity.[16a]

The structure of the cation also influences the viscosity of the ionic liquid. The lowest viscosities are usually obtained for melts with the 1-ethyl-3-methylimidazolium (EMIM) ion, in which a side chain with sufficient mobility is combined with a low molar mass. Longer or fluorinated alkyl chains result in higher viscosities because of stronger van der Waals interactions.[16a]

The viscosity of ionic liquids can be lowered, drastically in some cases, by only slight increases in temperature[40, 46] or by the addition of small amounts of organic cosolvents.[47]

3.5. Solvation Strength and Solubility Characteristics

The tuning of solubility properties of an ionic liquid by the careful choice of cation and anion deserves particular attention.

The influence of the cation, for example, is shown by investigations of the solubility of 1-octene in different tosylate melts (Figure 6).[25] It can be seen that with increasing nonpolar character of the cation, the solubility of 1-octene in the melt increases markedly. In methyl-tri-n-octylammonium tosylate a single-phase reaction mixture is obtained. This example shows that stepwise variation of the solubility properties can be achieved by variation of the alkyl group on the cation.

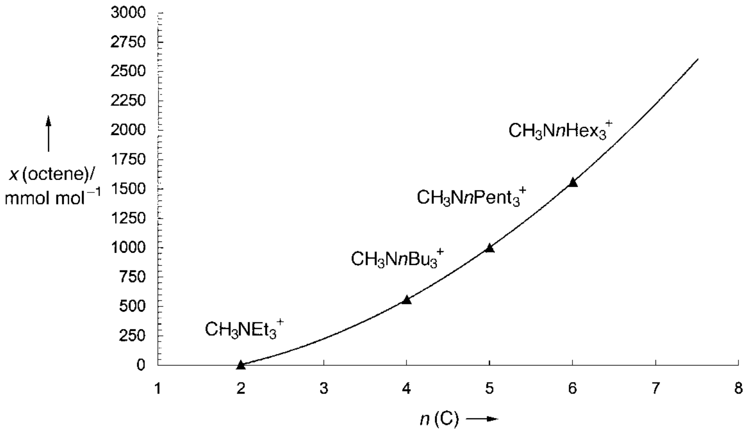


Figure 6. Solubility of 1-octene in four different tri-n-alkylmethylammonium tosylate melts at 80 °C. n(C) = number of C atoms of the alkyl residue.

The influence of the anion on the solubility characteristics of ionic liquids can be demonstrated in an impressive fashion by the example of the water solubility of different melts containing the BMIM ion. While [BMIM]Br, [BMIM]CF_3COO, and [BMIM]CF_3SO_3 are highly water-soluble, ionic liquids with the same cation but with a PF_6^- or $(CF_3SO_2)_2N^-$ ion form biphasic mixtures with water. The water content of the ionic liquid [BMIM]$(CF_3SO_2)_2N$ at 20 °C is only 1.4 weight percent.[16a]

Several ionic liquids showing a miscibility gap with water have been considered as interesting candidates for separation processes by liquid–liquid extraction. Rogers et al. investigated, for example, the solubility of different acids and bases in water/[BMIM]PF_6 at different pH values of the aqueous phase.[48] Interestingly, their results reveal a higher solubility of neutral substrates in the ionic liquid, while ionic species dissolve preferentially in the aqueous layer. The authors conclude that the solubility properties of [BMIM]PF_6 versus water show high similarity to organic solvents. The substitution of volatile organic solvents by ionic liquids in extractive separation processes may therefore be an interesting option.

Many ionic liquids are completely miscible with organic solvents if their dielectric constants exceed a characteristic limit. This limit appears to be specific for each cation/anion combination (Table 7).[16a]

The solubility of supercritical CO_2 in [BMIM]PF_6 that has recently been investigated by Brennecke's group is remarkable, too.[49] In the biphasic system $scCO_2$/[BMIM]PF_6 60 mol% of CO_2 dissolve in the ionic liquid at 80 bar CO_2 pressure. Hereby, the volume of the ionic liquid increases only by 10–20%, however. As a first application of this interesting biphasic system, the authors investigated the extraction of naphthalene from the ionic liquid. They succeeded in recovering the naphthalene quantitatively without any detectable contamination of the extract by the ionic liquid.

Without doubt, the key to the successful use of ionic liquids lies in the skillful exploitation of their exceptional solubility characteristics. Further systematic investigations are necessary, however, to take full advantage of this huge potential.

One very promising possibility is, for example, the investigation of the polarity of ionic liquids. The polarity of a solvent is usually determined in a purely empirical fashion. A well-understood, easily measurable and strongly solvent-dependent process is deter-

Table 7. Miscibility of various ionic liquids with the 1-ethyl-3-methylimidazolium (EMIM) ion in organic solvents with the dielectric constant ε.[a]

Solvent	ε	[EMIM]CF_3SO_3	[EMIM]CF_3COO	[EMIM]n-C_3F_7COO	[BMIM]CF_3COO[b]	[BMIM]n-C_3F_7COO
CH_2Cl_2	8.93	m	m	m	m	m
THF	7.58	m	m	m	m	m
ethyl acetate	6.02	m	pm	pm	m	m
toluene	2.38	im	im	im	im	im
1,4-dioxane	2.01	im	im	im	im	im

[a] m: miscible; pm: partially miscible; im: immiscible.

mined in a large number of different solvents, for example the spectral absorption of a solvatochromic dye. Empirical solvent polarity parameters are derived from the measured absorption maxima, which reflect the solvating ability of a solvent much more comprehensively than the individual physical constants.[50] Amongst the many empirical polarity scales, the $E_{(T)}(30)$ scale introduced by Dimroth et al. in 1963[51] and further developed by Reichhardt et al. in 1971 has proven successful, and is based on the solvatochromism of a pyridinium-*N*-phenolate betaine dye.[52] This method has also been used successfully to determine the polarity of a small number of ionic liquids. The results obtained confirm the considerable width of variation of solvent polarity of ionic liquids. While, for example, tetra-*n*-hexylammonium benzoate with an $E_{(T)}(30)$ value of 0.41 lies within the polarity range of DMF,[53] an $E_{(T)}(30)$ value of 0.95 was determined for ethylammonium nitrate corresponding to a polarity between CF_3CH_2OH and water.[4, 54] [BMIM]PF_6 was investigated by using the same method and its $E_{(T)}(30)$ value was found to correspond to a polarity in the range of methanol.[55]

However, recent work by Armstrong et al. gave rise to the question whether the chemical nature of the solvatochromic dye influences the result of the polarity determination of an ionic liquid. These authors coated GC columns with several ionic liquids and compared the retention times of a large number of substances.[56] The results of their study indicate different polarity of ionic liquids depending on the nature of the tested compounds.

While [BMIM]PF_6, for example, acts like an unpolar stationary phase versus unpolar molecules (like *n*-octane), very long retention times are observed with proton-donor compounds. The authors attribute a dual polarity behavior to the ionic liquids under investigation.

Unfortunately the number of systematic investigations concerning the polarity of ionic liquids is still very limited. More research in this field should be encouraged in order to establish efficient criteria to determine the right ionic liquid candidate for a given solvent application.

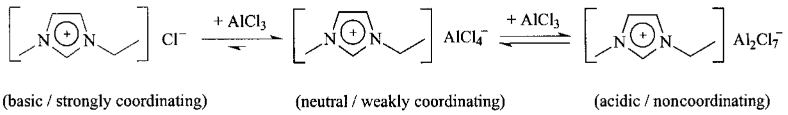
3.6. Acidity and Coordination Ability

The acidity and coordination properties of an ionic liquid are essentially determined by the nature of its anion. Many intermediate levels between "strongly basic/strongly coordinating" and "strongly acidic/practically noncoordinating" can be realized by careful choice of the anion (Table 8).[30]

Table 8. Coordinative characteristics of various anions.

Acidity/coordination basic/strongly coordinating	 neutral/weakly coordinating	 acidic/non-coordinating
Cl^-	$AlCl_4^-$	$Al_2Cl_7^-$
Ac^-	$CuCl_2^-$	$Al_3Cl_{10}^-$
NO_3^-	SbF_6^-	
SO_4^{2-}	BF_4^-	$Cu_2Cl_3^-$
	PF_6^-	$Cu_3Cl_4^-$

In this context, those ionic liquids have to be mentioned which form a neutral anion (e.g. $AlCl_4^-$) or an acidic anion (e.g. $Al_2Cl_7^-$) from a basic anion (e.g. Cl^-) by addition of a Lewis acid (e.g. $AlCl_3$). In Scheme 3 this behavior is illustrated by the example of a EMIM chloroaluminate melt.



Scheme 3. Control of the acidity of ionic liquids by the ratio of halide to Lewis acid examplified for 1-ethyl-3-methylimidazolium (EMIM) chloroaluminate melt.

Chloroaluminate melts are designated as basic when the molar ratio of $AlCl_3$ is smaller than 0.5. A neutral melt is referred to at an $AlCl_3$ ratio of exactly 0.5, where essentially only the anion $AlCl_4^-$ is present.[22a] Finally, an acidic chloroaluminate melt is one in which the $AlCl_3$ ratio is larger than 0.5. In such acidic melts, the anions $Al_2Cl_7^-$ and $Al_3Cl_{10}^-$ exist, which act as very strong Lewis acids.[27]

Two further phenomena in the field of acid/base chemistry of ionic liquids deserve to be mentioned. These are the so-called "latent acidity" and "superacidity" of protons in ionic liquids.

The latent acidity of ionic liquids arises when weak bases are added to buffered neutral chloroaluminate melts. Such melts are formed when, for example, excess alkali metal chloride (MCl) is added to an acidic chloroaluminate melt.[57] The alkali metal chloride MCl reacts according to Equation (4) with the acidic chloroaluminate dimers until the melt

$$Al_2Cl_7^- + MCl \rightleftharpoons 2\,AlCl_4^- + M^+ \qquad (4)$$

becomes neutral. A buffered melt is one in which the neutrality of the melt is maintained by reaction of excess alkali metal chloride when acid $AlCl_3$ is added. The latent acidity of this neutral system becomes noticeable when a weak base (B) such as *N,N*-dimethylaniline, pyrrole, or acetylferrocene is added.[58] An adduct is formed between the added base and $AlCl_3$ with precipitation of the alkali chloride MCl [Eq. (5)].

$$B + AlCl_4^- + M^+ \rightleftharpoons B\text{-}AlCl_3 + MCl\,(s) \qquad (5)$$

This reaction is not observed in the absence of excess alkali metal cations. The latent acidity of different ionic liquids has already been quantitatively measured.[59] In our group, ionic liquids with latent acidity have been successfully used as solvents in the Ni-catalyzed oligomerization of 1-butene (see Section 4.8).[60]

The superacidity of protons in several ionic liquids is also worth mentioning. It has been observed when strong mineral acids were dissolved in acidic chloroaluminate ionic liquids.[61] Smith and co-workers investigated the acidity of such protons in ionic liquids by the protonation of aryl compounds with a solution of HCl gas in acidic [EMIM]Cl/$AlCl_3$ melts. The acidity of the protons in the melt were measured quantitatively by UV spectroscopy.[61a] Acid strengths were obtained as a function of the melt's acidity which were clearly above the one of 100% sulfuric acid (Figure 7).[62]

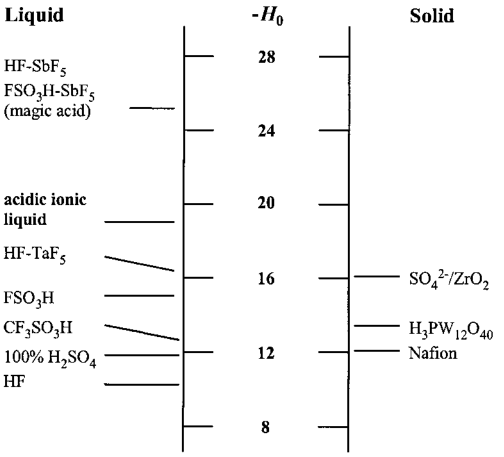


Figure 7. Comparison of the acid strength of superacid ionic liquids with those of conventional superacids.

The superacid properties of protons in acidic chloroaluminate melts have been explained by the reaction between the dissolved HCl and the acidic species in the melt, which releases protons with extremely low solvation and therefore very high reactivity [Eq (6)].

$$HCl + Al_2Cl_7^- \rightleftharpoons [H]^+_{nonsolvated} + 2\,AlCl_4^- \qquad (6)$$

In contrast to normal superacid systems, superacid ionic liquids are much easier and safer to handle.[61a] They could, therefore, represent very promising alternatives to the superacids normally used.

Finally we should note that the cation of an ionic liquid also has an influence on the acidity of the system. A weak Lewis acidity is, for example, attributed to the imidazolium ion itself. The catalytic effect of imidazolium bromide melts in Diels–Alder reactions is reported to be related to this weak acidity of the imidazolium ion.[63] Moreover, the H atom in the 2-position of an imidazolium ion possesses significant Brønsted acidity.[64] This is of special importance for reactions with transition metal complexes, since in the presence of bases in situ carbene complexes can be formed.[65]

3.7. Handling and Availability

The handling of ionic liquids depends essentially on the stability of the anion towards hydrolysis. Whereas ionic liquids with nitrate, benzenesulfonate, and [bis(trifluormethylsulfonyl]amide ions, for example, are air and water stable and can even be synthesized in water, systems with chloroaluminate anions must be classified as extremely hygroscopic and labile towards hydrolysis. More difficulties arise when traces of water in chloroaluminate melts react with the anions of the melt to release superacid protons. These cause unwanted side reactions and possess a considerable potential for corrosion. Since the preparation of a completely water-free chloroaluminate melt is difficult (for a detailed description of protic and oxidic impurities in chloroaluminate melts we recommend Welton's review[19]) the level of tolerable impurities has to be determined for each planned application. To sum up: the handling and stability of ionic liquids cannot be easily assessed, but it is mainly dependent on the nature of the anion.

The commercial availability of ionic liquids was very limited until recently. Only a small number of systems could be purchased from chemical distributors in small quantities (up to 25 g).[66] Since the end of 1999, a large variety of ionic liquids is now commercially available in up to 5 liter scale.[67] If demand for ionic liquids grows further, we suppose that in the near future particularly producers of ionic liquid precursor compounds (such as amines) will enter the market. In this case we expect drastically decreasing prices for ionic liquids.

In this context it should be mentioned that after most applications the used ionic liquid can be easily recovered, cleaned up—if necessary—and reused repeatedly. In an ideal case the cost for the ionic liquid can be therefore regarded as an one-time investment.

3.8. Enviromental Aspects

Recently ionic liquids have often been discussed as promising solvents for "clean processes" and "green chemistry".[36, 68] These two catchwords represent current efforts to reduce drastically the amounts of side and coupling products and also the solvent and catalyst consumption in chemical processes. The use of ionic liquids could make a contribution in this area, particularly with regard to solvent and catalyst usage.

In contrast to volatile organic solvents and extraction media, ionic liquids have no measurable vapor pressure. Therefore there is no loss of solvent through evaporation. Environmental and safety problems arising through the use of volatile organic solvents can also be avoided by the use of a nonvolatile ionic reaction medium.

With respect to efforts to reduce catalyst consumption, two aspects arise with the use of ionic liquids: First, the special solubility characteristics of an ionic reaction medium enables a biphasic reaction procedure in many cases. Exploitation of the miscibility gap between the ionic catalyst phase and the products allows, in this case, the catalyst to be isolated effectively from the product and reused many times. Second, the nonvolatile nature of ionic liquids enables a more effective product isolation by distillation. The possibility also exists here to reuse the isolated ionic catalyst phase. In both cases, the total reactivity of the applied catalysts is increased and catalyst consumption relative to generated product is reduced.

For environmental and safety reasons the use of ionic liquids could gain in significance particularly in processes with superacid catalysts. Substitution of HF by nonvolatile superacid ionic liquids presents a promising alternative in this context.

In the meantime, many examples have shown (see Section 4) that the application of ionic liquid solvents can result in significantly reduced environmental impact. Therefore we fully agree with the classification of ionic liquids as "green solvents". However, in this context it should be mentioned that aspects of their toxicity and their disposal have not been fully explored yet.

4. Ionic Liquids as Solvents for Transition Metal Catalyzed Reactions

Ionic liquids are able to dissolve organometallic compounds and are therefore possible solvents for reactions with homogeneous catalysts. Depending on the coordinative properties of the anion (see Section 3.6), the ionic liquid can be regarded as an "innocent" solvent or as a cocatalyst.

Ionic liquids with tetrafluoroborate or hexafluorophosphate ions, for example, have to be considered as inert solvents in most reactions (for exceptions see, for example, Section 4.5). In these cases the role of the ionic liquid is solely to provide a polar, weakly coordinating medium for the transition metal catalyst that additionally offers special solubility for feedstock and products. The use of ionic liquids often allows a combination of solvent properties which can not be realized with water or common organic solvents.

Ionic liquids formed by the reaction of a halide with a Lewis acid (e.g. chloroaluminate or chlorostannate melts) generally act as a cocatalyst. The reason for this is the Lewis acidity or basicity which is always present (at least latent), and which results in strong interactions with the catalyst complex. In many cases, the Lewis acidity of an ionic liquid is used to convert the neutral catalyst precursor into the corresponding cationic active form. The activation of $[Cp_2TiCl_2]$[13] in acidic chloroaluminate melts and the activation of $[(PR_3)_2PtCl_2]$ in chlorostannate melts are examples for this kind of activation [Eq. (7) and (8)].[31c]

$$[Cp_2TiCl_2] + [cation]^+ Al_2Cl_7^- \rightleftharpoons [Cp_2TiCl]^+ AlCl_4^- + [cation]^+ AlCl_4^- \quad (7)$$

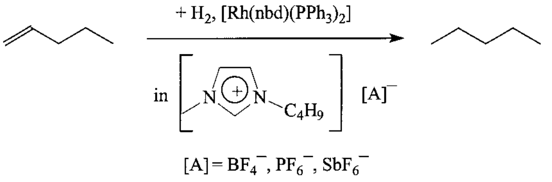
$$[(PR_3)_2PtCl_2] + [cation]^+ Sn_2Cl_5^- \rightleftharpoons [(PR_3)_2PtCl]^+ SnCl_3^- + [cation]^+ SnCl_3^- \quad (8)$$

There are many good reasons to study ionic liquids as alternative solvents in well-known transition metal catalyzed reactions. Besides the engineering advantage of their non-volatile nature, the investigation of new biphasic reactions with an ionic catalyst phase is of special interest. Here, the possibility to adjust solubility properties by different cation/anion combinations allows a systematical optimization of the biphasic reaction, for example, with regard to product selectivity. Attractive options to improve selectivity in multiphase reactions derive from the preferential solubility of only one reactant in the catalyst solvent or from the in situ extraction of reaction intermediates out of the catalyst layer. Finally, the ionic liquid may be in many cases a superior solvent for transition metal catalysis in comparison to water and common organic solvents especially when ionic complexes are used as catalysts. In these cases, significant enhancement of catalyst activity and stability is possible.

In our group we have been investigating the reactivity of ionic transition metal catalyst solutions since 1995 and are currently working on the hydrogenation, hydroformylation, oxidation, and oligomerization of functionalized and non-functionalized alkenes. In the following section an overview of recent developments in the field of transition metal catalysis in ionic liquids is presented.

4.1. Hydrogenations

The first successful hydrogenation reactions in ionic liquids were studied by the groups of de Souza[32] and Chauvin[15] in 1995. De Souza et al. investigated the Rh-catalyzed hydrogenation of cyclohexene in BMIM tetrafluoroborate. Chauvin et al. dissolved the cationic "Osborn complex" $[Rh(nbd)(PPh_3)_2]PF_6$ (nbd = norbornadiene) in ionic liquids with weakly coordinating anions (e.g. PF_6^-, BF_4^-, and SbF_6^-) and used the ionic catalyst solutions thus obtained according to Equation (9) for the biphasic hydrogenation of 1-pentene.



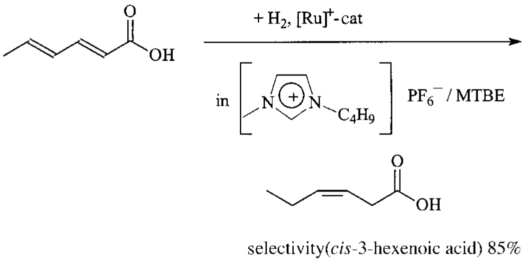
(9)

Although the reactants have only limited solubility in the catalyst phase, the rates of hydrogenation in $[BMIM]SbF_6$ are almost five times faster than for the comparable reaction in acetone. All ionic catalyst solutions tested could be reused repeatedly. The loss of rhodium through leaching into the organic phase lay below the detection limit of 0.02%. These results are of general importance for the field of biphasic catalysis since this was the first time that a rhodium catalyst could be "immobilized" in a polar solution without the use of specially designed ligands.

Moreover, Chauvin et al. described the selective hydrogenation of cyclohexadiene to cyclohexene by making use of the biphasic reaction system.[15] Since the solubility of cyclohexadiene in $[BMIM]SbF_6$ is about five times higher than the solubilty of cyclohexene in the ionic liquid, the latter was obtained in 98% selectivity at 96% conversion. The authors observed complete suppression of the hydrogenation activity however, if the used ionic liquid contained some Cl^- impurities.

Rhodium- and cobalt-catalyzed hydrogenation of butadiene and 1-hexene,[69, 32] and the Ru-catalyzed hydrogenation of aromatic compounds[18c] and acrylonitrile–butadiene copolymers[70] have also been reported to be successful in ionic liquids.

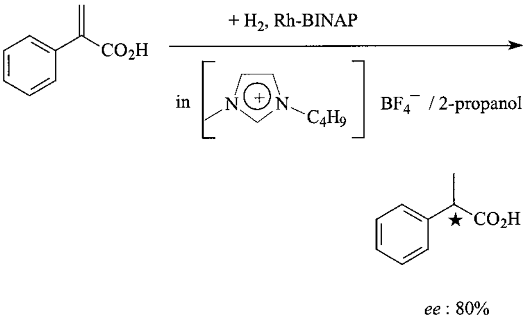
A stereoselective hydrogenation in ionic liquids was recently successfully carried out in our institute. Based on investigations in the biphasic system water/*n*-heptane,[71] the ruthenium-catalyzed hydrogenation of sorbic acid to *cis*-3-hexenoic acid according to Equation (10) in the system $[BMIM]PF_6$/MTBE (MTBE = methyl *tert*-butyl ether) was



(10)

studied.[72] In comparison to other polar solvents (e.g. glycol) a more than threefold increase in activity with comparable selectivity to *cis*-3-hexenoic acid was observed in the ionic liquid. After reaction, the ionic catalyst solution could be recovered by phase separation and reused repeatedly.

Enantioselective hydrogenation in ionic liquids is also possible. Chauvin et al. hydrogenated α-acetamidocinnamic acid in the presence of a [Rh(cod){(−)diop}] catalyst (cod = cycloocta-1,3-diene; diop = 4,5-bis[(diphenylphosphanyl)-methyl]-2,2-dimethyl-1,3-dioxolan-4,5-diol in a [BMIM]SbF$_6$ melt with 64 % *ee* to (*S*)-phenylalanine.[15] Dupont et al. were able to obtain up to 80 % *ee* in the reaction of 2-arylacrylic acid to (*S*)-2-phenylproprionic acid with Ru-BINAP catalysts (BINAP = 2,2′-bis(diphenylphosphanyl)-1,1′-binaphthyl)[73] in [BMIM]BF$_4$ melts [Eq. (11)]. Both reactions were carried out in two phases with the help of an additional organic solvent (e.g. *i*PrOH). The catalyst could be reused with the same activity and enantioselectivity after decanting the hydrogenation products.

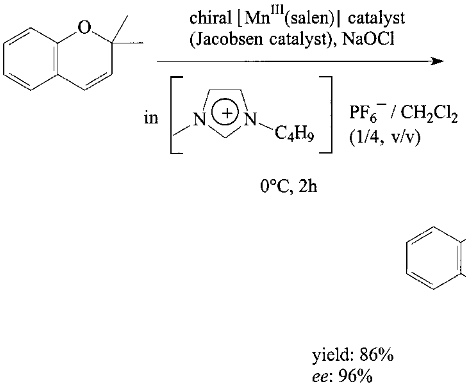


(11)

In general, transition metal catalyzed hydrogenation reactions in ionic liquids are judged to be particularly promising: On the one hand, a large number of known hydrogenation catalysts exist.[74] On the other hand, the solubility of hydrogen and many alkenes in the ionic liquid appears to be sufficiently high to achieve good reaction rates. At the same time, the miscibility gap between the saturated reaction products and the ionic liquid is large so that, in the majority of cases, a biphasic procedure is possible.

4.2. Oxidations

Recently published results by Song and Roh indicate that the use of ionic liquids is also of advantage in selective oxidation reactions.[75] They investigated the epoxidation of, for example, 2,2-dimethylchromene with a chiral Mn^{III}(salen) complex ([*N*,*N*′-bis(3,5-di-*tert*-butylsalicylidene)-1,2-cyclohexanediamine]manganese(III) chloride) in a mixture of [BMIM]PF$_6$ and CH$_2$Cl$_2$ (1:4 v/v) [Eq. 12]. The authors describe a clear enhancement of the catalyst activity by the addition of the ionic liquid to the organic solvent. In the presence of the ionic liquid an 86 % conversion of 2,2-dimethylchromene was observed after 2 h. Without the ionic liquid the same conversion was obtained only after 6 h. In both cases the enantiomeric excess was as high as 96 %.



(12)

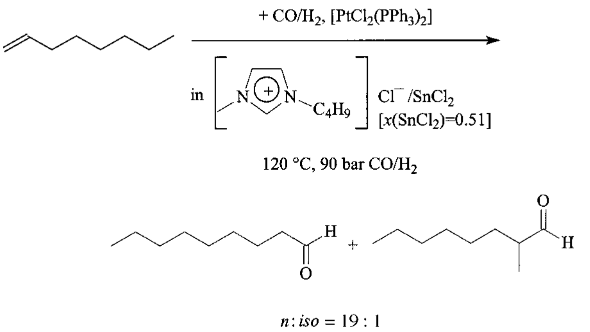
Moreover, the use of the ionic liquid solvent allows an easy catalyst recycle without the need of any catalyst modification. By washing the organic phase with water followed by extraction of the product with hexane, the ionic catalyst solution is recovered after reaction and can be reused. Though, after five recycles the conversion drops from 83 % to 53 % under identical reaction conditions. The authors explain this loss in activity by a slow degradation of the [Mn^{III}(salen)] complex.

To our best knowledge the publication of Song and Roh is the first published example of a transition metal catalyzed oxidation reaction in an ionic liquid. This is quite surprising taking in account that the ionic liquid concept appears particularly suitable for oxidation reactions. It is known from electrochemical studies that some ionic liquids show high oxidation stability.[16a] Moreover, recent studies in our laboratory showed that low melting imidazolium and pyridinium salts are stable even versus highly oxidizing media such as fuming sulfuric acid (30 % SO$_3$) if short alkyl chains are chosen at the cation.[76] The investigation of further oxidation reactions in ionic liquids looks therefore quite promising.

4.3. Hydroformylations

As early as 1972 Parshall described the platinum-catalyzed hydroformylation of ethene in tetraethylammonium trichlorostannate melts.[31a] The ionic liquid used in this case has, however, a rather high melting point of 78 °C. In addition, the publication does not contain details of the catalytic activity of the platinum catalyst dissolved in the melt.

In our group, we have therefore studied the platinum-catalyzed hydroformylation in chlorostannate melts anew. In BMIM trichlorostannate, which is liquid at room temperature, the hydroformylation of 1-octene, according to Equation (13), succeeded with remarkable *n*/*iso* selectivities.[31c] Despite the limited solubility of 1-octene in the ionic catalyst phase, a remarkable activity of the platinum catalyst was achieved (turnover frequency (TOF) = 126 h^{-1}]). The biphasic nature of the reaction enabled a very simple product isolation, leaching of the platinum catalyst into the product phase was not observed.

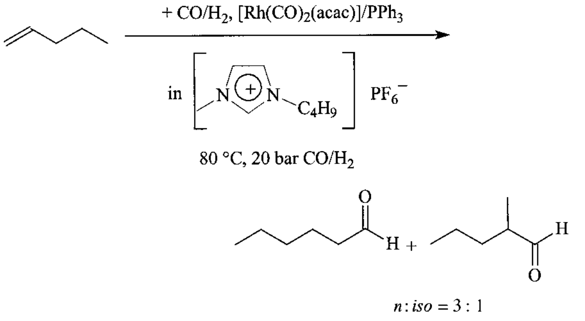


(13)

Ruthenium- and cobalt-catalyzed hydroformylation of internal and terminal alkenes in molten tetra-*n*-butylphosphonium bromide was investigated by Knifton.[23c] The author described a stabilization of the active ruthenium–carbonyl complex by the ionic medium. An increased catalyst lifetime at low synthesis gas pressures and higher temperatures was observed.

Recently the rhodium-catalyzed hydroformylation of 1-hexene was performed in higher melting (>70 °C) phosphonium salts, too.[24] The authors made use of the higher melting point of the salt to "pour off" the organic product from the solid catalyst medium at room temperature. After renewed heating above the salt's melting point, the catalyst could be reused with the same reactivity.

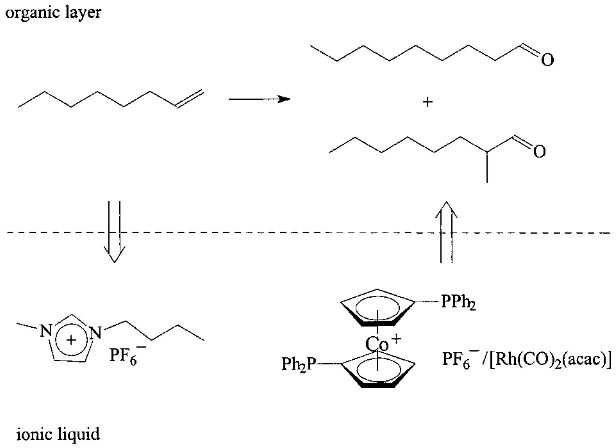
Investigations of the rhodium-catalyzed hydroformylation in room temperature liquid molten salts were published by Chauvin et al. in 1995.[15, 77] The hydroformylation of 1-pentene with [Rh(CO)$_2$(acac)]/PPh$_3$ (acac = acetylacetonate) succeeded, for example, in a [BMIM]PF$_6$ melt [Eq. (14)].



(14)

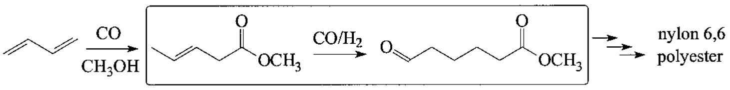
Compared with the reaction in toluene (TOF = 297 h^{-1}) a slightly improved activity (TOF = 333 h^{-1}) was achieved. In addition the biphasic procedure allows a simple product isolation. However, a slight leaching of the catalyst into the organic phase was observed. The use of a monosulfonated triphenylphosphane (tppms) ligand was able to suppress this completely but the activity of the system was significantly reduced (TOF = 59 h^{-1}).

This result gives rise to the question whether the observed deactivation with the tppms ligand is a result of the ionic liquid solvent or an effect of the sulfonated ligand. We have therefore investigated in our laboratories the application of other ionic ligands for the hydroformylation in ionic liquids. Cationic colbaltocenium diphosphane ligands proved to be particularly successful in the biphasic hydroformylation of 1-octene in [BMIM]PF$_6$ (Scheme 4).[78] The ligands used for our studies have been developed and synthesized by Salzer and Brasse.[79] Especially with the ligand 1,1′-bis(diphenylphosphanyl)cobaltocenium hexafluorphosphate the system shows activities that are at least remarkable for the biphasic hydroformylation of 1-octene (TOF = 810 h^{-1}). The selectivity for the linear aldeyde (*n*:*iso*: 16.2:1) was found to be in a technically interesting range, too. The catalyst leaching into the organic layer was less than 0.5 % and the recyclability of the ionic liquid catalyst solution could be proved in principle. Evidently, the Rh-catalyzed, biphasic hydroformylation of long-chain α-olefins in ionic liquids is possible in a highly active and selective manner if suitable (cationic) ligands are used.



Scheme 4. Biphasic, Rh-catalysed hydroformylation of 1-octene in 1-*n*-butyl-3-methylimidazolium(BMIM) hexafluorophosphate using a cationic cobaltoceniumdiphosphane ligand.

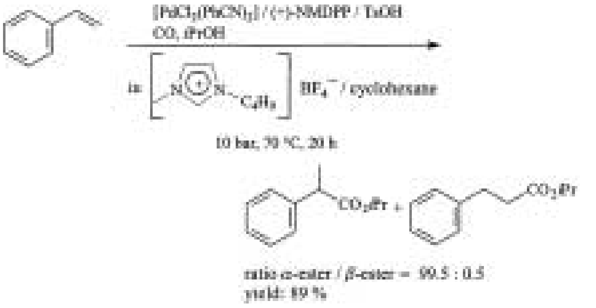
Interestingly not only biphasic hydroformylation reactions result in process engineering advantages if ionic liquids are applied. In the monophasic hydroformylation of methyl-3-pentenoate our group succeeded, by the use of [BMIM]PF$_6$ as the solvent, to stabilize the rhodium catalyst under the harsh product distillation conditions (0.2 mbar vacuum, 110 °C) in the reactor. The ionic catalyst phase was recycled ten times without significant loss in activity.[80] The total productivity of the rhodium catalyst used in this case could be increased tenfold in this way. The reaction has industrial significance as a step of an alternative synthesis route to produce adipic acid from butadiene [Eq. (15)].



(15)

4.4. Alkoxycarbonylations

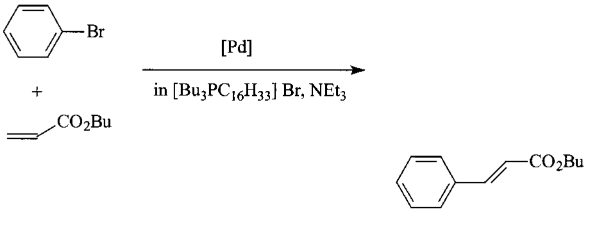
An interesting biphasic example of the palladium-catalyzed alkoxycarbonylation of styrene and styrene derivatives was published by Monteiro et al.[18a] In the system BMIM tetrafluoroborate/cyclohexane, styrene, isopropyl alcohol, and carbon monoxide were allowed to react to form 2-isopropyl phenylpropionate, for example. With (+)-neomenthyldiphenylphosphane ((+)-NMDPP) as the ligand, the product was obtained in high yield and very good regioselectivity. Despite the chiral phosphane ligands, the observed asymmetric induction was, however, very low ($ee < 5\%$) [Eq. (16)]. The ionic liquid allowed simplified product isolation due to the biphasic reaction procedure. Reuse of the ionic catalyst solution obtained by phase separation only succeeded if the conversion was previously restricted to <35%. With complete conversion of the substrate, the authors observed the partial or complete decomposition of the active palladium catalyst.



(16)

4.5. Heck Reactions

The use of ionic liquids as reaction media for the palladium-catalyzed Heck reaction was first described by Kaufmann et al. in 1996.[81] The reaction of bromobenzene with butyl acrylate to butyl *trans*-cinnamate succeeded in high yield in molten tetraalkylammonium and tetraalkylphosphonium bromide salts [Eq. (17)]. The authors describe a stabilizing effect of the ionic liquid on the palladium catalyst. In almost all reactions no precipitation of elemental palladium was observed even at complete conversion of the aromatic halide. The reaction products were isolated by distillation from the nonvolatile ionic liquid.



(17)

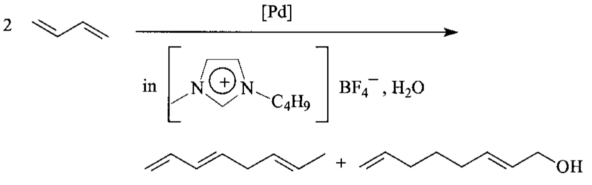
Extensive studies on the Heck reaction in low melting salts have been recently presented by Hermann and Böhm.[82] Their results indicate that the application of ionic solvents show clear advantages over commonly used organic solvents (such as DMF) especially for the conversion of the industrially interesting chloroarenes. With almost all tested catalyst systems an additional activation and stabilization was observed. Molten [NBu_4]Br (m.p. 103 °C) proved to be a particularly suitable reaction medium among the ionic solvent systems under investigation. In the reaction of bromobenzene with styrene using diiodobis(1,3-dimethylimidazolin-2-ylidene)palladium(II) as catalyst the yield of stilbene could be increased from 20% (DMF) to over 99% ([NBu_4]Br) under otherwise identical conditions. Again, a distillative product separation from the nonvolatile ionic catalyst solution was possible. The latter could be reused up to thirteen times without significant drop in activity. Additional advantages of the new solvent concept arise from the excellent solubility of all reacting molecules in the ionic solvent and the possibility to use cheap inorganic bases. The authors conclude that the application of ionic solvents could represent a standard procedure for Heck reactions in the future.

Other examples of the Heck reaction in ionic solvents were investigated by Seddon's group.[83] They described the option of a work-up procedure in the three-phase system [BMIM]PF_6/water/hexane. While the used catalyst [$(BMIM)_2PdCl_4$] remains in the ionic liquid, the products dissolve in the organic layer. The salt formed as a by-product of the reaction ($[Hbase]^+X^-$) is extracted into the aqueous phase. Interestingly, the authors observed significant differences in reactivity between the application of either imidazolium salts or pyridinium salts in the Heck reaction. They assume the abstraction of the 2-H-hydrogen atom at the imidazolium cation by the base of the Heck reaction and the formation of palladium–carbene complexes.

The in situ formation of palladium–carbene complexes in imidazolium melts under the reaction conditions of the Heck reaction was recently confirmed by a publication of Xiao et al.[65] They described a significantly enhanced reactivity of the Heck reaction in [BMIM]Br in comparison to the same reaction in [BMIM]BF_4 and explained this difference with the fact that only in the bromide melt the formation of palladium–carbenes was observed. From the bromide ionic liquid they could isolate and characterize the carbene complexes. The isolated complexes proved to be active catalysts in the Heck reaction when redissolved in [BMIM]Br.

4.6. Hydrodimerizations/Telomerizations

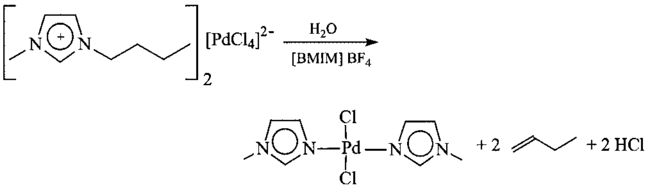
Dupont et al. investigated the hydrodimerization/telomerization of 1,3-butadiene with palladium(II) compounds in [BMIM]BF_4 melts.[84] In addition to 1,3,6-octatriene, the telomer octa-2,7-dien-1-ol was obtained [Eq. (18)]. The



(18)

activity of the catalyst was given with a turnover frequency (TOF) of 118 h^{-1} and could be increased to 204 h^{-1} by operating under CO_2 pressure. Interestingly, the reaction takes place in a monophasic reaction system at 70 °C; cooling to 5 °C induces the formation of an ionic catalyst phase and a product phase. In this way, simple product isolation becomes possible and the ionic catalyst phase can be recovered.

One of the catalyst precursors used for this reaction, the complex $[(BMIM)_2PdCl_4]$, was analyzed by X-ray spectroscopy. The authors describe the activation of this catalyst complex via a palladium(IV) compound, which is formed by oxidative addition of the imidazolium nitrogen atom and the alkyl group with cleavage of the C–N bond of the [BMIM] ion leading to a bis(methylimidazole)dichloropalladate (Scheme 5). This reaction was only observed in the presence of water, however.

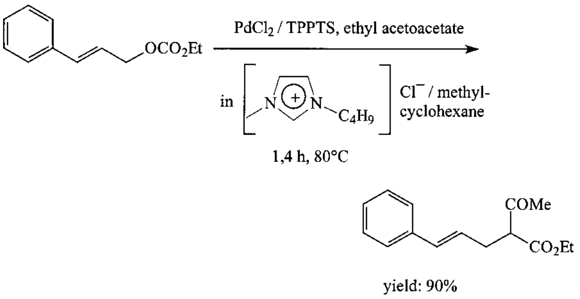


Scheme 5. Formation of the active catalyst from $[(BMIM)_2PdCl_4]$ for the hydrodimerization of 1,3-butadiene.

4.7. Trost–Tsuji Couplings

The nucleophilic, allylic substitution catalyzed by palladium(0) complexes is an attractive way to form C–C bonds in organic synthesis. The reaction could be successfully carried out in ionic liquids as well. Xiao et al. described the monophasic reaction of 3-acetoxy-1,3-diphenylprop-1-ene with dimethyl malonate in $[BMIM]BF_4$.[85] The reaction proceeded in 5 h (80 °C) to complete conversion with $Pd(OAc)_2/PPh_3$ (1/4) as catalyst system and K_2CO_3 as base. The desired coupling product could be isolated in 91 % yield. The possibility of generating the nucleophile in situ is regarded as a special advantage of the use of the ionic liquid solvent.

de Bellefon et al. investigated biphasic Trost–Tsuji coupling reactions.[86] They converted ethyl cinnamyl carbonate with ethyl acetoacetate in [BMIM]Cl/methylcyclohexane and compared the results to the identical reaction in the system butyronitrile/water [Eq. (19)]. Evidently, the reaction in the ionic catalyst solvent shows clear advantage over the reaction in the aqueous biphasic system. An enhancement of the catalytic activity by a factor of ten is observed in the ionic liquid mainly due to the much better solubility of the substrate molecules in the ionic liquid. Furthermore, the reaction in [BMIM]Cl/methycyclohexane shows significantly improved selectivity since the formation of cinnamyl alcohol (by reaction of water as nucleophile) and the formation of phosphonium salts (by reaction of the Pd-allyl complex with trisulfonated triphenylphosphane (tppts) as ligand) is suppressed and very much decreased, respectively, in the ionic liquid.



(19)

4.8. Oligomerizations

Many cationic transition metal complexes are known to be excellent oligomerization catalysts.[87] However, these complexes are often poorly soluble in unpolar solvents. With common organic solvents this situation usually requires a compromise between the solvation and the coordination properties of the solvent used. In order to achieve sufficient solubility of the metal complex a solvent of higher polarity is requested that may compete with the substrate for the coordination sites at the catalytic center. In this context some ionic liquids—especially those with chloroaluminate, hexafluorophospate, and tetrafluoroborate ions—offer a new perspective due to their ability to combine a certain solvent polarity with weak coordination to the metal centre in a unique way.

In our group we investigated, for example, the ethylene oligomerization with (η^3-methallyl)[bis(diphenylphosphanyl)methane-monoxide-κ^2-P,O]nickel(II) hexafluoroantimonate $[(\eta^3\text{-methallyl})Ni(dppmO)]SbF_6$ as catalyst in different solvents. CH_2Cl_2 proved thereby to be the best choice among the organic solvents studied.[88] By using the ionic liquid $[BMIM]PF_6$ the activity of the cationic Ni complex could be increased by about a factor seven.[85] The overall selectivity of the biphasic reaction to linear α-olefins was as high as 88 % which is even slightly higher than found in the monophasic reaction in CH_2Cl_2.

In tetrafluoroborate and hexafluorophosphate melts, the Pd-catalyzed dimerization of butadiene, for example, was performed as well.[18b] Again, the use of the ionic liquid enabled a biphasic reaction procedure. In addition, the authors observed a substantial increase in activity of the catalyst in comparison to the reaction in tetrahydrofuran.

The nickel-catalyzed oligomerization of short-chain alkenes in chloroaluminate melts is one of the best investigated applications of transition metal catalysts in ionic liquids up to the present. As early as 1990, Chauvin et al. published the first investigations of the dimerization of propene in ionic liquids of the type $[BMIM]Cl/AlCl_3/AlEtCl_2$.[12] Related systems have been used later for the oligomerization of ethene[90] and butenes.[91]

In general, the Ni-catalyzed oligomerization in chloroaluminate melts deserves particular attention since it is proposed for commercialization under the name "Difasol process" by the Institut Français du Pétrole (IFP).[36, 92] The first industrial application of ionic liquids is therefore in sight.

Some detailed aspects of this reaction are introduced in the following example of the dimerization of propene (Table 9).[12, 28a, 93] In basic melts (Table 9, entry a) no dimerization activity is observed. Presumably the basic chloride ions prevent the formation of free coordination sites on the nickel catalyst. In acidic chloroaluminate melts, an oligomerization reaction takes place even in the absence of a nickel catalyst (Table 9, entry b). However, not the desired dimers but a mix of different oligomers formed by cationic oligomerization reactions is obtained. Superacid protons and the reactivity of the acidic anions $Al_2Cl_7^-$ and $Al_3Cl_{10}^-$ are discussed as cause for this reactivity.[12, 60] The addition of alkylaluminum compounds suppresses this unwanted cationic oligomerization activity completely. In the presence of $NiCl_2$ as catalytic precursor, the ionic catalyst solution formed shows good activity in the dimerization of propene (Table 9, entry c). Without additional phosphane ligands however, a product distribution is obtained with no particular selectivity to the valuable highly branched products. With additional phosphane ligands, the product distribution depends on the steric demands of the ligand in question (Table 9, entry d). This corresponds well to results of earlier investigations by Wilke and Bogdanović in organic solvents.[94] Selectivities to the valuable highly branched dimer, 2,3-dimethylbutene, of up to 83% are achieved. At longer reaction times, however, a decrease in the selectivity to highly branched products is observed. It has been postulated that a competing reaction of the basic phosphane ligand with the hard Lewis acid $AlCl_3$ takes place [Eq. (20)]. This assumption is supported by the observation that the addition of a soft competing base such as tetramethylbenzene can prevent the loss in selectivity.

$$[HNiPR_3]^+ + Al_2Cl_7^- \rightleftharpoons [HNi]^+ + AlCl_3(PR_3) + AlCl_4^- \qquad (20)$$

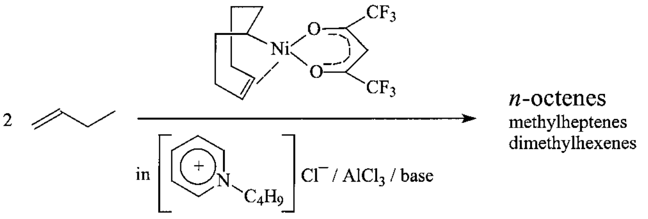
Unfortunately, investigations with ionic liquids containing high amounts of $AlEtCl_2$ reveal several limitations: The reductive effect of the alkylaluminum compound affects the temperature stability of the nickel catalyst. At very high alkylaluminum concentrations a precipitation of black metallic nickel is observed even at room temperature. In addition it has been observed with longer reaction times that small amounts of the alkylaluminum compound leach into the organic phase. This changes the composition and the chemical properties of the ionic liquid. At the border between the two phases the Equilibria (21) and (22) have been assumed.[28]

$$2\,Al_2Et_2Cl_5^- \rightleftharpoons 2\,AlCl_4^- + Al_2Et_4Cl_2 \qquad (21)$$

$$2\,Al_2EtCl_6^- \rightleftharpoons 2\,AlCl_4^- + Al_2Et_2Cl_4 \qquad (22)$$

Despite this, the biphasic IFP "Difasol" process, which uses chloroaluminate ionic liquids with small amounts of alkylaluminum compounds as catalyst, offers significant advantages over the industrially realized, homogeneous one-phase Dimersol process (25 Dimersol units are currently in operation producing octane booster for gasoline with a total processing capacity of 3.4 million tons per year).[92b] According to IFP, the novel ionic liquid process reduces drastically the consumption of Ni catalyst and alkylaluminum compounds. Additional advantages arise from the good performance obtained with highly diluted feedstocks and the significantly improved dimer selectivity of the biphasic ionic liquid process.[92]

In our group we have investigated the applicability of chloroaluminate ionic liquids as solvents for the linear dimerization of 1-butene with the catalyst (η-4-cycloocten-1-yl)(1,1,1,5,5,5,-hexafluoro-2,4-pentanedionato-*O*,*O'*)nickel [(Hcod)Ni(hfacac)] according to [Eq. (23)](Hcod = cyclooct-4-ene-1-yl). Hereby ionic liquids containing alkylaluminum compounds proved to be not suitable due to their strong isomerization activity.[91] Since only the α-olefin can be linked to form linear octenes, isomerization activity of the solvent inhibits the formation of the desired product.



(23)

We have therefore developed chloroaluminate melts that enable selective nickel-catalyzed C–C linkage in ionic liquids without the addition of alkylaluminum compounds.[60, 95] When weak organic bases such as quinoline or pyrrole are added to an acidic chloroaluminate melt, a reaction medium is obtained in which the Ni catalyst is much more active than in toluene, with only slightly lower linear selectivity (Table 10). The function of the added base is to buffer all the acid species in the ionic liquid that could catalyze the unselective, cationic oligomerization reaction (Scheme 6).

In addition to activation of [(Hcod)Ni(hfacac)] in the ionic liquid, we were principally interested in aspects of lifetime and overall activity of the ionic catalyst system. A continuous flow loop reactor was constructed for this purpose in our laboratories (Figure 8).[96] The ionic catalyst solution is placed in the loop at the start of reaction and the loop is filled with reactant. During the experiment, reactant is continuously

Table 9. Results for the dimerization of propene in ionic liquids at −15 °C.

Entry	Ionic liquid	Composition	Ni complex	Aktivity $[kg\,g(Ni)^{-1}\,h^{-1}]$	Product ratio DMB/M2P/*n*Hex[a]
a)	$[BMIM]Cl/AlCl_3$	1/0.8	$[NiBr_2L_2]$[b]	0	
b)	$[BMIM]Cl/AlCl_3$	1/1.5	–	–[c]	
c)	$[BMIM]Cl/AlEtCl_2$	1/1.2	$NiCl_2$	2.5	5/74/21
d)	$[BMIM]Cl/AlEtCl_2$	1/1.2	$[NiCl_2(iPr_3P)_2]$	2.5	74/24/2
e)	$[BMIM]Cl/AlCl_3/AlEtCl_2$	1/1.2/0.1	$[NiCl_2(iPr_3P)_2]$	12.5	83/15/2

$T = -15\,°C$. [a] DMB = dimethylbutene, M2P = methylpentene, *n*Hex = *n*-hexene. [b] L = 2-methylallyl. [c] Highly viscous cationic oligomers were obtained.

Table 10. Comparison of the linear dimerization of 1-butene with the [(Hcod)Ni(hfacac)] in toluene and in chloroaluminate melts.

Reaction in toluene	Reaction in [4-MBP]Cl/$AlCl_3$/quinoline (0.43/0.53/0.04)[a]
● single phase	● biphase, no detectable leaching of the catalyst
● no activity of the catalyst at $< 50\,^{\circ}C$	● obvious activity even at $-10\,^{\circ}C$
● results at $90\,^{\circ}C$[b]	● results at $25\,^{\circ}C$[b]
TOF = 500 h^{-1}	TOF = 1240 h^{-1}
dimer selectivity 85 %	dimer selectivity 98 %
linear selectivity 75 %	linear selectivity 64 %

[a] 4-MBP = 1-*n*-butyl-4-methylpyridinium ion. [b] At 20 % conversion.

$$Al_2Cl_7^- + B \rightleftharpoons B\text{-}AlCl_3 + AlCl_4^-$$

$$B\text{-}AlCl_3 + HCl \rightleftharpoons HB^+ + AlCl_4^-$$

$$Al_2Cl_7^- + HCl + B \rightleftharpoons HB^+ + 2\,AlCl_4^-$$

Scheme 6. Suppression of cationic side reactions in acidic chloroaluminate melts by addition of a weak organic base B.

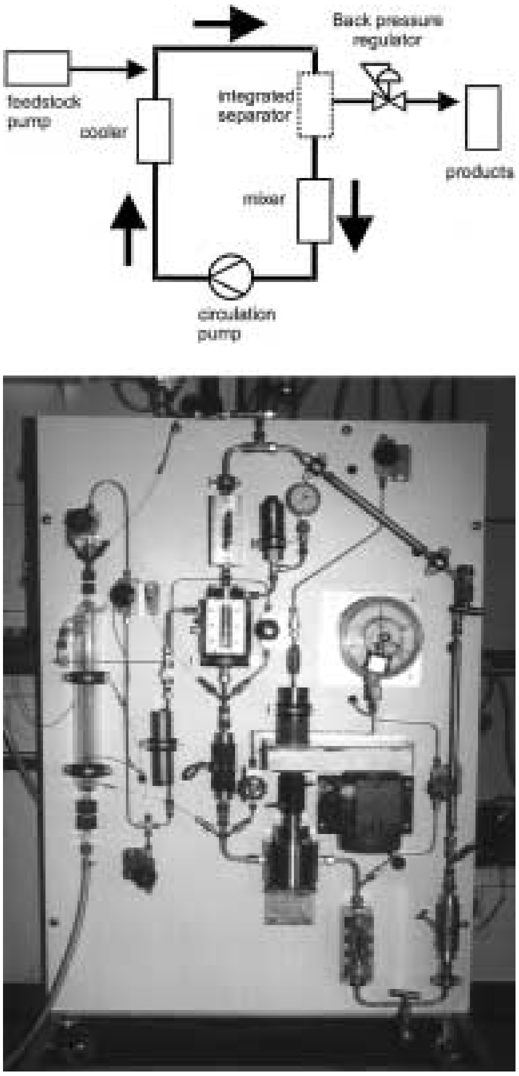


Figure 8. Schematic representation and view of a loop reactor for the investigation of the lifetime of ionic transition metal catalyst solutions.

refilled. The ionic catalyst solution and the organic product phase are separated in an integrated separator within the reactor loop. Since the ionic catalyst solution is present in the reactor loop at all times, any changes in the system can be registered by means of the collected products without time delay. Continuous experiments on linear dimerization of 1-butene resulted in an overall activity (turnover number) of over 18000 for the [(Hcod)Ni(hfacac)] catalyst.[97]

5. Summary and Outlook

Ionic liquids represent a unique class of new reaction media for transition metal catalysis. Their nonvolatile nature enables significant engineering advantages for distillative product separation and prevents uncontrolled evaporation. The possibility to specifically vary their physical and chemical properties make them ideal candidates for applications in biphasic catalysis.

The advantages mentioned above can be used in many applications to minimize solvent and catalyst consumption. Therefore it is highly justified to discuss ionis liquids as “green solvents”.[36, 68] In this respect, ionic liquids complete in a very attractive manner alternative „green solvent“ concepts like water or supercritical CO_2. While supercritical CO_2 covers applications commonly using unpolar solvents, ionic liquids can be considered as replacements for polar organic solvents. First results showing that both concepts can be combined successfully have already been published.[49]

Compared to water, ionic liquids will be—even in a long-term view—significantly more expensive. Therefore, they will be mainly used in those applications where aqueous systems are not possible or show serious drawbacks. In this context, the reactivity of water with many active catalyst complexes has to be considered as a limiting factor. Additionally, many substrates show low solubility in water.

In many applications ionic liquids with weakly coordinating anions and suitable substituted cations are attractive alternative „solutions“ to commonly used solvents. Switching from an organic solvent to an ionic reaction medium often results in an altered chemical reactivity of the dissolved catalyst. The examples presented show that well-known reactions can be accelerated in suitable ionic solutions and can proceed with improved selectivities. In some cases an increased stability of the catalyst is observed in the ionic liquid. In addition, the unusual properties of ionic liquids appear to possess enormous potential for transition metal catalysis: The formation of liquid crystal phases in some ionic liquids is, for example, well-known[1, 17a,d] and recently indications for an ordered surface structure of ionic liquids have been reported.[98] Will this enable new possibilities for the investigation of transition metal catalysts in highly ordered solvents? Is it possible to use the electrochemical properties of ionic liquids to actively maintain transition metal catalysts in certain unusual oxidation states? The use of ionic liquids as solvents for transition metal catalysis opens up a wide field for future investigations.

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