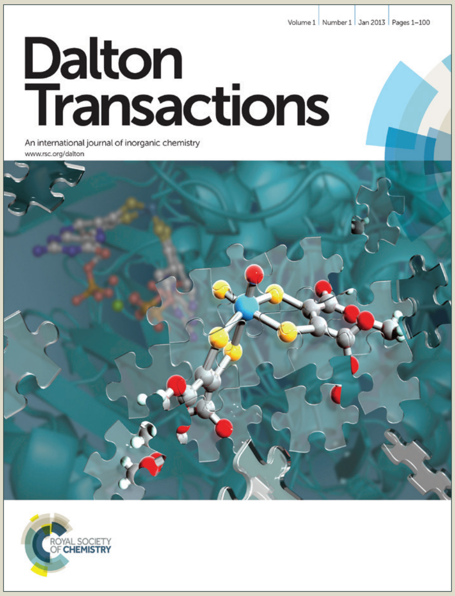
Dalton Transactions

Accepted Manuscript



ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/dalton

Dalton Transactions Perspective Paper

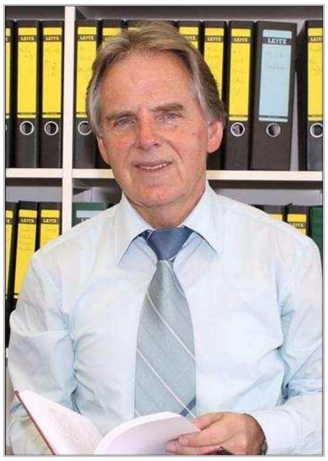
Elucidation of Inorganic Reaction Mechanisms in Ionic Liquids: The Important Role of Solvent Donor and Acceptor Properties

Matthias Schmeisser[a] and Rudi van Eldik[a,b]*

[a] Inorganic Chemistry, Department of Chemistry and Pharmacy, University of Erlangen-Nuremberg, Egerlandstr. 1, 91058 Erlangen, Germany
[b] Faculty of Chemistry, Jagiellonian University, Ingardena 3, 30-060 Krakow, Poland

*To whom correspondence should be addressed. E-mail: rudi.vaneldik@fau.de
Fax: +49(0)91318527387; Tel: +49(0)91318527357.

In this article, we focus on the important role of solvent donor and acceptor properties of ionic liquids in the elucidation of inorganic reaction mechanisms. For this purpose, mechanistic and structural studies on typical inorganic reactions, performed in ionic liquids, have been conducted. The presented systems range from simple complex-formation and ligand-substitution reactions to the activation of small molecules by catalytic-active complexes. The data obtained for the reactions in ionic liquids are compared to those for the same reactions carried out in conventional solvents, and are discussed with respect to the donor and acceptor properties of the applied ionic liquids. The intention of this perspective is to gain more insight into the role of ILs as solvent and their interaction with metal ions and complexes in solution.



***Rudi van Eldik** was born in Amsterdam, the Netherlands, and grew up in Johannesburg, South Africa. He received his chemistry education from the former Potchefstroom University, and completed his Habilitation in Physical Chemistry at the University of Frankfurt in 1982. He was appointed as Professor of Inorganic Chemistry at the Private University of Witten/Herdecke in 1987, and Professor of Inorganic and Analytical Chemistry at the University of Erlangen-Nuremberg in 1994. He has received five honorary doctoral degrees from universities in South Africa, Serbia, Poland and Russia. In 2009 he was awarded the Inorganic Reaction Mechanisms Award by the Royal Society of Chemistry. At present he is Emeritus Professor of Inorganic Chemistry at the University of Erlangen-Nuremberg and Professor of Inorganic Chemistry at the Jagiellonian University in Krakow, Poland.*

***Matthias Schmeisser** started his chemistry studies in 2001 at the Friedrich-Alexander-University of Erlangen-Nuremberg in Germany. During his doctoral studies under the supervision of Prof. Rudi van Eldik, he performed kinetic, mechanistic and structural studies on ligand substitution- and complex-formation reactions in ionic liquids to clarify the influence of these solvents on the mechanistic behavior. After he received his PhD in 2011, he remained in Erlangen as postdoctoral fellow to work on solvent-solute interactions in ionic liquids. He is co-author of a series of publications on mechanistic and structural studies performed in ionic liquids.*

Introduction

In recent years, the demand for environmental friendly and sustainable chemistry has led to a more detailed interest in solvent effects, and the search for customized solvents which are well-suited for the requirements of a specific application.[1, 2, 3] Because of their negligible vapor pressure and the resulting low volatility, ionic liquids (ILs) have been presented as a very promising class of new reaction media, since they also offer the possibility to tune their physicochemical properties such as conductivity, density, melting point, polarity or viscosity, through the combination of a large range of different possible cations and anions.[4] Today, between 300 and 400 different ILs are already commercially available[5] and some of these ILs are well established in new technologies.[6]

As a result of their ionic nature, ILs provide a completely different chemical environment for dissolved substances as compared to that of conventional organic solvents or water. But how do substrates really interact with such an exceptional environment? Since many groups consistently report unexpected observations, such as an increase or decrease in reactivity or even a complete inhibition of reactions, there is obviously still a lack of understanding of the unique interactions that take place between solvent cations, anions and dissolved substances.[7]

On considering possible solvent-solute interactions, the nucleophilicity of ILs plays a crucial role as most of the anions that form part of ILs, *e.g.* Cl^-, Br^-, SCN^-, NO_3^- or $N(CN)_2^-$, are potential Lewis bases. In particular, applications involving sensitive catalytic active metal complexes can seriously be affected by interactions with the anionic component of ILs, either by occupying a vacant coordination site necessary for binding substrates, or by displacing weaker coordinated ligands.[7, 8, 9, 10] Therefore, chemists have become more and more aware of the important role of the donor and acceptor properties of ILs, and a growing number of publications have attempted to generalize and categorize these properties.[11, 12] However, on the basis of the currently available data, it still remains difficult to make reliable predictions on the behavior of ILs and their role as solvents, catalysts or co-catalysts. Thus, studies on individual systems to learn more about possible effects and to obtain a feeling for the unique behavior of ILs still remain indispensable.[13]

As physical-inorganic chemists interested in chemical kinetics, reaction mechanisms and coordination chemistry, we started to investigate possible structural or mechanistic changes and the reasons therefore, when a typical inorganic reaction, extensively studied in conventional solvents before, is transferred into ILs. It was our intention to investigate a variety of different reaction types, such as complex-formation, ligand-substitution and the activation of small molecules, by applying conventional and specialized instrumental techniques. In this context, we first concentrated on the significant effect of a series of ionic liquids on ligand substitution reactions of Pt^{II} and Pd^{II} complexes.[14, 15] We then extended our studies to complex-formation reactions involving lithium ions,[16] a topic related to supramolecular and accumulator chemistry, and to the activation of small molecules, viz. carbon dioxide[17] and nitric oxide.[10, 18] The latter topic involves model systems of catalytically active, inorganic and bioinorganic transition metal complexes. During all these studies we often noticed a problematic influence of the applied ILs, either on the solubility of substrates or on the reactivity of the systems under investigation. Challenged through these problems, we further developed an interest in the understanding and quantification of donor and acceptor properties of ILs.[19] A selection of these studies is presented in this article and discussed with respect to the donor and acceptor properties of the applied ILs.

Donor and acceptor numbers for ionic liquids

Reaction rates, reaction mechanisms, the reactivity of dissolved substances or even the preferred products, can in general be influenced by solute-solvent interactions. Thus, a detailed knowledge of the physical and chemical properties of solvents is an important prerequisite for their efficient application in fundamental research and industrial processes. The type of interactions and their strength depend on various factors, such as the van der Waals forces, the ability of a solvent to form hydrogen bonds, the polarity of a solvent or, especially important in the case of ILs, the strength of intermolecular Coulomb interactions. To achieve a better understanding of these physico-chemical phenomena, numerous approaches have been proposed over the years to quantify solvent properties. Here, of widespread use, are the Dimroth and Reichardt $E_T(30)$ polarity-parameter and the three parameter set derived from Linear Solvent Energy Relationships (LSER) by Kamlet and Taft, consisting of α (hydrogen bond donating ability), β (hydrogen bond acceptance) and π* (polarity/polarisability).[20] Although, all these solvent parameters have originally been developed to describe conventional solvents, several groups have started to determine these parameters for ILs to be able to compare the properties and behavior of conventional solvents with that of ILs.[11, 12, 21, 22] However, the determination of these parameters relies on the successful application of solvatochromic dyes and their spectroscopic behavior in ILs, which in some cases is limited by solubility or stability restrictions. Moreover, there is still a controversial discussion on which set of solvatochromic dyes gives reasonable results, or whether the appropriate α, β and π* values can really be denoted as Kamlet-Taft parameters. Due to a partially very confusing presentation of all these methods and solvent parameters in the literature, it was our intention to find an easy and practical way to gain insight into the solvent properties of ILs and their interactions with metal ions and complexes. We therefore focused on Gutmann's "donor-acceptor concept" that established the donor (DN) and acceptor number (AN) to describe the ability of a solvent to donate or accept electron pairs, *i.e.* a measure of their nucleophilicity/electrophilicity, respectively. [23]

Gutmann originally determined the donor number calorimetrically by measuring the interaction enthalpy of $SbCl_5$ with an equimolar amount of the solvent under investigation, both dissolved in 1,2-dichloroethane (zero by definition).[23] The enthalpy change provides the donor number in kcal/mol. Later Ehrlich and Popov found that Gutmann's "solute state" donor numbers can be correlated linearly with the ^{23}Na chemical shift of $NaClO_4$ dissolved directly in the appropriate solvent.[24] In contrast to the calorimetric method, the application of ^{23}Na NMR offered several advantages, such as a fast acquisition of data and a high sensitivity due to the high abundance of the ^{23}Na nucleus (100 %). Based on the Ehrlich-Popov correlation between the DN of conventional solvents and the appropriate ^{23}Na chemical shift, we assigned donor numbers to various ILs by measuring the ^{23}Na chemical shift of $NaClO_4$ dissolved in the IL under investigation (see Table 1).[19, 24]

Table 1. NMR data and DNs for selected ILs. All measurements were done at 298 K (exceptions are given in brackets).

IL	Chemical shift of ^{23}Na [ppm]	Donor Number [kcal mol^{-1}]	IL	Chemical shift of ^{23}Na [ppm]	Donor Number [kcal mol^{-1}]
[emim][FAP]	-21.38	-12.3	[emim][PO(EtHex)$_2$]	-5.83	20.5
[emim][PF$_6$]	-18.51	-6.2	[emim][OctOSO$_3$]	-5.76	20.6
[emim][SbF$_6$]	-13.33	4.7	[emim][NO$_3$]	-5.01	22.2
[C$_{12}$mim][NTf$_2$]	-12.36	6.7	[emim][EtOSO$_3$]	-4.97	22.3
[emim][Pf$_2$N]	-12.14	7.2	[emim][HexOSO$_3$]	-3.15	26.1
[emim][BF$_4$]	-12.09	7.3	[emim][TCM]	-3.13	26.1
[C$_{10}$mim][NTf$_2$]	-12.00	7.5	[emim][BuOSO$_3$]	-2.95	26.5
[emim][ClO$_4$]	-11.95	7.6	[emim][(EtO)$_2$PO$_2$]	-0.68	31.3
[C$_8$mim][NTf$_2$]	-11.62	8.3	[emim][dca]	2.39	37.8
[C$_6$mim][NTf$_2$]	-11.50	8.5	[emim][NO$_2$] (348 K)	2.95	38.9
[C$_4$mim][NTf$_2$]	-10.70	10.2	[emim][SnCl$_3$]	3.17	39.4
[emim][NTf$_2$]	-10.22	11.2	[emim][Ac]	5.03	43.3
[emim][B(CN)$_4$]	-5.89	20.3	[emim][SCN]	6.26	45.9
[emim][OTf]	-5.84	20.4	[emim][MeOAc]	7.61	48.8

Since the electron pair donor ability of an IL is primarily controlled by the chemical nature of the anionic component, we mainly focused on the 1-ethyl-3-methylimidazolium cation based ILs with a wide range of different anions. Some obvious trends can be seen from the data presented in Table 1. Anions with a high nucleophilicity, such as thiocyanate or acetate, result in ILs with a high DN.. The introduction of an electron donating group, such as a methyl group, leads to an additional increase in the donicity as shown by [emim][MeOAc]. The donicity of this IL is similar to that of ethylendiamine (DN = 55). All these ILs will most likely coordinate to metal ions or replace weaker coordinated ligands. On the contrary, anions with weak donor ability result in weak coordinating or non-coordinating ILs. Here, the ILs [emim][PF_6] and [emim][FAP] have DNs even lower than the original zero point of Gutmann's scale, viz. 1,2-dichloroethane (DCE). Notably, the introduction of a fluorinated alkyl group leads to a significant decrease in the DN. [emim][PF_6] exhibits a DN of -6.2, whereas [emim][FAP] in which three fluorine atoms are replaced by $-CF_2CF_3$ groups, exhibits a DN of -12.3. These ILs could be interesting alternatives for organic solvents if the coordination of solvent molecules to a metal center has to be strictly avoided. Solvents with a slightly higher donicity feature DNs between 0 and 20 and are comparable to conventional solvents like nitromethane (DN = 2.7), acetonitrile (DN = 14.1) or acetone (DN = 17). Here, very popular representatives are the ILs [emim][BF_4] (DN = 7.3) or [emim][NTf_2] (DN = 11.2).[25, 26] As can be seen from a comparison of [emim][NTf_2] and [emim][NPf_2], the elongation of the fluorinated groups also leads to a decrease in the donicity. Other ILs containing fluorinated anions, such as SbF_6^-, TfO^-, and NPf_2^-, are also amongst the ILs with low DNs. All these anions are weak donors and therefore behave as almost innocent solvents. ILs in the DN range between 20 and 33 are weaker nucleophiles than water (DN = 33), but have donor atoms with free electron pairs that are known to coordinate to metal centers similar to $ROSO_3^-$ or $(RO)_2PO_2^-$. On dissolving a substrate in such an IL, the anions that are present in a large excess are able to substitute weaker coordinated ligands of a metal center.[27] These ILs are comparable to the donicity of DMSO (DN = 29.8), which can coordinate to metal complexes under the right conditions, but will easily be displaced if a stronger donor is added. In this context, it should be mentioned that the water content of an IL can significantly influence its nucleophilicity and can lead to an increase or decrease of its donicity. Therefore, water impurities should be carefully removed prior to the measurements to obtain reliable information on the donicity of ILs, which can help to predict the progress of reactions and to suggest new synthetic routes in ILs.

In an earlier publication, Linert *et al.* already presented DNs for several anions,[28] since Gutmann only determined DNs of molecular solvents. Besides other methods, they used [Cu(acac)(tmen)]BPh_4 (acac = acetylacetonate and tmen = tetramethylethylenediamine) dissolved in

DCE as a solvatochromic indicator to investigate the donicity of anions. The copper complex can interact in a competitive way with both the solvent (DCE) and the appropriate anion, which was added as a tetrabutylammonium salt. The equilibrium formed between these competitors results in a shift of the d-d absorption band and thus in a color change,[29] which leads to the DN of the appropriate anion. They found the sequence $PF_6^- \approx SbF_6^- < NTf_2^- < BF_4^- < ClO_4^- < CF_3SO_3^- < NO_3^- < I^- < Ac^- < SCN^-$. As illustrated by the correlation in Figure 1, their donicity sequence in general reflects the DNs of the corresponding [emim]-based ILs and is in good agreement with the results of Mudring *et. al.*[30]

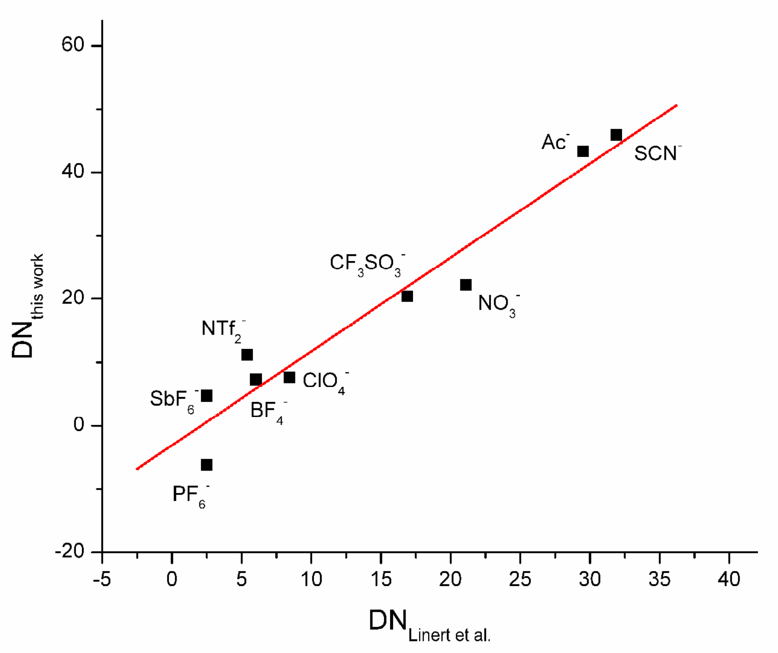


Figure 1. Correlation between DNs for anions determined by Linert et al. and those for the corresponding [emim]-based ILs.

In contrast to our results,[19] Linert found a DN of 2.5 for the PF_6^- anion (-6.2 in our study) and found the same value for SbF_6^- (4.7 according to our method). This discrepancy originates from the DN of the employed solvent DCE. The lowest DN assignable is the DN of the solvent used to dissolve the anions and the probe complex. If the anion is a weaker donor, a solvent molecule will coordinate to the Cu^{II} complex and thus “freeze” the experimentally determinable DN at a fixed value, in this case the DN of DCE. On the contrary, our solvent free method allows the determination of donicities even lower than that of DCE. With respect to Gutmann’s original DN scale, some ILs therefore exhibit negative DN values.

Since the donicity of ILs is mainly controlled by the anion, it was quite obvious to expect a response of the DN on modifications of the anionic component. However, a possible influence of structural changes on the cationic component could not be excluded. Therefore, we exemplarily studied the effect of an elongated alkyl chain of NTf_2^- based ILs and found systematic changes in the DNs. The longer the alkyl chain of the imidazolium cationic moiety, the lower the DN of the appropriate IL. This observation can be explained in terms of stronger van der Waals interactions and aggregation effects, which diminish the interaction with acceptors and lead to a lower donicity.[31, 32] On the contrary, an increase in temperature leads to an increase in the donicity (see Figure 2 and Table 2), as the higher mobility of the ions at higher temperature lead to a disintegration of cation-anion aggregates and, therefore, to stronger interactions with substrates.

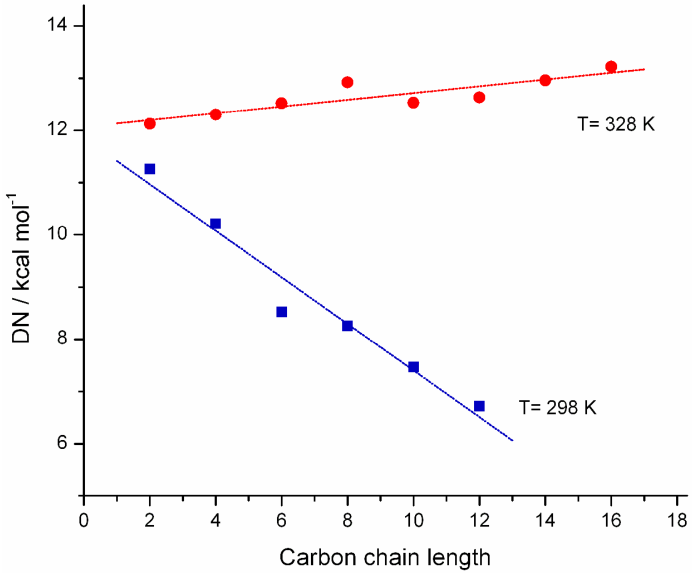


Figure 2. Change in the DN on elongation of the alkyl chain of the imidazolium cation at 298 and 328 K; $[C_{14}mim][NTf_2]$ and $[C_{16}mim][NTf_2]$ are solids at room temperature.

As a consequence, the temperature effect is much larger for ILs with long alkyl chains which form larger and more stable aggregates at room temperature. Such an influence of alkyl chain length and temperature on the donicity of ILs can, to a certain extent, be helpful to adjust the interactions between ILs and substrates. As the donicity influences the solubility of substrates and also the miscibility with other liquids, the arrangement of temperature switchable processes, such as a temperature-dependent variation of two-phase equilibria, may be possible. Similar effects have already been reported and established for conventional solvents.[33]

The LSER concept established by Kamlet and Taft is one of the most popular concepts to correlate solvent properties with different specific interactions such as the hydrogen bond donating ability (α), hydrogen bond acceptance (β), and the polarity/polarisability (π^*) of a solvent. [34] For a large selection of conventional solvents, Marcus showed that the β parameter, which is an expression for a molecule's electron pair donation ability to form a coordinative bond, can be correlated linearly with Gutmann's DN.[20] Such a correlation can be very useful to predict missing data of DNs or β parameters. Although a large number of Kamlet-Taft-parameters for organic solvents already exist and can facilitate a possible comparison, reliable data for ILs are still rather scarce. According to Marcus' approach,[20] we correlated our DNs with the appropriate Kamlet-Taft-β-parameters (see Table 2 and Figure 3).

Table 2. Kamlet-Taft-parameters for several imidazolium-based ILs

ionic liquid	π^*-parameter	α-parameter	β-parameter	DN [kcal mol^{-1}]
[emim][PF_6]	0.99	0.76	0.20	-6.2
[emim][BF_4]	1.03	0.70	0.26	7.3
[emim][ClO_4]	1.11	0.56	0.41	7.6
[C_8mim][NTf_2]	0.97	0.97	0.28	8.3
[C_6mim][NTf_2]	0.98	0.65	0.25	8.5
[C_4mim][NTf_2]	0.98	0.62	0.24	10.2
[emim][NTf_2]	0.90	0.76	0.28	11.2

[C$_4$mim][OTf]	1.01	0.63	0.46	20.5
[emim][OSO$_3$]	1.09	0.58	0.62	22.3
[emim][NO$_3$]	1.13	0.48	0.66	22.2
[emim][HexOSO$_3$]	0.98	0.65	0.71	26.1
[emim][OctOSO$_3$]	0.93	0.65	0.77	20.6
[emim][dca]	1.08	0.53	0.35	37.8
[emim][OAc]	1.09	0.40	0.95	43.3

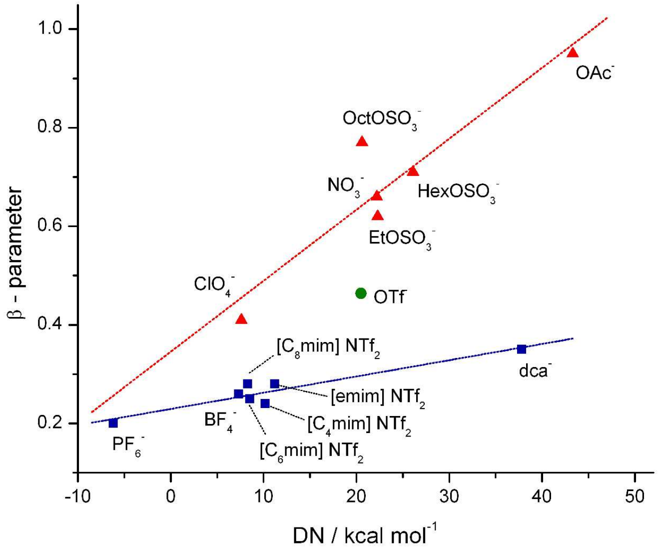


Figure 3. Correlation between β values (Table 3) and DNs for ILs; N-donor ILs generate one family together with fluorinated ILs.

At a first glance the DNs hardly correlate with the corresponding β-parameters and exhibit a large variance. However, a closer look reveals two separate correlations with an approximate linear behavior, and one exception. As shown in Figure 3, ILs consisting of O-donor anions appear to generate one family of ILs, whereas ILs consisting of N-donor atoms seem to generate another family along with the fluorinated ILs. Such family-dependencies were already reported by Kamlet and Taft for correlations between the β-values and other physical parameters.[34] Only [bmim][OTf] does not fit to one of these correlations. Interestingly, this IL is located exactly between both correlations, which could be accounted for by the fact that the triflate anion contains oxygen as well as fluorine atoms. On considering the different electro-negativity of nitrogen and oxygen, both correlations shown in Figure 3 could arise from different energy levels of the donor orbitals. Oxygen exhibits a higher electro-negativity than nitrogen, and as a result the energy levels of the free electron pairs, as well as the appropriate MOs generated on interaction with acceptors, should be lower than in the case of N-donors. However, to establish correlations which enable an accurate estimation/calculation of DNs or β-parameters according to Marcus' approach, there are presently not enough data available on both, DNs as well as β-parameters.

Similar to the correlations between DNs and β-parameters, we also observed a family-dependent behavior on comparing our DNs with the appropriate ion pair interaction energies ΔE calculated by DFT. Based on our earlier studies,[14] we determined ΔE as the energy difference between the ion-pair formed by the cation and anion, and the energy of the separated ions (see reaction (1)). To simplify the calculations, we used the 1,3-dimethylimidazolium cation ($[\mathrm{mmim}]^+$) instead of $[\mathrm{emim}]^+$. Although the energies are surely biased because of the Coulomb attraction and the fact that the values do not include dispersion, we obtained good correlations with the experimental data. The calculated structure of the ion-pairs (e.g. [mmim][NO_3], see Figure 4) accounts for the important role of the C-H···anion interactions that were previously verified by experiment.[14]

$$\underset{\text{separated ions}}{\mathbf{[mmim]^{+} + [anion]^{-}}} \rightleftharpoons \underset{\text{ion-pair}}{\mathbf{[mmim][anion]}} \qquad \mathbf{(1)}$$

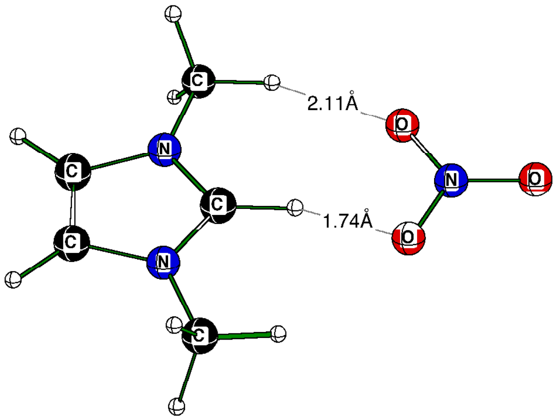


Figure 4. DFT (RB3LYP/LANL2DZp) calculated structure of [mmim][NO_3].

Depending on the anionic component of the investigated ILs, we also found large differences in the appropriate interaction energies. At first sight, only a very rough correlation can be observed, indicating that anions with a low interaction energy (ΔE) correspond to lower DNs, whereas anions with a high interaction energy correspond to higher DNs. However, a closer look at Figure 5 also points to the existence of two family-dependencies. In contrast to the results obtained for the β-parameter, there is no clear distinction between N- and O-donor anions, but rather between anions with and without cyano groups. Within the first family (anions containing cyano groups), the calculated interaction energy (ΔE) increases with decreasing number of cyanide substituents, following the same sequence $SCN^- > N(CN)_2^- > C(CN)_3^- > B(CN)_4^-$ as mentioned above for the DNs. Due to the pseudo-halogenide character of the cyanide groups, $AlCl_4^-$ is located amongst the cyanide containing anions next to the tricyanomethanide anion.[35], [36]

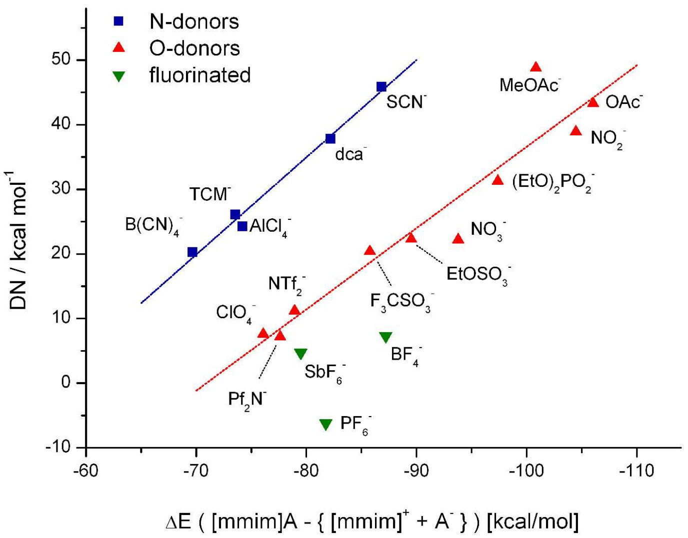


Figure 5. Correlation between the DNs and the DFT calculated interaction energy ΔE.

With respect to the second family of ILs, the O-donor anions exhibit the same sequence as found for the correlation between the DNs and the β-parameters. Only MeOAc$^-$ diverges and seems to have a too high DN in comparison to the calculated interaction energy. The calculated interaction energy of the acetate anion is higher despite its lower DN. This discrepancy might originate from the additional methoxide group in the MeOAc$^-$ anion. By applying DFT calculations, the electron withdrawing effect of this group is factorized and reduces the electron donation ability of the carboxyl group without considering the interactions between this electron rich group and the cation, which presumably exist in the liquid state, thus diminishing the actual overall interaction energy. Interestingly, the fluorinated ILs are located partly amongst and partly below the O-donor anions, but a clear correlation between the DN and the interaction energy was not observed. Due to specific electronic and structural features, such as electron delocalization over the whole molecule and the almost spherical shape, anions like SbF$_6^-$, PF$_6^-$ and BF$_4^-$ are rather weak electron donors and exhibit nearly the same interaction energy. Only BF$_4^-$ has a slightly higher DN and moderately higher interaction energy, which might be due to the stronger B-F bonds and lower coordination number. Anions with fluorinated alkyl groups such as NTf$_2^-$ and Pf$_2$N$^-$, are known to be weak donors because of the electron withdrawing effect of the CF_3 or C_2F_5 substituents. Though these anions offer different possible ways to coordinate to a metal center (monodentate, η^1-O, η^1-N or bidentate, η^2-O,O′, or even η^2-N,O), a preference for coordination via oxygen atoms can be observed from crystal structures and other investigation methods.[37] This can be ascribed to steric effects, but also to electronic features. Due to the electron withdrawing character of the CF_3 or C_2F_5 substituents, a large degree of pπ-dπ bonding within the N-S moiety could lead to charge delocalization over the whole anion and complicate coordination via the nitrogen donor.[38] All in all, the correlations in Figure 5 show a good agreement between DFT calculations and experimental data. The observed family dependencies should be considered as a useful tool for the interpretation and estimation of diverging or coinciding characteristics of other ILs.

To establish a method for quantifying the electrophilic properties of solvents, Gutmann *et al.* introduced the acceptor number (AN) as a counterpart to the DN and donicity. Since alternative methods to determine electrophilic interactions were complicated,[39] Gutmann devised a more advanced technique by selecting triethylphosphine oxide (Et_3PO) as probe molecule and ^{31}P-NMR as method of choice: (i) because of the high natural abundance and high NMR sensitivity of the ^{31}P nucleus, NMR measurements are very suitable; (ii) triethylphosphine oxide exhibits a high solubility and stability in many different solvents.[23] Moreover, the molecular structure of Et_3PO which assures an efficient electronic shielding of the ^{31}P nucleus without steric hindrance, turned out to be ideal as it leaves the oxygen atom as the only possibility to interact, excluding other effects such as contact contributions or multidentate coordination. To facilitate an extrapolation of the chemical shift to infinite dilution (δ_∞), Gutmann measured the ^{31}P signal of Et_3PO for 4 to 6 different concentrations. The AN scale was defined by assigning hexane, the solvent with the most pronounced high-field shift (1.68 ppm), the AN value of 0, whereas the chemical shift of the 1:1 Et_3PO-$SbCl_5$ adduct in 1,1-dichloroethane was taken as 100, in reference to the definition of the DN, and its original measurement procedure.

To compare the electrophilicity of ILs and molecular organic solvents, we conducted the same measurements using the same probe molecule, which turned out to be well soluble in all ILs under investigation. To determine the AN, the chemical shift of the ^{31}P nucleus was measured for 3 to 5 different concentrations of Et_3PO ranging from 0.027 to 0.5 M. On increasing the concentration of Et_3PO, the ^{31}P signal shifted to higher field in all ILs. Similar to Gutmann's observations, we also found that the plot of the concentration dependence of the chemical shift strongly depends on the appropriate solvent. In some cases the correlations were found to be linear, in others exponential, with very small or large changes in the chemical shift. The values of δ_∞ and the assigned ANs for the ILs under investigation are listed in Table 3. These values clearly show that most ILs have an AN between 25 and 33, and thus an electron accepting ability like aliphatic alcohols, viz. AN(*t*-butanol) = 27.1 and AN(*i*-propanol) = 33.5. Since the ILs under investigation all have the same cation (except for some variation in the alkyl chain), we expected the ANs to be similar for all ILs, showing only small differences due to the different strength of the cation-anion interactions. A slight dependence of the AN on the length of the alkyl chain of the cation can be seen for ILs with NTf_2^- anions. The longer the alkyl chain, the smaller the AN, which is consistent with our earlier observations in the case of the DNs and can be explained in terms of an increasing steric hindrance of the cation-anion interactions on increasing the chain length; this steric hindrance resulted from aggregation effects of the long chain imidazolium cations via van der Waals forces, thus impeding the solvent-solute interactions.

Table 3. ^{31}P chemical shifts and ANs for the ILs under investigation.

Solvent	^{31}P-NMR: δ_∞ [ppm]	AN	Solvent	^{31}P-NMR: δ_∞ [ppm]	AN
[emim][$EtOSO_3$]	-9.07	25.0	[emim][dca]	-11.94	31.7
[C_{12}mim][NTf_2]	-9.08	25.0	[emim][SCN]	-12.21	32.4
[C_8mim][NTf_2]	-9.32	25.6	[emim][BF_4]	-12.69	33.5
[emim][NTf_2]	-10.11	27.4	[emim][OTf]	-14.22	37.1
[emim][FAP]	-10.90	29.3	[emim][ClO_4]	-21.46	54.0

[emim][TCM]	-10.94	29.4	[emim][$SnCl_3$]	-30.59	75.4

Kimura *et al.* investigated the solvation properties of ILs by Raman spectroscopy using diphenylcyclopropenone as probe. They observed a drastic solvent dependence of the Raman band assigned to the C=C and C=O stretching modes.[40] Similar to their earlier work, they found a linear correlation between the AN and these frequencies, and were able to assign ANs to the ILs under investigation.[41] Amongst others, they also specified values for [bmim][BF_4] (AN = 26.9) and [bmim][NTf_2] (AN = 25.2), which are in good agreement with our data. However, some ILs seem to be much stronger acceptors than others, despite the same cation. [emim][OTf] (AN = 37.1) has a somewhat higher AN than the ILs mentioned above and accepts electron density as good as ethanol (AN = 37.1). [emim][ClO_4] (AN = 54.0) was found to be an IL with a really high electrophilicity and ranks, compared to molecular solvents, in the same range as acetic acid (AN = 52.9) and water (AN = 54.8). This high acceptor ability can account for the good solubility of some polar substrates and the miscibility with water and methanol, despite the low DN (only 7.6) of this solvent.[42] Other ILs, like [emim][NTf_2], which exhibit both a low DN and AN, are not miscible with water because of too weak interactions and their low polarity. In the case of [emim][ClO_4], it seems that the lack of electron donating ability is compensated by its accepting ability, and can thus be dissolved in water and methanol at room temperature, and in ethanol at temperatures above 60 °C. The IL with the highest AN measured in our study is [emim][$SnCl_3$] (1:1 mixture of [emim]Cl and $SnCl_2$; AN = 75.4) and a better acceptor than water, lying in the same range as 1,1,1,3,3,3-hexafluoro-*iso*-propanol (AN = 66.7) and formic acid (AN = 83.6). The high acceptor property originates from the high Lewis acidity of $SnCl_2$, making this IL a strongly electrophilic medium. This observation is in line with the results obtained by Seddon *et al.*,[43] who also determined ANs by applying Gutmann's procedure. They observed a change in the AN resulting from variations in the composition of the appropriate melts, using $InCl_3$, $GaCl_3$ and $AlCl_3$ as Lewis acids and [omim][Cl] as cation source.

The neutral melts, which all consist of [omim][MCl_4] and are therefore comparable to “normal” ILs, show very high ANs, viz. AN([omim][$GaCl_4$]) = 45.9, AN([omim][$InCl_4$]) = 57.1, and AN([omim][$AlCl_4$]) = 91.8. In contrast to the indium based IL, [emim][$SnCl_3$] has a higher AN despite the less metallic character of tin compared to indium. Seddon *et al.*[43] observed a strong dependence of the measured AN on the molar composition of the melt. We also predict such an effect for varying the molar ratios of $SnCl_2$ and [emim]Cl. Similar ANs were already reported by Osteryoung *et al.*, [35] who also investigated the AN of differently composed chloroaluminate melts, viz. [BuPy][$AlCl_4$] and [emim][$AlCl_4$]. They also found these ILs to be very electrophilic (AN([emim][$AlCl_4$] (1:1)) ≈ 98.3), with an AN close to that of trifluoroacetic acid (AN = 105.3).

Similar to his observations in terms of the DNs, Marcus also found an interrelation between Gutmann’s AN and the Kamlet-Taft-α parameter. For more than 50 organic solvents he was able to show that the ANs depend linearly on the appropriate α-values.[20] Although literature data are rather scarce, we tried to correlate our ANs with the already published α-values for these ILs. Unfortunately, we were not able to observe any reasonable correlation between these values. In order to have a larger set of data, we also applied the hydrogen-bond-donor-values (HBD-value) reported by Lungwitz *et al.*[12] However, a clear correlation between their parameters and our ANs was again not apparent. The fundamental discrepancy between our ANs and the hydrogen-bond-donation ability, either expressed by the Kamlet-Taft-α value or by the HBD value, could originate from the completely different probe molecules and measurement techniques used for the determination of the ANs, α- and HBD-values. Seddon *et al.*[43] already stated, “*it must be remembered that a Lewis acidity scale can never be universal, and will depend on, inter alia, the nature of the probe molecule*”. Therefore, a detailed comparison requires a much larger set of data, most suitably also for ILs with different cations, to obtain a better view of the overall picture and closer insight into the cation dependence of the AN and α, and also the DN and β.

Complex-formation on Li^+

A detailed understanding of fundamental processes in coordination chemistry, such as solvent exchange- or complex-formation reactions, is an important prerequisite for the selection of reaction media or the composition of solvent mixtures.[44] Moreover, such information can help to understand the reasons for and mechanisms of typical ligand exchange and substitution processes in various solvent environments. In many cases the equilibrium between ligands, solvent molecules and metal ions can generate molecular structures and coordination numbers in solution that can differ significantly from those found in solid-state structures. Due to their ionic nature and the resulting conductivity, ILs have often been discussed as electrolytes in the development of lithium accumulators. However, a successful application as electrolyte, strongly depends on the nucleophilicity of the anionic component and its coordination behavior/mode towards Li^+.[45] To learn more about the various effects of ILs and to comprehend resulting problems and opportunities, we investigated the influence of [emim][NTf_2] (DN = 11.2) and [emim][ClO_4] (DN = 7.6) used as solvents, on the complexation of lithium ions by the bidentate/tridentate N-donor ligands 2,2'-bipyridine (bipy) and 2,2':6',2''-terpyridine (terpy). Both ILs exhibit low coordination ability and are therefore expected to behave as innocent solvents. Despite their low coordination ability, [emim][ClO_4] has a hydrophilic nature[42, 46] and represents an interesting alternative to fluorinated ILs, such as [emim][BF_4] (DN = 7.3), which tend to undergo hydrolysis and generate hydrofluoric acid. The application of ILs allowed us to select lithium salts that exhibit the same anionic component as compared to the applied ILs. Therefore, a disturbing influence of other anions could be eliminated. Whereas X-ray diffraction can only reveal information on the solid-state structure, NMR spectroscopy has proven to be the method of choice to investigate the dynamics of such complex-formation processes in solution. To determine the number of coordinated ligand molecules, the chemical shift of the ^7Li NMR signal was studied as a function of the added ligand concentration and analyzed according to the molar ratio method.[47] Although such experiments cannot reveal unequivocal information to which extent a vacant coordination site is indeed occupied by an anion of the employed IL, we can at least determine the number of unoccupied coordination sites left for binding solvent anions.

In general, the successive addition of a chelate, bipy as well as terpy, leads to a significant downfield shift of the ^{7}Li NMR signal, indicating a strong interaction between the chelate molecules and Li^+ (see example given in Figure 6a). At higher chelate concentrations, the chemical shift becomes smaller, appears to reach a maximum and the first coordination sphere of Li^+ is practically saturated. As a result of the overall equilibrium (eq. (2)) between solvated and chelated lithium ions, the measured shifts do not depend linearly on the molar ratio [chelate]:[Li^+] (see Figure 6b), but exhibit a curvature typical for such complex-formation reactions. Depending on the nucleophilicity/donicity of the applied solvent and on the position of the equilibrium, i.e. either near to the reactant or near to the product state, the NMR data differ more or less from the applied linear fits, especially in the region of the observed discontinuities. These differences can be used to determine the stability constant β_2 of the generated lithium complexes and the appropriate standard reaction parameters $\Delta H°$ and $\Delta S°$ from the temperature dependence of β_2, respectively.[16]

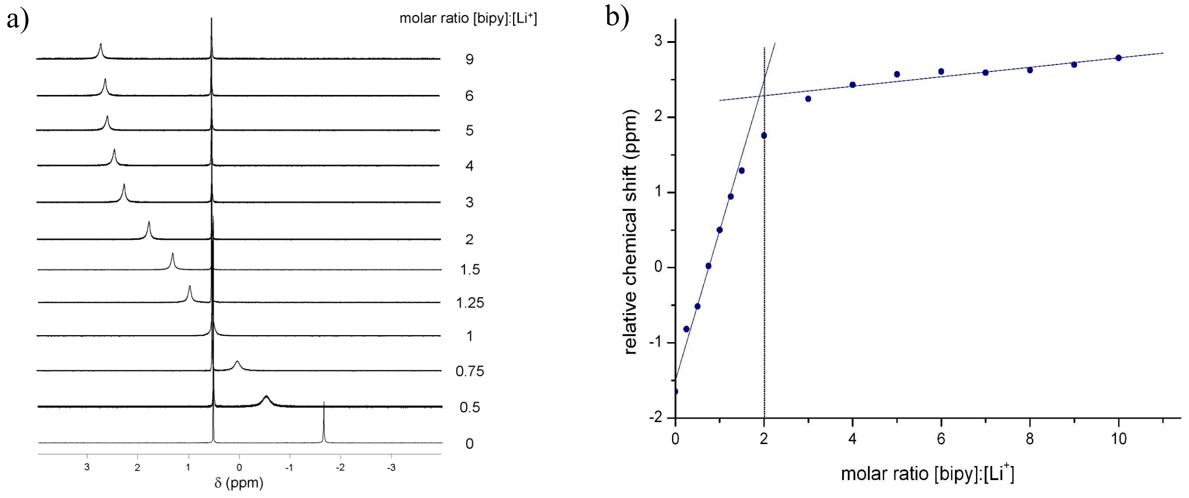


Figure 6. (a) ^{7}Li NMR spectra recorded as a function of the molar ratio [bipy]:[Li^+] in [emim][NTf_2] at 25 °C; (b) Chemical shift of the ^{7}Li signal as a function of the molar ratio [bipy]:[Li^+].

$$\mathrm{Li^+ + X\ terpy \rightleftharpoons [Li(terpy)_x]^+} \qquad (2)$$

In case of the ionic liquid [emim][NTf_2], the NMR experiments resulted in a maximum of two bipy ligands, occupying the first coordination sphere of Li^+. In terms of a coordination number of six, two sites can possibly be occupied by solvent anions. On the basis of results reported by other groups, lithium ions dissolved in [emim][NTf_2] exhibit a solvent shell of two NTf_2^- anions. These anions are coordinated as chelate ligands via the sulfonyl oxygen atoms and generate an overall tetrahedral coordination geometry at the Li^+ center.[48] Thus, the formation of $[Li(bipy)_2]^+$ occurs as a displacement of two NTf_2^- anions by two bipy molecules, and the occupation of further coordination sites by additional, sterical demanding NTf_2^- anion seems to be impossible. Similar to our observations in the case of bipy, the application of the terpy ligand likewise results in the formation of a cationic bis-ligand complex, viz. $[Li(terpy)_2]^+$. As indicated by a much larger overall chemical shift, the tridentate terpy ligand leads to a significantly more stable complex as compared to bipy. Interestingly, at sub-equivalent concentrations of terpy the ^7Li spectra exhibit significant line broadening. A closer look at these spectra revealed a coalescence of various NMR signals. This observation can be attributed to weak interactions between terpy and Li^+, as well as the presence of dynamic equilibria between different lithium ligated species in the IL solution. Because of these significantly broadened signals, the coordination number with respect to the terpy ligand can only be roughly determined at room temperature. To resolve this complication, the measurements were repeated at 50 °C. Although the overall equilibrium between solvated and coordinated lithium ions (eq. (2)) is influenced by the elevated temperature (the chemical shift becomes smaller, indicating an exothermic complex-formation reaction), the signals at sub-equivalent concentrations become significantly sharper due to the accelerated exchange between the different lithium species.

However, the ^{7}Li NMR data clearly reveal that also a maximum of two terpy molecules can occupy the first coordination sphere of Li^+ in [emim][NTf_2] under the selected conditions.

In terms of the ionic liquid [emim][ClO_4], the stepwise addition of bipy resulted in a clear discontinuity of the chemical shift at a molar ratio of [bipy]:[Li^+] = 2:1, and similar to the results obtained for [emim][NTf_2] the formation of the cationic complex $[Li(bipy)_2]^+$ could be observed. Due to the low coordination ability of ClO_4^-, its coordination behavior towards Li^+ in the solute state is still unclear. Although most studies on related systems indicate that Li^+ is four-fold coordinated in solution, several crystal structures exhibit Li^+ ions coordinated in an octahedral mode by six monodentate bound ClO_4^- anions.[49] Therefore, we cannot completely exclude the additional coordination of a maximum of two ClO_4^- anions within the first coordination sphere of $[Li(bipy)_2]^+$. In contrast to bipy, the coordination of two terpy ligands leads to a saturation of the first coordination sphere and the coordination of additional solvent anions can therefore be excluded. Similar to the observations in terms of the IL [emim][NTf_2], the successive complexation of Li^+ in [emim][ClO_4] also resulted in a significant line-broadening of the NMR signals at sub-equivalent concentrations of terpy. Though these broad signals clearly indicate the presence of equilibria between different lithium ligated species, the exchange rate between these species seems to be much higher as compared to [emim][NTf_2], and the formation of intermediate species (i.e. more than one signal) cannot be observed in the spectra. This observation can be ascribed to the smaller size of ClO_4^- as compared to the sterically demanding NTf_2^- anion and the lower donicity of ClO_4^-. These effects lead to a much faster exchange between terpy and ClO_4^- on Li^+, which in turn will lower the stability of the resulting terpy complexes.

As outlined by the data presented in Table 4, the stability of $[Li(ligand)_2]$ complexes in general increases on using terpy instead of bipy. This observation can be explained by the stronger chelate-effect of the terpy ligand, which results from the additional N-donor atom. The largest increase in the complex stability can be observed for the formation of $[Li(terpy)_2]^+$ using the non-ionic solvent nitromethane.[50] Here, β_2 was found to be eleven times higher as compared to the formation of $[Li(bipy)_2]^+$. As a consequence of the low polarity and the low coordination ability of nitromethane, solvent-solute interactions are very weak and the stability constants determined from nitromethane best reflect the influence of the chelate effect. In terms of the employed ILs, β_2 increases significantly more (on going from $[Li(bipy)_2]^+$ to $[Li(terpy)_2]^+$) for [emim][NTf$_2$] than for [emim][ClO$_4$], despite the lower DN of [emim][ClO$_4$]. This effect originates from the smaller size of the perchlorate anion and its lower coordination ability. Both lead to a much faster exchange between terpy and ClO_4^- on Li^+, and thus to a lower stability of $[Li(terpy)_2]^+$ in [emim][ClO$_4$]. A similar observation can be made in terms of $[Li(bipy)_2]^+$. Although for both ILs, the observed stability constants are of the same order of magnitude, β_2 should be definitely higher in the case of [emim][ClO$_4$] with respect to the lower donicity of this solvent.

Table 4. Overall stability constants β_2 for Li(bipy)$_2$ and Li(terpy)$_2$ complexes.[16]

Complex	Solvent	Donor Number	β_2 [M^{-2}]	log β_2	$\Delta H°$ [kJ mol^{-1}]	$\Delta S°$ [J K^{-1} mol^{-1}]
$[Li(bipy)_2]^+$	[emim][NTf$_2$]	11.2	$(29 \pm 3) \times 10^3$	4.46	-30.8 ± 0.1	+18.1 ± 0.3
$[Li(bipy)_2]^+$	[emim][ClO$_4$]	7.6	$(28 \pm 3) \times 10^3$	4.45	-26.4 ± 0.3	-3.5 ± 1
$[Li(bipy)_2]^+$	nitromethane	2.7	$(57 \pm 8) \times 10^3$	4.76	-16.1 ± 0.3	+37 ± 1
$[Li(terpy)_2]^+$	[emim][NTf$_2$]	11.2	$(156 \pm 10) \times 10^3$	5.19	-30.9 ± 0.1	-4.1 ± 0.3
$[Li(terpy)_2]^+$	[emim][ClO$_4$]	7.6	$(48 \pm 11) \times 10^3$	4.68	-6.9 ± 0.1	+66.6 ± 0.4
$[Li(terpy)_2]^+$	nitromethane	2.7	$(635 \pm 204) \times 10^3$	5.80	-24.3 ± 0.4	+30 ± 1

However, the data clearly show that complex stability in general decreases on applying ionic reaction media. Besides a specific influence of the appropriate anions of an IL, such as their Lewis basicity or steric effects, this observation can be attributed to stronger solvent-solute interactions as a consequence of the ionic character and the higher polarity. In agreement with the experimental observation that the overall chemical shift becomes smaller on increasing the temperature, the determination of the standard reaction parameters resulted in negative values for $\Delta H°$, viz. an exothermic complex-formation reaction. Although, a standard reaction enthalpy of $\Delta H° = -6.9 \pm 0.1$ kJ mol^{-1} for the formation of $[Li(terpy)_2]^+$ in [emim][ClO_4] seems to be small compared to the other data, this value can be explained in terms of a high lability as a consequence of the fast exchange between terpy and ClO_4^- on Li^+. The activation enthalpy $\Delta H^{\neq}$ for both, the forward and the backward reaction in eq. (2) seem to be of the same order of magnitude, thus resulting in the small value of $\Delta H°$. On the contrary, this system exhibits an exceptionally high standard reaction entropy of $\Delta S° = +66.6 \pm 0.4$ J K^{-1} mol^{-1}, which suggests that the formation of $[Li(terpy)_2]^+$ in [emim][ClO_4] is an entropy driven process. Notably, the same reaction behaves the other way around on using [emim][NTf_2] as solvent. Here, the standard reaction enthalpy $\Delta H° = -29.9 \pm 0.1$ kJ mol^{-1} was found to be large, whereas the standard reaction entropy $\Delta S° = -4.1 \pm 0.3$ J K^{-1} mol^{-1} was found to be close to zero. Therefore, complex-formation of $[Li(terpy)_2]^+$ becomes an enthalpy driven process on applying [emim][NTf_2] instead of [emim][ClO_4] as IL. In contrast to the non-ionic solvent nitromethane, lithium ions, or more generally speaking metal ions, dissolved in ILs exhibit an anionic solvent shell. Thus, the complex-formation reaction involves a change in the overall charge on going from $[Li(anion)_n]^{-(n-1)}$ to $[Li(terpy)_2]^+$, and leads to a spreading out of the second coordination sphere of Li^+. Although the presented values of $\Delta S°$ are influenced by these bonding and solvation effects, the large difference between $\Delta S°$ determined for the formation of $[Li(terpy)_2]^+$ in [emim][NTf_2] and [emim][ClO_4] can also be explained by the number of solvent anions, substituted during the complex-formation process. In the case of [emim][NTf_2], two solvent anions were found to occupy the first coordination sphere of Li^+.[48] Therefore, the complex-formation reaction of $[Li(terpy)_2]^+$ involves substitution of two solvent anions by two ligand molecules. In total, there is no change in the number of free molecules which would lead to an increase in the disorder of the system. Unfortunately, there is no clear information available on how many ClO_4^- anions are coordinated to Li^+ in [emim][ClO_4]. On considering a number of four to six ClO_4^- anions that occupy the first coordination sphere of Li^+ dissolved in [emim][ClO_4],[49] the formation of $[Li(terpy)_2]^+$ involves the displacement of four to six solvent anions by two ligand molecules. In total, the number of free molecules increases by two to four per lithium ion which will lead to a significant increase in the disorder of the system, and therefore to a notably higher value of $\Delta S°$. In terms of the formation of $[Li(bipy)_2]^+$, the interpretation of the standard reaction entropy is very difficult. Due to the smaller size of the bipy ligand, the first coordination sphere of Li^+ is not completely saturated and a coordination (or at least partial coordination) of one or more solvent anions should be considered.

Based on the NMR studies, crystals were grown with a threefold excess of chelate over Li^+, to determine the coordination behavior of bipy/terpy in the solid state and to investigate the influence of the applied ILs on the crystallization process. In general, it could be observed that both π stacking and charge neutralization mainly control the solid state structure.[16] Although ClO_4^- and NTf_2^- exhibit a low donicity, both anions were found to coordinate to Li^+ in the solid state. Depending on the interplay between ligand size, anion size and their coordination behavior, the formation of either monomeric or dimeric or polymeric lithium species could be observed. As shown in Figure 7a, the coordination of bipy to Li^+ in $[emim][ClO_4]$ leads to the formation of crystals which exhibit a monomeric lithium species. In agreement with the NMR data, each lithium ion is coordinated by two bipy molecules. Due to the small size of ClO_4^-, the polyhedron exhibits enough space for the additional coordination of a η^2-bound ClO_4^- anion and charge neutralization does not disturb the complex-formation of $[Li(bipy)_2]$ in the solid state. On the contrary, the application of $[emim][NTf_2]$ leads to the formation of the discrete dimeric lithium species $[Li(bipy)(NTf_2)]_2$ (see Figure 7b), in which each lithium cation is formally coordinated by only one bipy ligand and one NTf_2^- anion.[16] On considering the size of the NTf_2^- anion, the formation of a monomeric species as observed for $[emim][ClO_4]$ is not possible. Although the NTf_2^- anion offers different possible ways to coordinate to a metal center (N-donor as well as O-donor), a large degree of pπ-dπ bonding within the N-S moiety leads to charge delocalization over the whole NTf_2^- anion and to a preference for coordination via oxygen atoms instead of the nitrogen atom.[51] In combination with a bidentate ligand such as bipy, the electronic and steric properties of the NTf_2^-

anion lead to the formation of the observed dimeric structure. Similar results were already reported by Davidson et al. on the coordination of TMEDA to Li^+ in the presence of NTf_2^-.[52] Thus, the obtained crystal structure does not support the complex-formation process in solution.

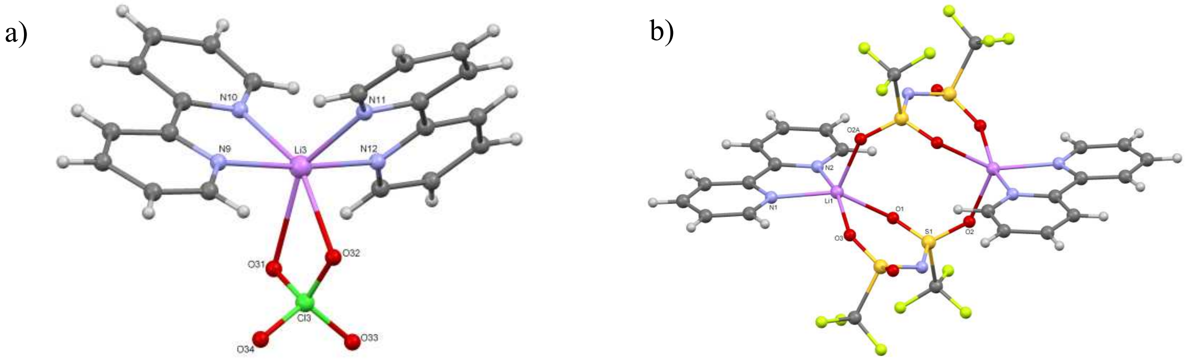


Figure 7. (a) Molecular structure of $Li(bipy)_2ClO_4$; (b) Molecular structure of $[Li(bipy)(NTf_2)]_2$.

Notably, the coordination of terpy to Li^+ in $[emim][ClO_4]$ resulted in similar dimeric species (see Figure 8a) as observed for $[Li(bipy)(NTf_2)]_2$. To generate such a structure, the anionic component must at least be able to act as bridging ligand, otherwise dimerisation would not be possible. In the case of $[Li(terpy)(ClO_4)]_2$**,** the tridentate terpy ligand is much larger as compared to the bidentate bipy ligand. However, the larger size of the terpy ligand is compensated by the smaller size of the ClO_4^- anion. The same observation can be made with respect to the occupied coordination sites. Although the terpy ligand requires an additional coordination site on Li^+, this site is in principle provided by the ClO_4^- anion. Due to its tetrahedral structure, ClO_4^- can only act as bidentate or bridging ligand; compared to the structure presented in Figure 7b, one coordination site on Li^+ is not used and can therefore be occupied by the third N-donor atom of the terpy ligand. On using $[emim][NTf_2]$ as solvent, the coordination of terpy leads to the formation of the polymeric lithium species $[Li(terpy)(NTf_2)]_n$ (see Figure 8b). Interestingly, NTf_2^- behaves in this case as a bis-monodentate ligand bridging the individual Li^+ ions with *trans*-positioned oxygen atoms of different sulfonyl subunits. This observation can be ascribed to the strong chelate effect of the terpy ligand and the sterical demanding nature of the NTf_2^- anion. In contrast to the dimeric species presented in Figure 7b, the required additional coordination site at the lithium center is already occupied by the third N-donor atom of the terpy ligand and, in addition, the NTf_2^- anion is much too voluminous to generate a similar dimeric lithium complex.

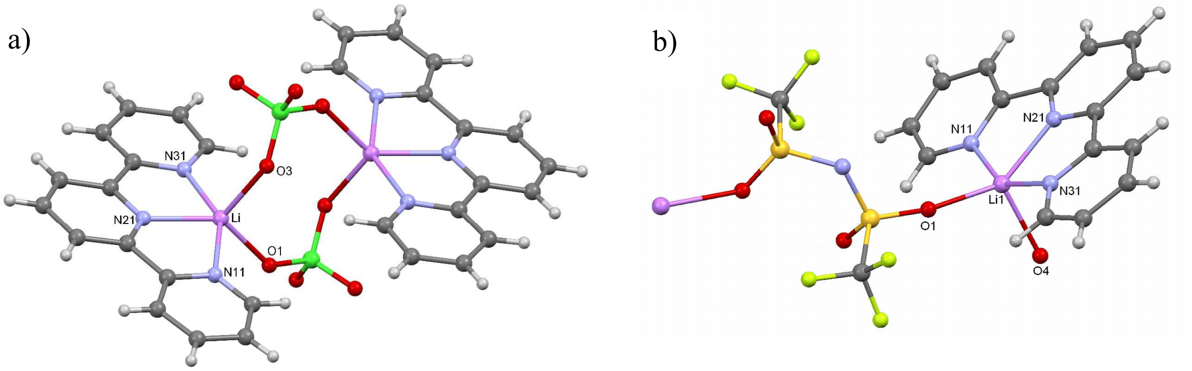


Figure 8. (a) Molecular structure of $[Li(terpy)(ClO_4)]_2$; (b) Molecular structure of $[Li(terpy)(NTf_2)]_n$.

Activation of small molecules

As a result of both, steric factors as well as repulsive and attractive interactions between identical and different charged ions, ILs have a very specific inner structure with empty cavities between their cations and anions. Since these cavities can be occupied by small molecules, ILs exhibit a high solubility for several gases.[53] However, systematic investigations clearly showed that gas solubility in ILs rather depends on the polarity and polarisability of a gas than on the size of the molecule or the size of the cavities.[54] Therefore, polar gases like carbon dioxide (CO_2) tend to be excellently soluble in most ionic liquids, whereas hydrogen tends to be only moderately soluble, despite its much smaller molecular size.[55] In terms of chemical reactions that involve dissolved gases, such as carboxylation, hydroformylation or hydration, ILs can be an interesting alternative to conventional solvents, since they allow the application of a much higher gas-saturation in the solute state. Based on our own interest in the activation of small molecules[56] such as nitric oxide (NO) or CO_2, we started to transfer inorganic and bioinorganic model reactions, extensively studied in conventional solvents before, into ILs to investigate the influence of their unique properties on the reactivity of these systems.[10, 17, 18]

Activation of NO

The interaction of NO with aquated Fe^{II} is one of the easiest examples of NO activation and has become the famous brown-ring-test in introductory freshman laboratory courses. Nevertheless, fundamental details of the underlying reaction, such as the electronic properties of the Fe^{II}–NO adduct have not been well understood in the past and even misinterpreted in undergraduate text books. Detailed mechanistic and spectroscopic studies later showed that the generated nitrosyl complex can be best described as high spin Fe(III) (S = 5/2) antiferromagnetically coupled to NO^- (S = 1) and the previous assumption of the presence of $[Fe^{I}(H_2O)_5(NO^+)]^{2+}$ has proven to be wrong.[57] Since many biological processes take advantage of the unique Red/Ox behavior of Fe-complexes, which is tuned by the appropriate ligand shell,[58] the question arises to which extent the reactivity of the brown-ring-test is influenced by the appropriate solvent shell. In terms of ILs used as solvent, the question is even more fundamental and must be formulated as: How do iron-salts dissolve in ILs? We therefore transferred the classical brown-ring-reaction into ILs, to study the influence of the solvent nucleophilicity on the reactivity of the dissolved Fe^{II}-ions.[18]

Despite its relatively high DN of 37.8, we selected the ionic liquid [emim][dca] (1-ethyl-3-methylimidazolium dicyanimide), since it exhibits a low viscosity and readily dissolves $FeCl_2$. In contrast to acidic aqueous solution in which Fe^{II} is dissolved as $[Fe(H_2O)_6]^{2+}$, three different ligands are possible on applying [emim][dca] viz. Cl^- from the iron salt, H_2O present as contaminant in the hygroscopic IL and dca^-. However, crystal structure analysis clearly showed that Fe^{II} exhibits distorted octahedral coordination geometry, in which the equatorial positions are occupied by four dca^- anions and the axial positions by one dca^- and one Cl^- anion. Notably, the equatorial bound dca¯ ligands are coordinated via the cyano N atoms, whereas the axial dca¯ ligand is coordinated via the amido-N atom.[18]

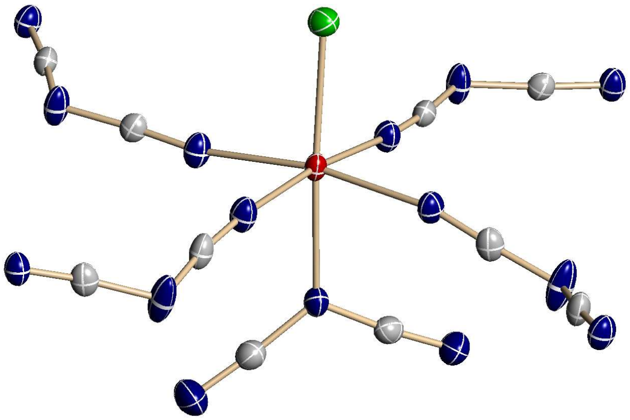


Figure 9. Crystal structure of $[Fe(dca)_5Cl]^{4-}$

In terms of the axial bound dca¯ ligand, the strong σ–donor effect of the cyano groups leads to a labilisation of the *trans*-positioned chloride ligand through the amido-N atom (see Figure 9) which can be seen from an elongation of the Fe-Cl bond. We, therefore, assume that the chloride ligand is substituted by NO to result in $[Fe(dca)_5NO]^{3-}$. This assumption is in agreement with a significantly faster reaction rate as compared to aqueous medium and a mechanistic shift from I_d to D, as discussed in more detail below.

Exposure of a degassed solution of $FeCl_2$ in [emim][dca] to nitric oxide leads to a significant increase in absorbance, resulting in band maxima at 465 and 630 nm. Although these absorbance changes are shifted to longer wavelength, as compared to aqueous solution (viz, 451 and 585 nm), the typical greenish-brown color of the resulting solution indicates the formation of an Fe–NO adduct similar to the brown-ring-test.[57] Bubbling an inert gas through the solution leads to reversed spectral changes indicating a complete reversibility of reaction (3).

$$[\mathrm{Fe(dca)_5Cl}]^{4-} + \mathrm{NO} \underset{k_{off}}{\overset{k_{on}}{\rightleftharpoons}} [\mathrm{Fe(dca)_5NO}]^{3-} + \mathrm{Cl}^{-} \tag{3}$$

With respect to the high velocity of the binding of NO to $[\mathrm{Fe(dca)_5Cl}]^{4-}$, the kinetics was studied on applying laser-flashlight photolysis instead of stopped flow techniques. Irradiation at 532 nm induces a dissociation of the nitrosyl complex and a rapid release of NO (bleaching of the solution) which is followed by a subsequent relaxation of the system back to the original position of the equilibrium. Kinetics was studied under pseudo-first-order conditions with at least a 10-fold excess of $\mathrm{Fe^{II}}$ over NO as a function of temperature and pressure. The excess of $\mathrm{Fe^{II}}$ is necessary to avoid the formation of higher nitrosyl-adducts.[57] The observed rate constants k_{obs} resulted in linear concentration dependences which allowed a determination of k_{on} and k_{off} from slope and intercept, respectively. The appropriate rate constants and activation parameters $\Delta H^{\neq}$, $\Delta S^{\neq}$ and $\Delta V^{\neq}$ are summarized in Table 5 in compared to the data derived from aqueous solution.[57]

Table 5. Rate constants and activation parameters for the reversible binding of NO to $\mathrm{Fe^{II}}$ in [emim][dca] and H_2O.[18, 57]

solvent	**k_{on} [$\mathrm{M^{-1}\,s^{-1}}$] at 298 K**	**$\Delta H^{\neq}_{on}$ [kJ mol^{-1}]**	**$\Delta S^{\neq}_{on}$ [J K^{-1} mol^{-1}]**	**$\Delta V^{\neq}_{on}$ [cm^3 mol^{-1}]**
[emim][dca]	$(2.3 \pm 0.2) \times 10^7$	27 ± 4	-14 ± 12	+14.3 ± 0.5
H_2O	$(1.42 \pm 0.04) \times 10^6$	37.1 ± 0.5	-3 ± 2	+6.1 ± 0.4

solvent	**k_{off} [s^{-1}] at 298 K**	**$\Delta H^{\neq}_{off}$ [kJ mol^{-1}]**	**$\Delta S^{\neq}_{off}$ [J K^{-1} mol^{-1}]**	**$\Delta V^{\neq}_{off}$ [cm^3 mol^{-1}]**
[emim][dca]	$(1.0 \pm 0.6) \times 10^5$	66 ± 3	+73 ± 9	+25 ± 2
H_2O	$(3.2 \pm 0.7) \times 10^3$	48 ± 1	-15 ± 5	+1.3 ± 0.2

Since k_{off} is obtained by extrapolation from plots of k_{obs} vs. $[\mathrm{Fe(dca)_5Cl}]^{4-}$, and the determination of $\Delta S^{\neq}$ involves an extrapolation to 1/T = 0, especially the $\Delta S^{\neq}$ values for the "off" reaction are subjected to large error limits. Therefore, it is difficult to draw mechanistic conclusions based on the reported $\Delta S^{\neq}$ values. In this context, the activation volume $\Delta V^{\neq}$, which describes the effect of hydrostatic pressure on the rate constant, is a more reliable parameter.[59] A volume profile, constructed on the basis of the high pressure kinetic data is shown in Figure 10. The standard reaction volume $\Delta V° = -11 \pm 2$ cm^3 mol^{-1}, indicates that there is an overall decrease in the partial molar volume during the substitution of Cl$^-$ by NO. Both, the forward and the back reaction of (3) occur according to a dissociative mechanism. A comparison of the appropriate rate constants derived from [emim][dca] and aqueous solution shows that both the "on" and the "off" reactions are significantly faster in the applied IL than in aqueous medium (see Table 5). In some previous studies on ligand substitution reactions of Pt^{II} complexes[14] and on the reversible binding of NO to a monohydroxo ligated Fe^{III} porphyrin,[10] we observed significant deceleration effects caused by the polarity and nature of the applied ILs. Here, the substitution of the chloro-ligand is significantly influenced by donicity of the *trans*-positioned dca$^-$ ligand. The strong σ-donor effect of the two cyano groups leads to a labilisation of the chloro ligand through the coordinated amido-nitrogen atom and to a significant acceleration of the substitution reaction. The release of NO during the "off" reaction exhibits a much higher activation enthalpy as compared to the "on" reaction, and is characterized by a more positive activation entropy, suggesting that solvent reorganization plays an important role in this process. A further consequence of the labilizing effect of the *trans*-positioned dca$^-$ ligand is a mechanistic change from an I$_d$ observed for aqueous solution to a limiting D mechanism in the case of the IL. This can be clearly seen from a comparison of the volume profiles established for [emim][dca] and water (see Figure 9). The $\Delta V^{\neq}$ values found for the "on" and "off" reactions in [emim][dca] confirm the dissociative nature of both reactions and are close to the partial molar volumes of the Cl$^-$ (16.45 cm^3 mol^{-1})[60] and of NO (27 cm^3 mol^{-1}).[61] The overall negative reaction volume $\Delta V°$ found for [emim][dca] as compared to the positive reaction volume found for aqueous medium (see Figure 9) can be accounted for in terms of the contribution of the very positive activation volume of the "off" reaction in [emim][dca]. The latter is also related to a strong labilization of NO by the *trans*-positioned dca$^-$ ligand similar to the chloro ligand in the case of $[Fe(dca)_5Cl]^{4-}$.

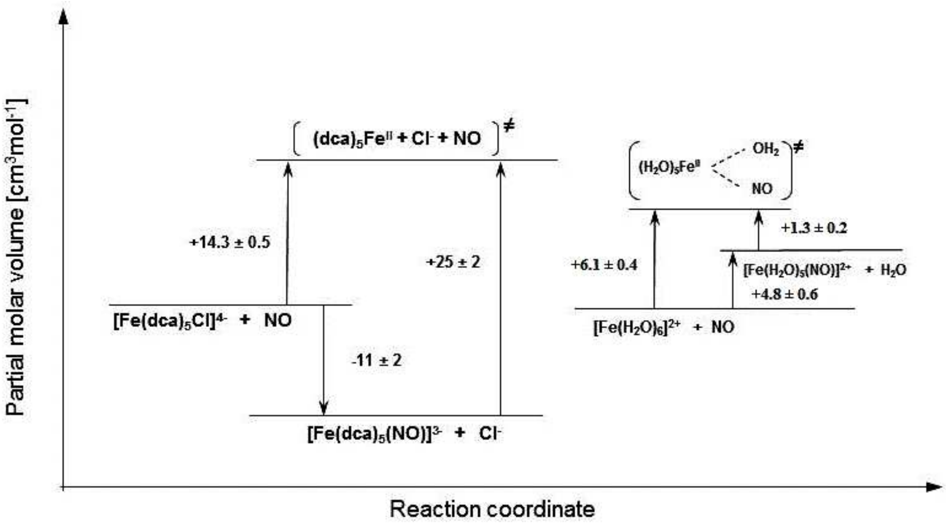


Figure 10. Volume profile for reaction (3) based on the determined volumes of activation (left), and by way of comparison the corresponding volume profile for the same reaction in aqueous medium (right).

The X-Band EPR spectrum of the nitrosylated Fe^{II} solution clearly reveals two EPR active species present in the frozen solution. Besides some low intensity signals in the region between g = 2.16 and g = 2.10, which point to small impurities of Fe^{III}, a very asymmetric broad signal centered at about g = 1.98 is typical for “free” NO molecules in frozen solution. The low g-value and the large width of this S = 1/2 species indicate the presence of substantial spin-orbit interaction, as expected for the NO radical. The low-field part of the spectrum together with the signal at g = 2.04 could be assigned to an iron nitrosyl complex with g values of 4.05, 4.05 and 2.04, which are typical for a spin quartet species (S = 3/2) with dominating zero-field splitting, D >> *hν* (0.3 cm^{-1} at X-band), and vanishing rhombicity, E/D = 0. Similar spectra have been observed for solutions of [Fe(edta)(NO)],[62] and $[Fe(H_2O)_5NO]Cl_2$.[57] Therefore, the sub-spectrum assigned to the nitrosylated iron-dca complex confirms the S = 3/2 ground state of the $\{FeNO\}^7$ core.

The zero-field Mössbauer spectrum of the nitrosylated Fe^{II} solution can be deconvoluted into two overlapping quadrupole doublets with an intensity ratio of about 1:4. The major doublet shows a very large isomer shift, $\delta = 1.25$ mm s^{-1}, and a large quadrupole splitting, $|\Delta E_Q| = 2.28$ mm s^{-1}, similar to the precursor $[Fe(dca)_5Cl]^{4-}$. These parameters were also observed in other Fe^{II}-dca species and are indicative of a high-spin Fe^{II} ion in an octahedral ligand environment.[63] Thus, the contribution (79.3%) can be assigned to non-reacted $[Fe(dca)_5Cl]^{4-}$, which nicely agrees with that expected for a saturated NO solution. The Mössbauer parameters of the second doublet, $\delta = 0.74$ mm s^{-1} and $|\Delta E_Q| = 2.07$ mm s^{-1}, are similar to those found for $[Fe(H_2O)_5NO]^{2+}$ ($\delta = 0.76$ mm s^{-1} and $|\Delta E_Q| = 2.1$ mm s^{-1})[57] and can therefore be assigned to the nitrosyl complex $[Fe^{III}(dca)_5NO^{-}]^{3-}$.

Both, the Mössbauer and EPR parameters of the resulting nitrosyl complex closely resemble those of other well-characterized nitrosyl complexes. We therefore suggest, that the electronic structure of $[Fe^{III}(dca)_5NO^{-}]^{3-}$ can best described by a high-spin Fe^{III} center ($S = 5/2$) antiferromagnetically coupled to NO^{-} (S = 1) yielding the observed spin quartet ground state ($S_t = 3/2$).

Activation of CO_2

Over the past decade, carbon dioxide has extensively been discussed in terms of its role as greenhouse gas and its contribution to the overall global warming process. In this context, current research pursues two main objectives: i) a general decrease in the CO_2 emission[64] and ii) a recovery of CO_2 in terms of a reduction to methanol. One possible way of such a recovery could be the activation by a hydride transfer reaction in which CO_2 is first reduced to formic acid, followed by further reduction.[65] The insertion of CO_2 in $[Ru(bipy)(terpy)H]^{+}$ (Ru–H) to result in the appropriate formate complex $[Ru(bipy)(terpy)OCHO]^{+}$ (see Figure 11), is a very interesting example of CO_2 activation, since the reactivity of the hydride complex Ru–H strongly depends on the acceptor properties of the applied solvent.[66, 67] Depending on the ability of a solvent to accept electron density, the hydridic character of Ru–H decreases or increases, as an effect of a stabilization or destabilization of the hydride ligand. However, the application of an IL used as solvent offers the combination of two very interesting aspects: i) the possibility to work at much higher maximum gas/CO_2 saturation and ii) the possibility to exemplarily investigate the influence of the acceptor properties of an IL. We therefore selected the IL [emim][NTf_2] since it exhibits a low viscosity, a high optical purity and a moderate AN of 27.4. In addition to our studies applying [emim][NTf_2], we reinvestigated some literature data concerning conventional solvents such as water or short chain alcohols.

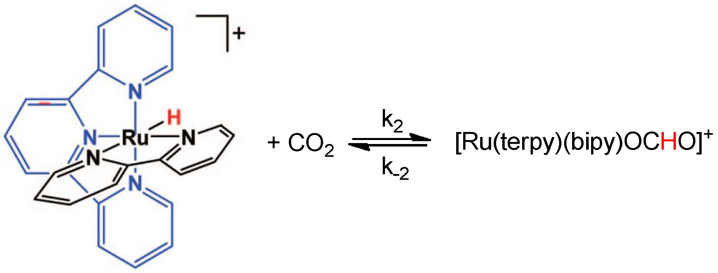


Figure 11. Reaction of Ru–H with CO_2 leading to the formation of a formate complex.

In general, the insertion of CO_2 in Ru–H was studied under pseudo-first-order conditions as a function of the CO_2 concentration, temperature and pressure, to determine the rate constants and activation parameters $\Delta H^{\neq}$, $\Delta S^{\neq}$ and $\Delta V^{\neq}$, respectively. Although, the application of ILs could be problematic in terms of their higher viscosity[15] as compared to conventional solvents, in the case of [emim][NTf_2] the stopped-flow kinetics were not affected by the viscosity and showed single-exponential behavior. For all solvents under investigation, the observed rate constants k_{obs} resulted in linear concentration dependences, with no significant intercept. Therefore, the insertion of CO_2 is an irreversible process and the presence of an equilibrium between $[Ru(bipy)(terpy)H]^+$ and $[Ru(bipy)(terpy)OCHO]^+$ could not be observed. The corresponding second-order rate constants and activation parameters are summarized in Table 6.

Table 6. Rate constants (at 25 °C) and activation parameters for the reaction between CO_2 and Ru–H.17

Solvent	k_2 [M^{-1} s^{-1}]	k_2 (literature)	$\Delta H^{\neq}$ [kJ mol^{-1}]	$\Delta S^{\neq}$ [J K^{-1} mol^{-1}]	$\Delta V^{\neq}$ [cm^3 mol^{-1}]	AN
[emim][NTf_2]	0.447 ± 0.004	–	33.8 ± 0.5	-138 ± 2	-14.4 ± 1.8	27.4
EtOH	0.05 ± 0.01	0.464 *	40.7 ± 0.5	-114 ± 2	-35.9 ± 1	37.1
MeOH	4.08 ± 0.01	4.69 *	34.6 ± 1.0	- 116 ± 3	-39.3 ± 0.8	41.3
water	1320 ± 30	850 *	59.1 ± 0.6	+14 ± 2	-5.9 ± 0.6	55

* These values were taken from ref. 66

Due to the autoprotolysis of water and the formation of hydrogen carbonate HCO_3^-, the measurements performed in aqueous solution turned out to be very complex and will therefore be discussed in more detail. On dissolving Ru–H in pure water, protons provided by the autoprotolysis lead to the generation of molecular hydrogen and therefore to a decomposition of the Ru–H complex.[68] Although, this process is slow because of the low proton concentration at pH 7, the time slot of the complex stability is not sufficient to perform temperature or pressure dependence studies. On increasing the pH to 9.5, the complex turned out to be stable for several hours, but the concentration of reactive CO_2 significantly decreased as a consequence of the formation of HCO_3^-. To accommodate this complication, a pH jump approach appeared to be reasonable, since the formation of HCO_3^- is significantly slower than the insertion of CO_2. Therefore, the CO_2 solution was buffered at pH 5.8 before mixing with Ru–H in the stopped-flow apparatus. Our first idea, to use CO_2 itself to create a buffer with added sodium bicarbonate seemed to be tricky, since the equilibrium between CO_2 and HCO_3^- (reaction (4)) is very sensitive towards temperature and pressure changes.[69] On going from ambient pressure up to 130 MPa, the pH value decreases from pH 5.8 to pH 5.2. However, due to the high excess of the added CO_2, the effect of the pH change turned out to be very small and therefore negligible.

$$CO_2 + 2\,H_2O \rightleftharpoons H_2CO_3 + H_2O \rightleftharpoons HCO_3^- + H_3O^+ \qquad (4)$$

In contrast to the CO_2/HCO_3^- system, the buffer-equilibrium of MES (2-(*N*-morpholino)-ethansulfonic-acid) is almost independent of pressure.[70] Although the proton concentration was kept constant on using MES instead of bicarbonate, the pressure-induced shift in the CO_2/HCO_3^- equilibrium significantly affected the concentration of reactive CO_2 which decreased from 1.75 mM at ambient pressure to 1.07 mM at 130 MPa. Due to the fact that both buffer equilibria nearly exhibit the same pK_a change as a function of temperature, MES as well as bicarbonate resulted in the same values for $\Delta H^{\neq}$ and $\Delta S^{\neq}$ and a correction of the appropriate CO_2 concentrations was not necessary.[70, 71]

The activation volume $\Delta V^{\neq}$ consists of two components. One part, the intrinsic volume change, is generated by bond formation and bond cleavage processes, whereas the other part is caused by solvational changes such as a spreading out or contraction of the solvent shell as an effect of changes in the overall charge.[72] In contrast to ligand substitution processes, the insertion of CO_2 does not result in a leaving ligand and the intrinsic volume change has to be largely negative. Moreover, $\Delta V^{\neq}$ should mainly reflect the associative nature of the insertion process, since there is no change in charge on going through the transition state and the effects of solvation are therefore expected to be small. As summarized in Table 6, for all solvents under investigation, the pressure dependence resulted in negative values of $\Delta V^{\neq}$, but only in the case of methanol and ethanol the observed activation volume is in the order of the partial molar volume of CO_2. In terms of water and [emim][NTf_2] as solvent, the interpretation of $\Delta V^{\neq}$ seems to be difficult, since the activation volume is significantly more positive. Unfortunately, reliable data on the partial molar volume of CO_2 in ILs are still scarce. A molecular dynamics study by Huang et al. showed that the partial molar volume of supercritical CO_2 dissolved in [bmim][PF_6] and other ILs is very low as compared to that of bulk supercritical CO_2.[73] They account for this behavior in terms of the cavities between the cations and anions of an IL, which can excellently be occupied by polar molecules such as CO_2. This may also explain the smaller activation volume in the case of [emim][NTf_2], but the effect of the partial molar volume of gas dissolved in ILs is still not completely understood and the interpretation of the activation volume is therefore uncertain. In the case of water, the activation volume becomes even more positive as compared to [emim][NTf$_2$], indicating that the insertion of CO$_2$ must be controlled by other factors than simple bond formation processes. Since hydrogen-bonded water molecules play an important role in the insertion process, the observed activation volume can be explained in terms of a rearrangement of the solvent shell. Although the intrinsic volume change is expected to be the same as for the other solvents under investigation, the formation and cleavage of hydrogen bonds could affect local charge-formation/neutralization processes and so contribute towards the observed activation volume in terms of changes in the solvent shell. Similar effects also account for the significantly more positive activation entropy value.

As outlined above, the hydridic character of Ru–H strongly depends on the ability of the surrounding molecules to accept electron density and Konno et al. noticed a dependence of ln k_2 on the AN of the applied solvent (see Figure 12).[66] Although, the AN of ethanol is larger than [emim][NTf$_2$], the corresponding k_2 values are of the same order of magnitude. Nevertheless, the AN of the applied IL and the resulting rate constant fit very well. In terms of the high reaction rate observed on applying water as solvent, several studies concerning the hydrogenation of carbon dioxide revealed that water, either as ligand or as solvent, has a decisive impact on the reactivity by generating hydrogen bonds with the reactants.[74, 75] In our case, the presence of a water ligand can be excluded, due to a lack of vacant coordination sites on the Ru–H complex. However, theoretical studies by Creutz *et al*. on the reaction mechanism clearly showed that water molecules have a crucial influence on the transition state of the reaction by forming hydrogen bonds with the oxygen atoms of the inserting carbon dioxide molecule.[68] Notably, the AN of water seems to account for this influence quite accurately.

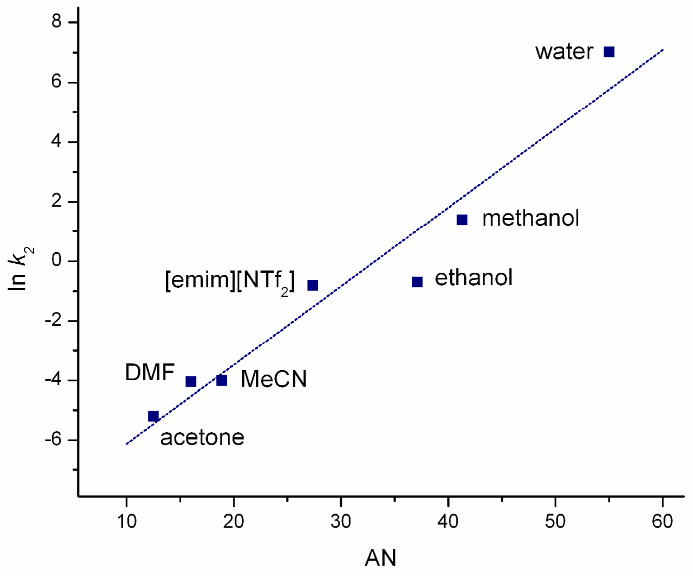


Figure 12. Relationship between ln k_2 and the acceptor number (AN) for various solvents; the appropriate data for acetone, DMF and MeCN were taken from Kono et. al. (ref. 66).

Conclusions

This perspective outlines the important role of the donor and acceptor properties of ILs used as solvent. In terms of typical inorganic reactions, the reactivity and the mechanistic behavior of dissolved metal complexes can seriously be influenced by the donicity of ILs, which mainly results from the nature of the anionic component. Besides electrostatic interactions which can lead to a shift of charge density, anions with a high nucleophilicity can occupy vacant coordination sites or even displace weaker bound ligands. In most cases, such donor interactions were reported to cause a loss of reactivity, but some reactions also seem to benefit as shown by the “brown-ring-reaction” performed in [emim][dca].

Since typical inorganic reactions involve charged metal complexes, many effects observed on applying ILs, can be ascribed to the donicity of the ILs. However, some observations can only be explained in terms of the acceptor properties of the applied solvents. Especially, anionic metal complexes or complexes which exhibit regions of high electron density can be influenced by interactions with the cationic component of ILs. These interactions are comparatively weak, since most ILs consist of organic cations, with a high degree of steric hindrance and charge delocalization. Therefore, the insertion of CO_2 in $[Ru(bipy)(terpy)H]^+$ was found to be the slowest on applying the IL [emim][NTf_2] as solvent despite the positive charge of the [emim] cation.

Although the Donor and Acceptor concept cannot describe all aspects of solvent properties, our work nicely shows that the donor and acceptor numbers can be used as a proper indication to predict the coordination of ILs used as solvents. However, due to the large variety of different ILs already available, this article could only focus on a very small selection of ILs and their possible interactions. Therefore, our understanding of how metal salts dissolve in ILs or how ILs interact with substrates, still remains rather limited. Although a good understanding of the role of conventional solvents has been developed during the past decades, much more remains to be done to reach a similar understanding in the case of ILs.

Acknowledgements

The authors gratefully acknowledge continued financial support from the Deutsche Forschungsgemeinschaft.

---

(1) P. Knochel, (ed) *Modern Solvents in organic Synthesis*, Springer-Verlag, Berlin, 1999.

(2) D. J. Adams, P. J. Dyson and S. J. Tavener, in *Chemistry in Alternative Reaction Media*, Wiley: Chichester, 2004.

(3) T. Mandai, K. Yoshida, K. Ueno, K. Dokko and M. Watanabe, *Phys. Chem. Chem. Phys.*, 2014, 16, 8761-8772.

(4) P. Wasserscheid and T. Welton, (eds) *Ionic Liquids in Synthesis*, Whiley-VCH, Weinheim 2008.

(5) http://www.iolitec.de/en/Ionic-Liquids/custom-synthesis.html, http://www.intermediates.basf.com/chemicals/ionische-fluessigkeiten/faq

(6) a) S. Doherty, P. Goodrich, C. Hardacre, V. Parvulescu and C. Paun, *Adv. Synth. Catal.*, 2008, **350**, 295-302; b) A. Paczal and A. Kotschy, *Monatshefte für Chemie*, 2007, **138**, 1115-1123; c) R. Gienoth, *Top. Curr. Chem.*, 2007, **276**, 1-23; d) M. Maase, *Multiphase Homogeneous Cataysis.* 2005, **2**, 560-566; e) R. Sheldon, *Chem. Comm.*, 2001, **23**, 2399-2407.

(7) a) A. Shirai and Y. Ikeda, *Inorg. Chem.,* 2011, **50**, 1619-1627; b) J. McNulty, S. Cheekoori, T. Bender and J. Coggan, *Eur. J. Org. Chem.,* 2007, **9**, 1423-1428; c) A. Vidis, G. Laurenczy, E. Küsters, G. Sedelmeier and P. Dyson, *Phys. Org. Chem*., 2007, **20**, 109–114; d) C. Daguenet and P. Dyson, *Organometallics*, 2006, **25**, 5811-5816.

(8) a) M. J. Earle, U. Hakala, B. J. McAuley, M. Nieuwnhuyzen, A. Ramani and K. R. Seddon, *Chem Comm.*. 2004, **12**, 1368-1369; b) L. Magna, Y. Chauvin, G. P. Niccolai, J. M. Basset, *Organometallics*, 2003, **22**, 4418-4425.

(9) a) J. P. Hallett and T. Welton, *Chem. Rev.*, 2011, **11**, 3508-3576; b) P. Illner, A. Zahl, R. Puchta, N. van Eikema Hommes, P. Wasserscheid and R. van Eldik, *J. Organomet. Chem.*, 2005, **690**, 3567–3576; c) Ch. F.Weber, R. Puchta, N. van Eikema Hommes, P. Wasserscheid and R. van Eldik, *Angew. Chem.*, 2005, **117**, 6187–6192.

(10) M. Schmeisser and R. van Eldik, *Inorg. Chem.*, 2009, **48**, 7466-7475.

(11) a) C. Chiappe, C. S. Pomelli and S. Rajamani*, J. Phys. Chem. B,* 2011, **115**, 9653-9661; b) M. A. Ab Rani, A. Brant, L. Crowhurst, A. Dolan, M. Lui, H. Niedermeyer, J. M. Perez-Arlandis, M. Schrems, T. Welton and R. Wilding, *Phys. Chem. Chem. Phys.* 2011, **13**, 16831-16840; c) T. V. Doherty, M. Mora-Pale, S. E. Foley, R. J. Lienhardt and J. S. Dordick, *Green Chem.*, 2010, **12**, 1967-1975; d) C. Chiappe, and D. Pieraccini, *J. Phys. Org. Chem.*, 2005, **18**, 275-297; e) N. Llewellyn and T. Welton, *J. Org. Chem.*, 2004, **69**, 5986-5992; f) L Crowhurst, P. R. Mawdsley, J. M. Perez-Arlandis, P. A. Salter and T. Welton, *Phys. Chem. Chem. Phys.*, 2003, **5**, 2790-2794.

(12) a) M. Holzweber, R. Lungwitz, D. Doerfler, S. Spange, M. Koel, H. Hutter and W. Linert, *Chem. Eur. J.*, 2013, **19**, 288-293; b) R. Lungwitz, V. Strehmel and S. Spange, *New J. Chem.*, 2010, **34**, 1135-1140; R c) R. Lungwitz and S. Spange, *New J. Chem.*, 2008, **32**, 392-394; d) Lungwitz, M. Friedrich, W. Linert and S. Spange, *New J. Chem.*, 2008, **32**, 1493-1499.

(13) C. D. Hubbard, P. Illner and R. van Eldik, *Chem. Soc. Rev.*, 2011, **40**, 272-290.

(14) a) P. Illner, S. Begel, S. Kern, R. Puchta and R. van Eldik, *Inorg. Chem.*, 2009, **48**, 588-597; b) S. Begel, P. Illner, S. Kern, R. Puchta and R. van Eldik, *Inorg. Chem.*, 2008, **47**, 7121-7132; c) P. Illner, S. Kern, S. Begel and R. van Eldik, *Chem. Comm.*, 2007, **45**, 4803-4805.

(15) S. Kern, P. Illner, S. Begel and R. van Eldik, *Eur. J. Inorg. Chem.*, 2010, **29**, 4658-4666.

(16) a) M. Schmeisser, F. W. Heinemann, P. Illner, R. Puchta, A. Zahl and R. van Eldik, *Inorg. Chem.*, 2011, **50**, 6685-6695; b) K. Pokorny, M. Schmeisser, F. Hampel, A. Zahl, R. Puchta and R. van Eldik, *Inorg. Chem.*, 2013, **52**, 13167-13178.

(17) S. Kern and R. van Eldik, Inorg. Chem., 2011, **51**, 7340-7345.

(18) S. Begel, F. W. Heinemann, G. Stopa, G. Stochel and R. van Eldik, *Inorg. Chem.*, 2011, **50**, 3946-3958.

(19) a) M. Schmeisser, P. Illner, R. Puchta, A. Zahl and R. van Eldik, *Chem. Eur. J.*, 2012, **18**, 10969-10982; b) M. Schmeisser, P. Illner, R. Puchta, A. Zahl and R. van Eldik, *Chem. Eur. J.*, 2013, **19**, 16835-16836.

(20) a) C. Reichardt, *Chem. Rev.*, 1994, **94**, 2319-2358; b) M. J. Kamlet and R. W. Taft, *J. Am. Chem. Soc.*, 1976, **98**, 377-383; c) Y. Marcus, *Chem. Soc. Rev.*, 1993, **22**, 409-416; b) Y. Marcus, *J. Solution Chem.*, 1984, **13**, 599-624.

(21) C. Reichardt, *Green Chem.*, 2005, **7**, 339-351.

(22) A. F. M. Claudio, L. Swift, J. P. Hallett, T. Welton, J. A. P. Coutinho and M. G. Freire, *Phys. Chem. Chem. Phys.*, 2014, **16**, 6593-6601.

(23) a) V. Gutmann, (Ed) *The Donor– Acceptor Approach to Molecular Interaction*, Plenum, New York, 1978; b) V. Gutmann, *Electrochim. Acta*, 1976, **21**, 661-670 c) U. Mayer, V. Gutmann and W. Gerger, *Monatsh. Chem.*, 1975, **106**, 235-1257.

(24) R. H. Erlich and A. I. Popov, *J. Am. Chem. Soc.*, 1971, **93**, 5620-5623.

(25) J. S. Wilkes and M. J. Zaworotko, *J. Chem. Soc. Chem. Comm.*, 1992, 965-967.

(26) P. Bonhôte, A.-P. Dias, N. Papageorgiou, K. Kalyanasundaram and M. Grätzel, *Inorg. Chem.* 1996, **35**, 1168-1178.

(27) S. Antoniotti, V. Dalla and E. Dunach, *Angew. Chem.*, 2010, **122**, 8032-8060; *Angew. Chem. Int. Ed.*, 2010, **49**, 7860-7888.

(28) a) W. Linert, A. Camard, M. Armand and C. Michot, *Coord. Chem. Rev.*, 2002, **226**, 137-141; b) W. Linert, R. F. Jameson and A. Taha, *J. Chem. Soc. Dalton Trans.*, 1993, 3181-3186.

(29) K. Ueno, T. Fukai, T. Nagatsuka, T. Yasuda and M. Watanabe, *Langmuir*, 2014, **30**, 3228-3235.

(30) a) S. Pitula and A.-V. Mudring, *Phys. Chem. Chem. Phys.*, 2010, **12**, 7056-7063; b) J. Bartosik and A.-V. Mudring, *Phys. Chem. Chem. Phys.*, 2010, **12**, 4005-4011.

(31) a) J. N. A. Canongia Lopes and A. A. H. J. Padua, *J. Phys. Chem. B*, 2006, **110**, 3330-3335; b) Y. Wang and G. A. Voth, *J. Am. Chem. Soc.*, 2005, **127**, 12192-12193.

(32) a) A. Triolo, O. Russina, H.-J. Bleif and E. D. Cola*, J. Phys. Chem.*, B 2007, **111**, 4641-4644.

(33) a) J. Jiang, Y. Wang, C. Liu, Q. Xiao and Z. Jin, *J. Mol. Catal. A*, 2001, **171**, 85-89; b) A. Behr, G. Henze and R. Schomaecker, *Adv. Synth. Catal.*, 2006, **348**, 1485-1495; c) N. Pinault and D. W. Bruce, *Coord. Chem. Rev.*, 2003, **241**, 1-25.

(34) a) J. M. Kamlet, J.-L. M. Abboud, M. H. Abraham and R. W. Taft, *J. Org. Chem.*, 1983, **48**, 2877-2887; b) M. Kamlet and R. W. Taft, *J. Chem. Soc. Perkin Trans. 2* 1985, 1583-1589.

(35) T. A. Zawodzinski and R. A. Osteryoung, *Inorg. Chem.*, 1989, **28**, 1710-1715.

(36) J. Estager, J. D. Holbrey and M. Swadźba-Kwaśny, *Chem. Soc. Rev***.,** 2014, **43**, 847-886.

(37) a) A. Babai and A.-V. Mudring, *Z. Anorg. Allg. Chem.*, 2008, **634**, 938-940 b) N. Mézailles, L. Ricard and F. Gagosz, *Org. Lett.*, 2005, **7**, 4133-4136; c) D. B. Williams, M. E. Stoll, B. L. Scott, D. A. Costa and W. J. Oldham, *Chem. Comm.*, 2005, 1438-1440; d) A. Babai and A.-V. Mudring, *Inorg. Chem.*, 2006, **45**, 3249-3255; e) K. Fujii, Y. Soejima, Y. Kyoshoin, S. Fukuda, R. Kanzaki, Y. Umebayashi, T. Yamaguchi, S. Ishiguro, and T. Takamuku, *J. Phys. Chem. B*, 2008, **112**, 4329-4336.

(38) A. Haas, Ch. Klare, P. Betz, J. Bruckmann, C. Krueger, Y.-H. Tsay and F. Aubke, *Inorg. Chem.*, 1996, **35**, 1918-1925.

(39) a) R. Alexander, A. J. Parker, J. H. Sharp and W. E. Waghorne, *J. Am. Chem. Soc.*, 1972, **94**, 1148-1158; b) B. G. Cox, G. R. Hedwig, A. J. Parker and D. W. Watts, *Austral. J. Chem.*, 1974, **27**, 477-501; c) V. Gutmann, G.

Gritzner, K. Danksagmueller, *Inorg. Chim. Acta*, 1976, **17**, 81-86.

(40) T. Fujisawa, M. Fukuda, M. Terazima and Y. Kimura, *J. Phys. Chem. A*, 2006, **110**, 6164-6172.

(41) Y. Kimura, M. Fukuda, T. Fujisawa and M. Terazima, *Chem. Lett.*, 2005, **34**, 338-339.

(42) M. Schmeisser, P. Keil, J. Stierstorfer, A. König, T. M. Klapötke and R. van Eldik, *Eur. J. Inorg. Chem.*, 2011, 4862-4868.

(43) J. Estager, A. A. Oliferenko, K. R. Seddon and M. Swadźba-Kwaśny, *Dalton Trans.*, 2010, **39**, 11375-11382.

(44) L. Helm and A. E. Merbach, *Chem. Rev.*, 2005**, 105**, 1923-1959.

(45) a) K. Ueno , J.-W. Park , A. Yamazaki , T. Mandai , N. Tachikawa , K. Dokko and M. Watanabe, *J. Phys. Chem. C*, 2013, **117**, 20509-20516; b) J.-W. Park, K. Ueno, N. Tachikawa, K. Dokko, and M. Watanabe, *J. Phys. Chem. C* 2013, 117, 20531−20541; c) Q. Zhou, W. A. Henderson, G. B. Appetecchi and S. Passserini, *J. Phys. Chem. C*, 2010, **114**, 6201-6204; d) Q. Zhou, K. Fitzgerald, P. D. Boyle and W. A. Henderson, *Chem. Mater.*, 2010, **22**, 1203-1208 e) T. Frömling, M. Kunze, M. Schönhoff, J. Sundermeyer and B. Roling, *J. Phys. Chem. B*, 2008, **112,** 12985-12990.

(46) T. M. Klapötke, J. Stierstorfer, H. D. B. Jenkins, R. van Eldik and M. Schmeisser, *Z. Anorg. Allg. Chem.*, 2011, **637**, 1308-1313.

(47) a) E. Schmidt, A. Hourdakis and A. I. Popov, *Inorg. Chim. Acta*, 1981, **52**, 91-95. b) K. Momoki, J. Sekino, H. Sato and N. Yamaguchi, Anal. Chem., 1969, 41, 1286-1298.

(48) a) I. Nicotera, C. Oliviera, W. A. Henderson, G. B. Appetecchi and S. Passerini, *J. Phys.Chem. B*, 2005, **109**, 22814-22819; b) J. Lassègues, T. Grondin and D. Talaga, *Phys. Chem. Chem. Phys.*, 2006, **8**, 5629-5632; c) Y. Umebayashi, T. Mitsugi, S. Fukuda, T. Fujimori, K. Fujii, R. Kanzaki, M. Takeuchi and S. Ishiguro, *J. Phys. Chem. B*, 2007, **111**, 13028-13032.

(49) a) M. S. Wickleder, *Z. Anorg. Allg. Chem.*, 2003, **629**, 1466-1468; b) W. A. Henderson and N. R. Brooks*, Inorg. Chem.*, 2003, **42**, 4522-4524.

(50) These values were calculated from the data presented in: M. Schmeisser, A. Zahl, A. Scheurer, R. Puchta and R. van Eldik, *Z. Naturforsch.*, 2010, **65b***,* 405-413.

(51) A. Haas, Ch. Klare, P. Betz, J. Bruckmann, C. Krueger, Y.-H. Tsay and F. Aubke, *Inorg. Chem.*, 1996, **35**, 1918-1925.

(52) M. G. Davidson, P. R. Raithby, A. L. Johnson and P. D. Bolton, *Eur. J. Inorg. Chem.*, 2003, **18**, 3445-3452.

(53) F. Bresme and J. Alejandre, *J. Chem. Phys*., 2003, **118**, 4134-4139

(54) a) J. L. Anthony, J. L. Anderson, E. J. Maginn and J. F. Brennecke, *J. Phys. Chem. B*, 2005, **109**, 6366-6374. b) P. J. Carvalho, V. H. Alvarez, I. M. Marrucho, M. Aznar and J. A. P.Coutinho, *J. Supercrit. Fluids*, 2009, **50**, 105-111.

(55) a) M. J. Muldoon, S. N. V. K. Aki, J. L. Anderson, J. K. Dixon and J. F. Brennecke, *J. Phys. Chem. B*, 2007, **111**, 9001-9009. (b) J. L. Anderson, J. K. Dixon, E. J. Maginn and J. F. Brennecke, *J. Phys. Chem. B*, 2006, **110**, 15059-15062. (c) J. L. Anderson, J. K. Dixon and J. F Brennecke, *Acc. Chem. Res*, 2007, **40**, 1208-1216.

(56) a) A. Franke and R. van Eldik, *Eur. J. Inorg, Chem.*, 2013, **4**, 460-480, b) D. A. Pixton, C. A. Petersen, A.

Franke, R. van Eldik, E. M. Garton and C. R. Andrew, *J. Am Chem. Soc.*, 2009, **131**, 4846-4853; c) A. Franke, F. Roncaroli and R. van Eldik, *Eur. J. Inorg, Chem.*, 2007, 6, 773-798; d) F. Franke, N. Hessenauer-Ilicheva, D. Meyer, G. Stochel, W.-D. Woggon and R. van Eldik, *J. Am Chem. Soc.*, 2006, 128, 13611-13624; M. Wolak and R. van Eldik, *J. Am Chem. Soc.*, 2005, **127**, 13312-13315.

(57) A. Wanat, Th. Schneppensieper, G. Stochel, R. van Eldik, E. Bill and K. Wieghardt, *Inorg. Chem.*, 2002, **41**, 4-10.

(58) a) A. Franke, E. Hartmann, I. Schlichting and R. van Eldik, *J. Biol. Inorg. Chem.*, 2012, **17**, 447-463; a) A. Franke, M. Wolak and R. van Eldik, *Chemistry*, 2009, **15**, 10182-10198.

(59) a) R. van Eldik, *Coord. Chem. Rev.*, 2007, **251**, 1649-1662; b) L. M. Harwood, *Angew. Chem. Int. Ed.*, 2003, **42**, 4852; c) R. van Eldik and C. D. Hubbard, *Chemie in unserer Zeit*, 2000, **34**, 306-317; d) R. van Eldik, C. D. Hubbard, *Chemie in unserer Zeit*, 2000, **34**, 240-252.

(60) The partial molar volume was obtained from density measurements reported in: F. J. Millero, in R. A. Horne, (Ed.), *Water and Aqueous Solutions: Structure, Thermodynamics and Transport Processes*, Wiley-Interscince, London, 1972, Chapter 13.

(61) A. V. Plyasunov, J. P. O'Connell and R. H. Wood, *Geochim. Cosmochim. Acta,* 2000, **64**, 495-512.

(62) a) C. A. Brown, M. A. Pavlosky, T. E. Westre, Y. Zhang, B. Hedman, K. O. Hodgson and E. I. Solomon, *J. Am. Chem. Soc*., 1995, **117**, 715-732; b) T. E. Westre, A. Di Cicco, A. Filipponi, C. R. Natoli, B. Hedman, E. I. Solomon and K. O. Hodgson, J. *Am. Chem. Soc*., 1994, **116**, 6757-6768.

(63) P. M. van der Werff, S. R. Batten, P. Jensen, B. Moubaraki, K. S. Murray and J. D. Cashion, *Crystal Growth und Design*, 2004, **4**, 503-508.

(64) M. Roeper, in *Chemie über den Wolken*, Whiley-VCH, Weinheim 2011, 43-45.

(65) E. E. Benson, C. P. Kubiak, A. J. Sathrum and J. M. Smieja, *Chem. Soc. Rev.*, 2009, **38**, 89-99.

(66) H. Konno, A. Kobayashi, H. Sakamoto, F. Fagalde, N. E. Katz, H. Saitoh and O. Ishitani, *Inorg. Chim. Acta*, 2000, **299**, 155-163.

(67) a) C. Creutz and M. H. Chou, *J. Am. Chem. Soc*., 2007, **129**, 10108-10109; b) C. Creutz and M. H. Chou, *J. Am. Chem. Soc*., 2009, **131**, 2794-2795.

(68) C. Creutz, M. H. Chou, H. Hou and J. T. Muckermann, *Inorg. Chem.*, 2010, **49**, 9809-9822.

(69) a) D. A. Palmer and R. van Eldik, *Chem. Rev.*, 1983, **83**, 651-731; b) R. van Eldik and D. Palmer*, J. Solution Chem.*, 1982, 11, 339-346.

(70) Y. Kitamura and T. Itoh, *J. Solution Chem.*, 1987, **16**, 715-725.

(71) R. N. Robert, N. Kishore and R. M. Lennen, J. Phys. Chem. Ref. Data, 2002, **31**, 231-370.

(72) C. D. Hubbard and R. van Eldik, *Inorg. Chim. Acta*, 2010, **363**, 2357-2374.

(73) X. Huang, C. J. Margulis, Y. Li and B. J. Berne, *J. Am. Chem. Soc.*, 2005, **127**, 17842-17851.

(74) C. Yin, Z. Xu, S.-Y. Yang, S. M. Ng, K. Y. Wong, Z. Lin and C. P. Lau, Organometallics, 2001, **20**, 1216-1222.

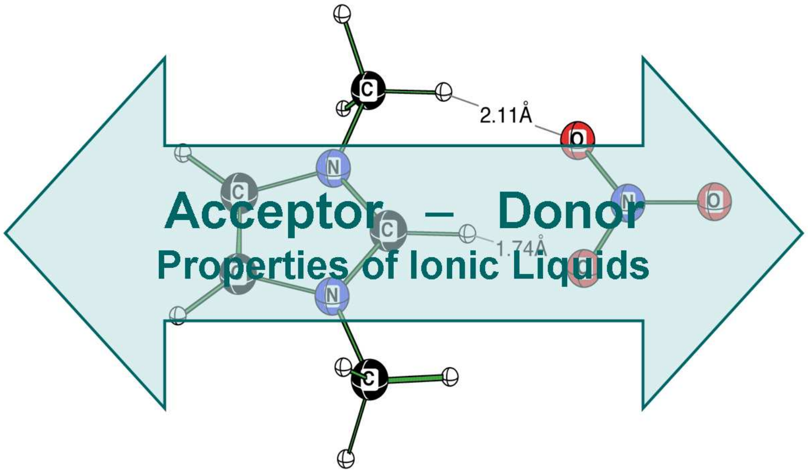
(75) H. Hayashi, S. Ogo and S. Fukuzumi, *Chem. Comm.*, 2004, 2714‒2715.

Graphical Abstract

Elucidation of Inorganic Reaction Mechanisms in Ionic Liquids: The Important Role of Solvent Donor and Acceptor Properties

Matthias Schmeisser[a] and Rudi van Eldik[a,b]*

[a] Inorganic Chemistry, Department of Chemistry and Pharmacy, University of Erlangen-Nuremberg, Egerlandstr. 1, 91058 Erlangen, Germany
[b] Faculty of Chemistry, Jagiellonian University, Ingardena 3, 30-060 Krakow, Poland



Solvent donor and acceptor properties play an important role in the elucidation of inorganic reaction mechanisms studied in ionic liquids