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Gutmann Donor and Acceptor Numbers for Ionic Liquids

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Abstract: We present for the first time Gutmann donor and acceptor numbers for a series of 36 different ionic liquids that include 26 distinct anions. The donor numbers were obtained by ^{23}Na NMR spectroscopy and show a strong dependence on the anionic component of the ionic liquid. The donor numbers measured vary from $-12.3\,\mathrm{kcal\,mol^{-1}}$ for the ionic liquid containing the weakest coordinative anion [emim][FAP] (1-ethyl-3-methylimidazolium tris(pentafluoroethyl)trifluorophosphate), which is a weaker donor than 1,2-dichloroethane, to $76.7\,\mathrm{kcal\,mol^{-1}}$ found for the ionic liquid [emim][Br], which exhibits a coordinative strength in the range of tertiary amines. The acceptor numbers were measured by using ^{31}P NMR spectroscopy and also vary as a function of the anionic and cationic component of the ionic liquid. The data are presented and correlated with other solvent parameters like the Kamlet–Taft set of parameters, and compared to the donor numbers reported by other groups.

Keywords: donor–acceptor systems · ionic liquids · NMR spectroscopy · nucleophilicity · solvent effects

Introduction

Ionic liquids (ILs) and their properties have extensively been discussed over the past decade. The number of scientific publications and established industrial applications have increased yearly.[1–4] Due to specific properties of this new class of solvents, such as the extremely low vapor pressure, the large electrochemical window and many other unique characteristics, ILs have turned out to be a very exciting field of research. In particular, the possibility to tune the properties of these solvents, thereby creating "tailor made" ILs through modification of structural features, has enabled a wide range of applications.

However, an efficient and realistic employment of ILs in scientific research and technical applications requires exact knowledge on the physical data and properties of the selected solvent. One important aspect is the specific interaction of solvent molecules with dissolved substrates. The reactivity of dissolved substances, reaction rates, reaction mechanisms and even the preferred product(s) of a reaction can in general be influenced by solvent–solute interactions.[5]

These interactions and their strength is influenced by many different factors, such as the strength of intermolecular van der Waals forces, the ability of a solvent to form hydrogen bonds, the polarity of the solvent, and especially important for ILs, the strength of intermolecular Coulomb interactions. The quantification of these solvent characteristics can be an important tool to understand physicochemical phenomena and chemical behavior in solution. For this purpose many different solvent parameters have been proposed over the years to express and quantify solvent properties. Of widespread use is the Dimroth and Reichardt $E_T(30)$ parameter[6] and the three parameter set derived from an LSER (linear solvation energy relationship) by Kamlet and Taft, consisting of α, β and π^*.[7] In the past, such values have been obtained for a wide range of organic solvents,[8] and some groups have also started to determine these parameters for ILs.[9,10] A complete data set will provide a deeper understanding of the properties of ILs and will enable a better comparison between organic solvents and ILs. In this way conclusions about solubility and reactivity of dissolved substrates can be drawn in comparison with organic solvents that exhibit similar parameters.

The $E_T(30)$ value of ILs can be determined analogously to the procedure for organic solvents by using Reichardt's dye if it is soluble or stable in the appropriate ILs. A comprehensive set of data of this parameter for several different ILs including a variety of cations and anions, is already available.[11] The Kamlet–Taft parameters are determined in a similar manner by dissolving different dyes in the ILs, but there is still a controversial discussion on which set of solvatochromic dyes really give reasonable results. Therefore, the

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obtained values for α, β and π^* vary depending on the set of solvatochromic dyes used.[9,10]

Another approach to express and quantify solvent properties is the so-called "donor–acceptor concept" invented by Victor Gutmann.[12] He defined the donor number, DN (also referred to as "donicity"), as a quantitative measure for the tendency to donate electron pairs to acceptors, and its counterpart, the acceptor number (AN),[13] as a measure for the electrophilic properties of a solvent, namely the ability to accept electron pairs or at least electron density. Information on the donor number of ILs would allow an estimation of the strength of the interactions between the IL anion and dissolved metal ions or complexes, or other Lewis acids. It could further help to predict the probability for the coordination of IL anions to metal centers or other electrophilic substrates. Such modifications in the coordination sphere of a metal complex could lead to a blockage of catalytic active site(s) and inhibition of the catalytic activity. Information on the acceptor number of ILs could help to predict the intermolecular interactions of nucleophiles and other electron-rich substrates with the IL cations. Electron-rich nucleophiles or substrates that are supposed to react with electrophilic metal centers could also react or interact with IL cations, depending on their acceptor strength, and thus also slow down or even inhibit chemical reactions.

Therefore, the aim of this study is to gain more insight into these interactions, to quantify and compare interactions in ILs and molecular solvents, and to achieve a better understanding of the complex solvent–solute relationship in ILs.

Results and Discussion

Donor number (DN): The donor number was originally determined calorimetrically by measuring the interaction of $SbCl_5$ with an equimolar amount of the appropriate solvent in 1,1-dichloroethane.[12] The observed enthalpy change provides the donor number in $kcal\,mol^{-1}$. The values varied from 0 $kcal\,mol^{-1}$ for 1,1-dichloroethane (by definition) to 38.8 $kcal\,mol^{-1}$ measured for HMPTA (hexamethylphosphoramide), the strongest donating solvent measurable with this method. Later Popov and Erlich showed by ^{23}Na NMR spectroscopy that the chemical shift of the ^{23}Na nucleus of dissolved $NaClO_4$ depends linearly on the solvents DN.[14]

Based on Popov's finding, DNs of several other solvents that could not be determined calorimetrically, could be assessed. Finally, correlations with other solvent parameters could be used to calculate and estimate DNs for some not studied solvents.[8]

The determination of DNs by ^{23}Na NMR spectroscopy has several advantages. 1) The ^{23}Na nucleus is the only natural stable isotope and has a high NMR sensitivity, which enables a straightforward measurement procedure without the need for prior enrichment. Despite the sometimes very low solubility of $NaClO_4$ in the investigated ILs, the observed signals were always of sufficient quality for the assignment of DNs (Figure S1 in the Supporting Information). 2) The chemical shift of ^{23}Na in $NaClO_4$ is not concentration dependent[14] (at least not in the selected concentration range) and thus no extrapolation to infinite dilution is necessary, which drastically reduces the quantity of IL used in each measurement. 3) In contrast to the solvatochromic dyes that are in some cases not commercially available, $NaClO_4$ is a cheap and readily available chemical.[10]

We started the investigation of DNs of ILs by selecting only imidazolium-based derivates as cations for an easy comparability of the results (Figure 1). In most cases the 1-ethyl-3-methylimidazolium cation ([emim]$^+$) could be used, and only in some cases 1-butyl- or 1-octyl-3-methylimidazolium cations were used because of the unavailability of the ethyl-containing derivatives. However, since the electron pair donor ability should be mainly controlled by the chemical nature of the IL anion, we did not expect large deviations in the DN of the IL on exchanging ethyl against another alkyl group. Nevertheless, the influence of changing the alkyl chain length on the DN of the IL was studied systematically and will be discussed further below.

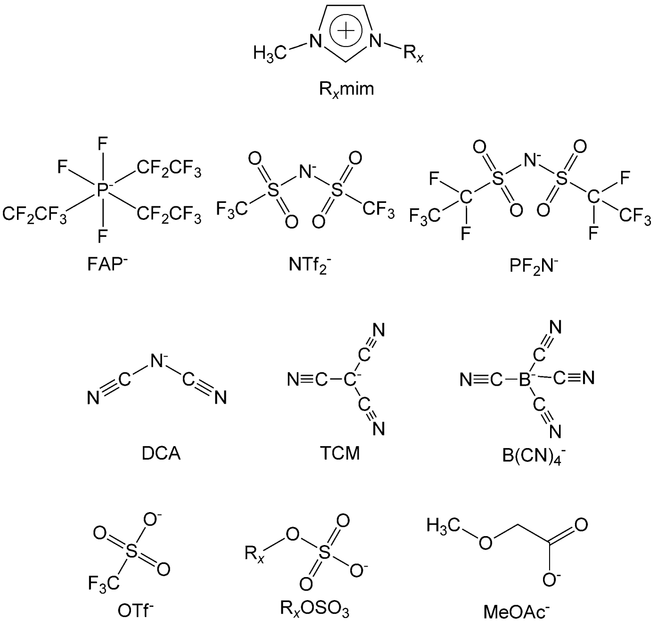

Figure 1. Structures of some imidazolium-based ionic liquids used in this study.

We first remeasured some of the values for the ^{23}Na chemical shift reported by Popov and Erlich[14] to check our experimental procedures and to report comparable and trustworthy results. We found a very good agreement between our and the earlier results, and selected 16 different organic solvents for the compilation of a linear calibration used for the assignment of the DN (for details see the Experimental Section, Table S1 and Figure S2 in the Supporting Information). For these measurements, the appropriate amount of $NaClO_4$ was dissolved in the IL and transferred into an NMR tube with a reference capillary containing a solution of NaCl. $NaClO_4$ dissolved readily in most of the investigated ILs, except for the very nonpolar ILs containing non-coordinating anions, such as PF_6^-, which resulted in very low DNs. The determined values and the assigned DNs based on the calibration line are given in Table 1. At first sight there are obvious trends that can be seen from the data for particular ILs with different anions. Anions that are strongly coordinating in aqueous solution (or other solvents) like the halogenides or good nucleophiles like thiocyanate, produce very strong donating ILs. If one compares the values measured for the strongest donating ILs with the value for bulk water (33 kcal mol^{-1}) or triethylamine (61 kcal mol^{-1}), it can be seen that some ILs are only slightly stronger donors than water (e.g., [emim][dca] or [emim]-[Ac]), whereas others are really strong donors ([emim][halogenides]) and even more likely to donate electron density than tertiary amines. Presumably, the anions of these ILs will most likely coordinate to metal centers if their existing ligands are weaker donors.

Table 1. NMR spectroscopy data and DNs for the investigated ILs. All measurements were carried out 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]	−21.378	−12.3	[emim][B(CN)$_4$] (328 K)	−5.646	20.8
[emim][PF_6]	−18.509	−6.2	[emim][NO_3]	−5.010	22.2
[emim][SbF_6]	−13.326	4.7	[emim][$EtOSO_3$]	−4.966	22.3
[C_{12}mim][NTf_2]	−12.356	6.7	[emim][$HexOSO_3$]	−3.146	26.1
[emim][Pf_2N]	−12.145	7.2	[emim][TCM]	−3.131	26.1
[emim][BF_4]	−12.086	7.3	[emim][$BuOSO_3$]	−2.954	26.5
[C_{10}mim][NTf_2]	−12.000	7.5	[emim][$(EtO)_2PO_2$]	−0.683	31.3
[emim][ClO_4]	−11.951	7.6	[emim][DCA]	2.389	37.8
[C_8mim][NTf_2]	−11.622	8.3	[emim][NO_2] (348 K)	2.946	38.9
[C_6mim][NTf_2]	−11.497	8.5	[emim][$SnCl_3$]	3.166	39.4
[C_4mim][NTf_2]	−10.696	10.2	[emim][Ac]	5.030	43.3
[emim][NTf_2]	−10.220	11.2	[emim][SCN]	6.257	45.9
[C_8mim][OTf]	−6.712	18.6	[emim][MeOAc]	7.610	48.8
[emim][B(CN)$_4$]	−5.895	20.3	[omim][I]	12.605	59.3
[emim][OTf]	−5.840	20.4	[C_{10}mim][Cl] (328 K)	16.030	66.5
[emim][PO(EtHex)$_2$]	−5.828	20.5	[omim][Cl]	17.327	69.2
[C_4mim][OTf]	−5.826	20.5	[emim][Cl] (358 K)	18.981	72.7
[emim][$OctOSO_3$]	−5.761	20.6	[emim][Br] (358 K)	20.858	76.7

A remarkable observation is that the ILs formed by halogenides exhibit higher DNs than the ILs with thiocyanate or other anions, which are much stronger nucleophiles in water and other solvents, and are supposed to donate electron density better to solvated substrates. One reason for this apparent discrepancy might originate from the measurement technique itself, namely the use of Na^+ as "sensor". A more effective interaction between the halogenides and the sodium cation being both ball-shaped with a high charge density might lead to an overestimation of the DNs. The difference between "bulk" solvents and the separated solvent molecules in solution has already been addressed by Gutmann who found a higher DN for bulk water than for water dissolved in dichloroethane. He ascribed this to the intermolecular effects in bulk liquid, like the formation of hydrogen bonds, etc., that lead to an altered solvation ability of the bulk solvent compared to the interaction ability of one separated molecule/anion.[12]

In a chloride-containing IL, or generally speaking halogenide-containing IL, it has to be taken into account that there are no separated ions dissolved in, and thus solvated by, a neutral solvent, but the formation of ion clusters dissolved in a highly charged medium consisting of identical ions and/or ion-pairs does occur. In water, for example, in which chloride is a weaker donor and nucleophile than thiocyanate, chloride is solvated by water molecules and thus the effective charge or electron density available for interaction with substrates is shielded by the solvating molecules, thus lowering the electron donicity of solvated chloride. On the contrary, in ILs the chloride anions are supposed to be far less interacting with the imidazolium cations (because of the diffuse electron density delocalized around the ring and the steric shielding of the alkyl chains) and are thus "naked" and readily donating/coordinating to any acceptor ion or molecule present in solution.[15]

On the other side of the IL compilation, one finds anions that are very weak donors and thus, combined with imidazolium cations, also result in strongly non-coordinating ILs. Outstanding are the liquids [emim][FAP] (DN = −12.3 kcal mol^{-1}) and [emim][PF_6] (DN = −6.2 kcal mol^{-1}), both of which have DNs even lower than that of the former zero point of the DN scale, namely 1,1-dichloroethane. These ILs could be formidable alternatives for organic solvents in cases where coordination of the solvent has to be strictly avoided, for example, in catalytic processes in which vacant coordination sites on metal complexes vital for substrate processing, are present that could easily be blocked by even weak coordinating anions.

Solvents with slightly higher electron donor ability are located between DNs of 0 to 20. Here one finds [emim][BF_4] (DN = 7.3 kcal mol^{-1}), one of the first ILs to become popular with widespread use,[16] and one of the most famous and best studied ILs, namely [emim][NTf_2] (DN = 11.2 kcal mol^{-1}). The NTf_2^- anion was always stated to be an "innocent" anion, useable for many applications for which coordination ability is of great importance.[17–19] Other ILs containing anions with fluorinated groups, namely SbF_6^-, TfO^-, and NPf_2^-, are also amongst the ILs with low DNs. These anions are all very weak donors and therefore show only weak interactions with acceptor molecules or substrates, and behave like innocent solvent components. Of course, given the required conditions, one could force even NTf_2^- to coordinate to a metal complex. If the ligands of a metal complex are weaker donors than the IL anion, then the latter is very likely to coordinate.[20,21]

The ILs in the DN range between 20 and 33 are weaker than water, 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 an IL, the anions are present in a large excess and these weaker donors are able to substitute the coordinated ligands of a metal center. These anions are comparable to DMSO ($DN = 29.8\ kcal\,mol^{-1}$), which can coordinate to metal complexes under the right conditions, but will be easily displaced when a stronger donor is added. The information on the exact donating ability of ILs will therefore help to predict reaction progress and suggest new synthesis routes in ILs.

In summary, one can conclude that there are ILs with every possible DN for organic solvents, so that substitutes for these solvents with the same coordinating and/or donating ability can be found amongst the ILs. In addition, there are also ILs with extreme values that could not be achieved so far with common solvents; this could facilitate new prospects for possible application and use of ILs.

Comparison of the DNs measured in this work with values obtained by Linert et al.: Besides other methods, Linert et al. used $[Cu(acac)(tmen)]BPh_4$ (acac = acetylacetonate and tmen = tetramethylethylenediamine) dissolved in 1,2-dichloroethane (DCE) as a solvatochromic indicator to investigate the donicity of anions since Gutmann only determined DNs of molecular solvents. This 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 that leads to the DN of the appropriate anion. They found the sequence $PF_6^- \approx SbF_6^- < NTf_2^- < BF_4^- < ClO_4^- < CF_3SO_3^- < NO_3^- < I^- < Ac^- < SCN^- < Br^- < Cl^-$, which in general reflects the sequence found for ILs.[22,23] As illustrated in Figure 2, a correlation between the anion DNs assigned by Linert and the DNs of the corresponding [emim]-based ionic liquids, shows an approximate linear behavior with the exception of the halides.

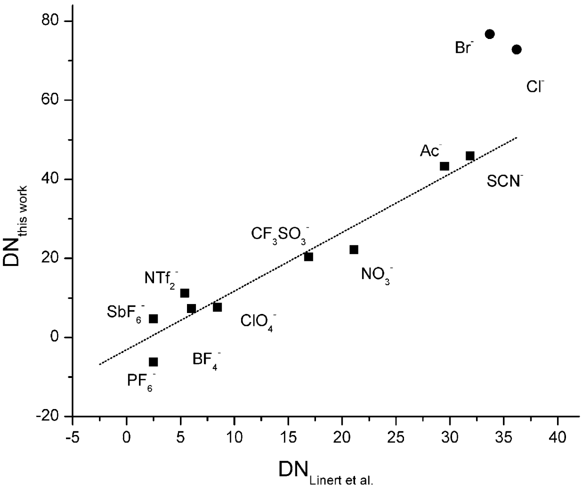

Figure 2. Correlation between DNs for anions determined by Linert et al.,[23] and those for the corresponding [emim]-based ILs.

Taking into account that the [emim]halides are solids, whereas the other [emim]salts shown in this correlation are room temperature ILs, this deviation can be attributed to the higher temperature (358 K) used in the determination of the DNs of the [emim]halide ILs. A further contribution to this deviation could arise from the solvation of the anions. Though DCE is a weak-coordinating solvent, there should be at least some interaction with the anions, shielding the negative charge, reducing the mobility of the anions and thus decreasing the effective donicity of the anion. In our measurement procedure, there are no additional solvent molecules and only weak and ineffective coordinating cations (at least for small ball-shaped anions like the halogenides), which force the anion to interact with the "Na^+" probe.

In contrast to our measurements, the value for PF_6^- was assigned to be 2.5 (−6.2 in our measurement), which is the same value as for SbF_6^- (4.7 in our measurement). 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, since if the anion is even weaker coordinating than DCE, a solvent molecule will coordinate to the Cu^{II} complex and thus "freeze" the experimentally determinable DN at a fixed value, which is the DN value of DCE. In contrast, in our solvent-free method a lower donicity can be detected and even negative DNs of ILs with a lower donicity than DCE could be assigned.

DN variation by alteration of structural features of the IL anions and cations: Structural changes on the IL anion, like the introduction of electron donating or withdrawing atoms or groups and the introduction of fluorinated groups, can have large effects on the resulting donor ability of the IL. The $[emim][NO_3]$ IL ($DN = 22.2\ kcal\,mol^{-1}$) has a much lower DN than $[emim][NO_2]$ ($DN = 38.9\ kcal\,mol^{-1}$), which could be caused by the absence of the free electron pair located on nitrogen in case of the NO_3^- anion and the delocalization of the electron density over three oxygen atoms. The distribution of negative charge over more atoms leads to a weaker interaction between the anion and a substrate (in the DN measurements the Na^+ ion) and thus a lower donor strength. A similar effect can be seen in the DNs that follow the sequence $SCN^- > N(CN)_2^- > C(CN)_3^- > B(CN)_4^-$ with DNs of 45.9, 37.8, 26.1 and $20.3\ kcal\,mol^{-1}$, respectively. As the number of cyanide groups attached to the different central atoms increases, the DN of the appropriate IL decreases despite the growing number of possible sites for interaction. The negative charge is distributed between the central atoms and the cyanide groups through mesomeric effects.

The more cyanide groups are present, the smaller the overall charge on each group and thus the electron density required for the interaction with substrates. In the case of $B(CN)_4^-$ there is no free electron pair to be distributed at all, and only polarization of the bonds can occur, thus transferring some electron density to the cyano groups.

The introduction of fluorinated alkyl groups leads to a decrease in the DN, which can be seen in the examples of [emim][PF_6] (−6.2 kcal mol^{-1}) and [emim][FAP] (−12.3 kcal mol^{-1}) in which three fluorine atoms are replaced by $-CF_2CF_3$ groups. A similar effect is observed for the elongation of the fluorinated groups, namely [emim][NTf_2] (11.2 kcal mol^{-1}) exhibits a higher DN than [emim][NPf_2] (7.2 kcal mol^{-1}). The low polarizability of the fluorinated groups weakens the interactions with the acceptors and lowers the donor ability of the IL.

The introduction of an electron-donating group on the anion can increase the donor ability as can be shown with the pair [emim][Ac] (43.3 kcal mol^{-1}) and [emim][MeOAc] (48.8 kcal mol^{-1}). The inductive effect of the MeO group results in a higher electron density on the carboxylate group, and thus a stronger interaction with the sodium nucleus, and a more effective charge transfer. We specially synthesized [emim][MeOAc] to check the influence of electron-donating groups on macroscopic properties, like electron donicity.

It was quite obvious to expect a response of the DN towards the modification of the IL anions, but we also wanted to investigate the influence of structural changes on the cation. We elongated the alkyl chain of ILs consisting of NTf_2^- and Cl^- anions and found systematic changes in the DNs (Figure 3), namely the longer the alkyl chain of the imidazolium moiety, the lower the DN of the appropriate IL. Longer alkyl chains lead to a higher hydrophobicity of the ILs,[24] thus diminishing the interaction with the sodium nucleus. Furthermore, due to stronger van der Waals interactions and aggregation of the nonpolar alkyl chain aggregates,[25] the interactions with acceptors are weakened. In addition, there could also be steric effects resulting from partial blocking of the sites predestined for interaction with the long alkyl chains. Thus, it seems possible to tune the DN like many other physical properties, by structural modifications of cations or anions of the IL. This may help to create ILs with exact defined DNs to reproduce the donicity of a molecular solvent that should be substituted by an IL.

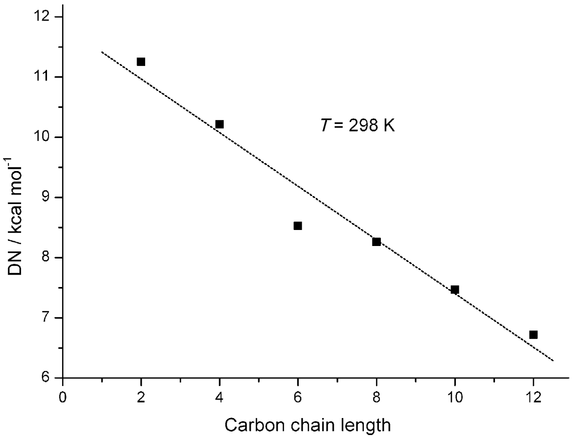

Figure 3. Change in DN on elongation of the alkyl chain of the imidazolium cation at 298 K.

DN variation with temperature: The temperature dependence of physical parameters is quite important for various purposes. Water shows a slight linear decrease in DN with increasing temperature (Figure S3 the Supporting Information). To elucidate the temperature dependence of the DN of ILs, we investigated several different ILs. The ILs studied all show a linear increase in the DN on increasing the temperature in the selected temperature range. This can be accounted for in terms of a higher mobility of the ions at higher temperature, leading to a disintegration of cation–anion aggregates[25] in the IL and a stronger interaction with a substrate. Figure 4 displays the temperature-dependent change in the DN for [C_{12}mim][NTf_2]. The difference is quite significant ($\Delta DN \approx 5$ kcal mol^{-1}) since it increases the DN of this IL to over that of [emim][NTf_2].

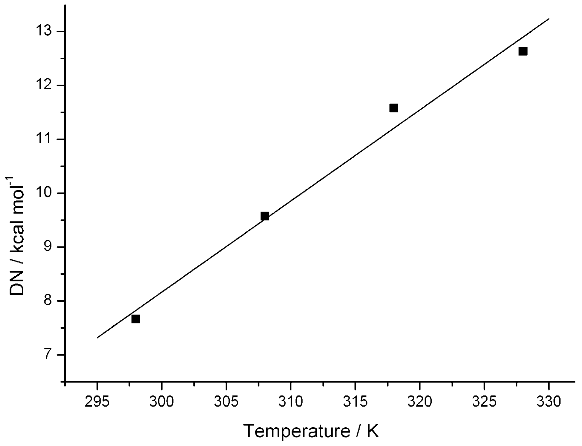

Figure 4. Temperature-dependent change in DN observed for [C_{12}mim][NTf_2].

We also studied the temperature dependence of the DN for other [$C_x$mim][NTf_2] ILs and found the magnitude of variation in the DN to depend on the alkyl chain length, namely the longer the alkyl chain, the larger the increase in DN with increasing temperature (Table 2). This might be connected with the aggregation of the IL cations through van der Waals interactions.[26] Cations with long alkyl chains form large and stable aggregates at room temperature, which restricts the mobility of the anions and leads to their fixation. The stability of these aggregates decreases at higher temperature, resulting in a higher mobility of the anions and therefore in a better interaction between the anions and substrates. In consequence, the temperature-dependent variation in the DN is larger for ILs with long alkyl chains, which form more stable aggregates.

Table 2. DNs of [C$_x$mim][NTf$_2$] at 298 and 328 K as a function of the alkyl chain length.

Alkyl chain length of [C$_x$mim][NTf$_2$]	Chemical shift of ^{23}Na [ppm] at 298 K	DN [kcal mol^{-1}] at 298 K	Chemical shift of ^{23}Na [ppm] at 328 K	DN [kcal mol^{-1}] at 328 K
2	−10.201	11.3	−9.787	12.1
4	−10.696	10.2	−9.705	12.3
6	−11.497	8.5	−9.600	12.5
8	−11.622	8.3	−9.409	12.9
10	−12.000	7.5	−9.594	12.5
12	−12.356	6.7	−9.548	12.6
14	–[a]	–[a]	−9.393	13
16	–[a]	–[a]	−9.267	13.2

[a] [C$_{14}$mim][NTf$_2$] and [C$_{16}$mim][NTf$_2$] are solids at room temperature.

As a result of the above-mentioned effect, all the [C$_x$mim][NTf$_2$] ILs exhibit nearly the same DN of about 12.6 kcal mol^{-1} at 328 K (Figure 5). However, such an influence of the temperature and alkyl chain length on the donicity of ILs can, to a certain extend, 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 may be possible, for instance as a temperature-controlled transfer of substrates from one liquid phase to another, or the temperature-dependent variation of two-phase equilibria. These effects are already reported and established for conventional solvents.[27–29]

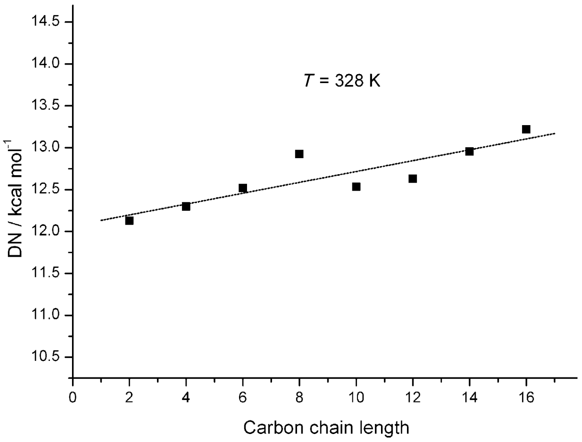

Figure 5. DN dependence on the elongation of the alkyl chain length of the imidazolium cation moiety for [C$_x$mim][NTf$_2$] at 328 K.

Variation of the anion also influences the temperature dependence of the DN. The IL [emim][(EtO)$_2$PO$_2$] shows a distinctive change in the DN on variation of the temperature ($\Delta DN \approx 0.194\,K^{-1}$), which was found to be even larger than observed for [C$_{12}$mim][NTf$_2$] ($\Delta DN \approx 0.169\,K^{-1}$; Figure 6 and Table S2 in the Supporting Information).

It follows that the temperature dependence of the DN depends on both the cationic and anionic components of the IL. Some combinations like [emim][NTf$_2$] ($\Delta DN \approx +0.029\,K^{-1}$) result in an IL with a relatively low temperature sensitivity, whereas others with longer alkyl chains or different anions show changes up to six-times larger, namely [emim][(EtO)$_2$PO$_2$]. At 298 K [emim][(EtO)$_2$PO$_2$] has a slightly smaller DN than water, but at temperatures above 360 K its DN reaches the value of amines, enabling it to coordinate much more effectively to metal centers or other acceptor sites. A systematic variation of cations and anions that facilitate a higher temperature dependence can lead to an IL that could exhibit an extremely high temperature sensitivity. In this way the coordination of an IL to any acceptor site could be controlled by simple temperature variation. The IL could act as a "thermal-controlled-on-off-switch", blocking or enabling access to a coordination site and thus inhibiting or permitting a catalytic reaction through temperature variation. This tunable feature provides potential for interesting future applications.

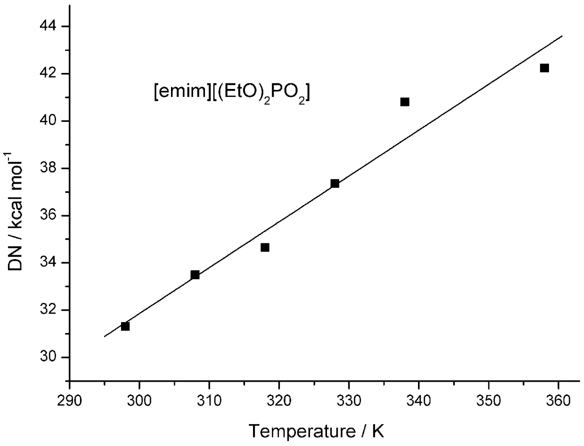

Figure 6. Temperature dependence of the DN for [emim][(EtO)$_2$PO$_2$].

Comparison with other solvent parameters: We compared the obtained DNs with other recently determined solvent parameters for ILs to verify our results and to investigate the possibility to estimate missing values for other ILs through the extrapolation of existing data.

Kamlet–Taft β-parameters: Over the years several concepts have been suggested to empirically describe solvent properties. The LSER concept established by Kamlet and Taft is one of the most popular and successful concepts, and relates solvent properties to different specific interactions, such as the hydrogen bond donating ability (α), hydrogen bond acceptance (β), and the polarity/polarisability (π^*). 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.[8] This correlation can be especially useful to predict missing data of DNs or β-parameters.

Although for organic solvents a large number of Kamlet–Taft parameters already exist that facilitate this comparability, reliable data for ILs, especially for [emim]-based ILs, are rather scarce. On the basis of Marcus' suggestion, we tried to correlate our DNs with the Kamlet–Taft β-parameters (Table 3 and Figure 7).

Table 3. Kamlet–Taft parameters (π^*, α, and β) for several imidazolium-based ILs used in this study.

IL	π^*	α	B	DN [kcal mol^{-1}]	Ref.
[emim]PF_6	0.99	0.76	0.20	-6.2	[30]
[emim]BF_4	1.03	0.70	0.26	7.3	[31]
[emim]ClO_4	1.11	0.56	0.41	7.6	[30]
[C_8mim]NTf_2	0.97	0.97	0.28	8.3	[32]
[C_6mim]NTf_2	0.98	0.65	0.25	8.5	[32]
[C_4mim]NTf_2	0.98	0.62	0.24	10.2	[9]
[emim]NTf_2	0.90	0.76	0.28	11.2	[30]
[C_4mim]OTf	1.01	0.63	0.46	20.5	[9]
[emim]OSO_3	1.09	0.58	0.62	22.3	[33]
[emim]NO_3	1.13	0.48	0.66	22.2	[30]
[emim]HexOSO_3	0.98	0.65	0.71	26.1	[34]
[emim]OctOSO_3	0.93	0.65	0.77	20.6	[34]
[emim]DCA	1.08	0.53	0.35	37.8	[30]
[emim]OAc	1.09	0.40	0.95	43.3	[30]

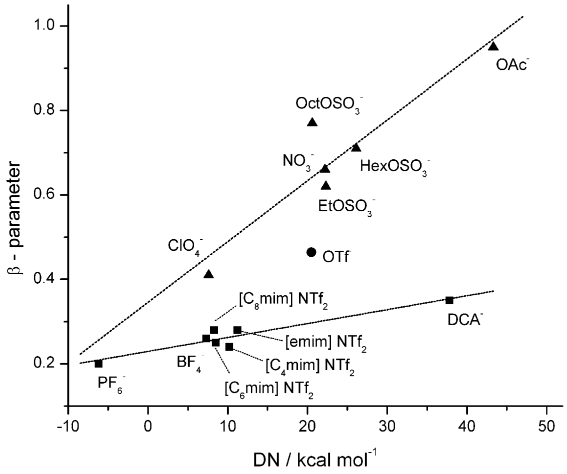

Figure 7. Correlation between β-values (Table 3) and DNs for ILs: O- and N-donors.

At first sight the DNs hardly correlate with the corresponding β-parameters and exhibit a large variance, but a closer look reveals two separate correlations with an approximate linear behavior, and one exception. As shown in Figure 7, 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.[35] Only [bmim][OTf] does not seem to fit to one of these correlations. Interestingly, this IL is located exactly between both correlations, which could be due to the fact that the triflate anion contains oxygen as well as fluorine atoms. Lungwitz et al.[10] also found a divergent behavior for this IL with respect to several physical properties, but no plausible explanation has been offered so far.

On considering the different electronegativity of nitrogen and oxygen, the two correlations shown in Figure 6 could arise from different energy levels of the donor orbitals. Oxygen exhibits a higher electronegativity 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. A similar observation can be made on applying the hydrogen-bond-acceptance-parameters of Lungwitz et al.[10] A correlation between their values and our DNs (Figure S4 in the Supporting Information) also resulted in two separate dependencies, and [bmim][OTf] was located between both of them. However, in contrast to Figure 7, the perfluorinated ILs do not fall in line with the fluorinated N-donors and other N-donor ILs.

Though interesting correlations between the β-parameters and the DNs could also be observed for ILs, there is presently not enough data available to establish correlations that allow an accurate estimation/calculation of DNs or β-parameters as done by Marcus.[8]

DFT calculations of donor numbers: We also observed a family-dependent behavior on comparing the DNs of the ILs with the appropriate interaction energies, ΔE, calculated by DFT. Following our earlier studies,[5a–e] 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 Equation (1) and Table S3 in the Supporting Information). To simplify the calculations we used the 1,3-dimethylimidazolium cation ([mmim]$^+$) instead of [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], Figure 8) account for the important role of the C–

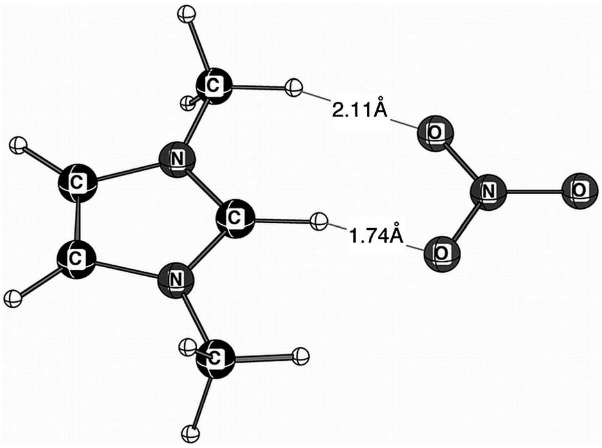

Figure 8. DFT calculated (RB3LYP/LANL2DZp) structure of [mmim]-[NO_3].

H···anion interactions that were previously verified by experiment.[5]

$$\underset{\text{separated ions}}{[\text{mmin}]^+ + [\text{anion}]} \rightarrow \underset{\text{ion pair}}{[\text{mmin}][\text{anion}]} \tag{1}$$

In agreement with our earlier work,[5a–e] we also found large differences in the interaction energies that depend on the anionic component of the ILs. As shown in Figure 9, a correlation between the DN and ΔE appears to be similar to the correlation between the DN and β-parameters (Figure 7).

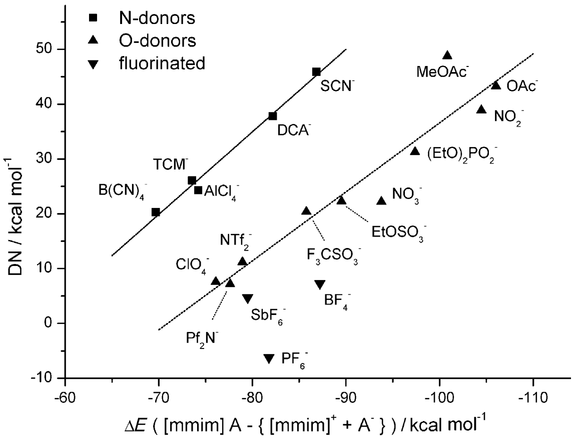

Figure 9. Correlation between the DNs and the calculated (DFT) interaction energy ΔE.

At first sight, there seems to be only a very rough correlation indicating that anions with a lower interaction energy ΔE correspond to a lower DN, whereas ILs with higher interaction energies exhibit higher DNs. However, a closer look at Figure 9 also points to the existence of two family dependencies. In contrast to Figure 7 there is no clear distinction between N- and O-donor anions, but rather between anions with and anions 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, $AlCl_4^-$[36] is located amongst the cyanide containing anions, next to the tricyanomethanide anion.

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 ΔE. 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 nearly 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 a moderately higher interaction energy, which might be connected with the stronger B–F bonds and lower coordination number.

Anions with fluorinated alkyl groups, such as NTf_2^- and Pf_2N^- 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 centre (monodentate, η^1-O, η^1-N or bidentate, η^2-O,O', or even η^2-N,O), a preference for coordination through oxygen atoms can be observed from crystal structures[37–40] and other methods.[41,42] 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 $p\pi$–$d\pi$ bonding within the N–S moiety could lead to charge delocalization over the whole anion and complicate coordination via the nitrogen donor.[43]

All in all, the correlations in Figure 9 show the good agreement between the DFT calculations and the experimental DNs. The family-dependent almost linear dependence should be kept in mind and investigated further as it could be useful for the interpretation and estimation of diverging or coinciding characteristics of other ILs.

Donicity and DNs in terms of the HSAB concept: The tendency of anions to coordinate to a metal center is strongly related to their Lewis basicity. Though Pearson's concept of hard and soft acids and bases (HSAB) elucidates only one aspect that contributes to the overall stability of Lewis acid–base complexes,[44] this concept has often been stated to be useful for qualitative predictions of the extent of such Lewis acid–base interactions. In this context a discussion of DNs in terms of the HSAB concept seems to be relevant.

As outlined before, our DNs were determined by NMR measurements of the chemical shift of the ^{23}Na nucleus. According to Pearson's definition of hardness and softness, Na^+ is a small cation with a high charge density and therefore a hard Lewis acid.[45] Thus, the DNs should somehow reflect the relative stability of acid–base complexes generated by a hard Lewis acid (Na^+) and Lewis bases (anions) of different hardness or softness. Soft anions should lead to less stable complexes and lower DNs, whereas hard anions should lead to more stable complexes and higher DNs, in case no further effects, such as symmetry, sterical hindrance or charge delocalization play a dominating role. On considering typical anions of ionic liquids, such as NTf_2^-, OTf^- or BF_4^-, the donor atom is either shielded by steric hindrance and/or the negative charge is delocalized over the anion structure. Therefore, many of these anions, which are actually hard bases, interact only weakly with the sodium cation and yield low DNs. These ionic liquids cannot be understood from the perspective of the HSAB concept, as the effect of "chemical hardness" is dominated by other effects; [emim][ClO_4] is one of the best examples. Due to a complete delocalization of the negative charge over four oxygen atoms, the perchlorate anion exhibits a perfect tetrahedral structure (Cl–O bond length = 146 pm), behaves almost innocent and results in a low DN for [emim][ClO_4], despite being a hard base.[46] Other ionic liquids, which consist of smaller anions, such as [emim][Ac], [emim][NO_3] or [emim][SCN], exhibit significantly higher DNs; this points to a strong interaction between Na^+ and the appropriate anions. On considering the relative hardness of these anions, the DNs roughly reflect the hardness of these anions.[47] However, it is in general difficult to estimate DNs by applying Pearson's HSAB concept. Especially in the case of room temperature ILs, the electronic properties of the anions, which facilitate the liquid state of these salts,[48] dominate over the influence of "chemical hardness or softness".

Watanabe's "ionicity" concept:[49] Since ILs only consist of ions, Coloumbic interactions are expected to be predominant. Intermolecular interactions can lead to the formation of clusters and aggregates,[24,25] and thus influence a large variety of physicochemical properties. Solvation of and interaction with dissolved substrates are also influenced by these phenomena. The understanding of "ionicity" ("ionic nature" or "dissociativity") can give valuable insight into the understanding and also the prediction of the chemical properties of ILs. Since the DN also reflects the interaction between the ions in ILs, similar trends and correlations should be observed in terms of the ionicity. The ionicity of ILs was already compared to the solvent polarity and several other physicochemical properties by some groups,[50,51] amongst them Watanabe et al.[52] They used the molar conductivity ratio ($\Lambda_{imp}/\Lambda_{NMR}$) approach for different ILs with imidazolium cations and the most common anions, like TfO^-, BF_4^- and NTf_2^-. In agreement with our results, they also observed a proportional change in the "ionicity" on elongation of the alkyl chain of the imidazolium moiety (Figure 10). The ionicity of the ILs decreases significantly with increasing chain length, even though the decrease in DN is relatively small. This can be ascribed to the predominant anion dependence of the DN and the only marginal influence of the cation. On the contrary, the ionicity is affected by van der Waals interactions of the alkyl chains and the formation of nonpolar aggregates. The displacement of anions affects both the ionicity and DN, and results in a linear correlation of both values (Figure 11). An increasing DN means a stronger electron donating ability and thus a higher Lewis basicity that intensifies the cation–anion interaction in the IL and thus reduces the ionicity by the formation of ion pairs or larger aggregates. The results obtained in our measurements are thus in line with Watanabe's investigations, and demonstrate the applicability of our findings.

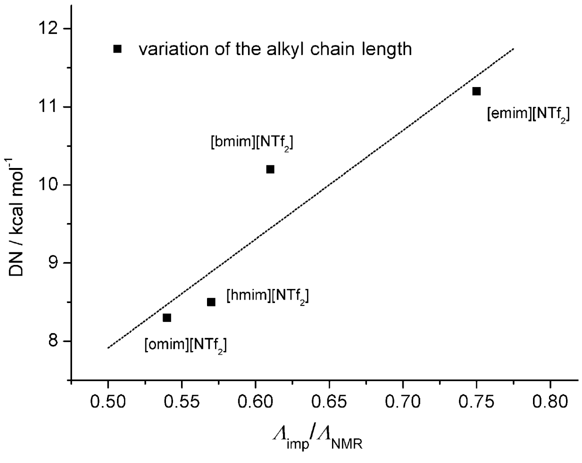

Figure 10. Correlation between the DNs and ionicity (values taken from ref. [49]) for different ILs: effect of the imidazolium alkyl chain length.

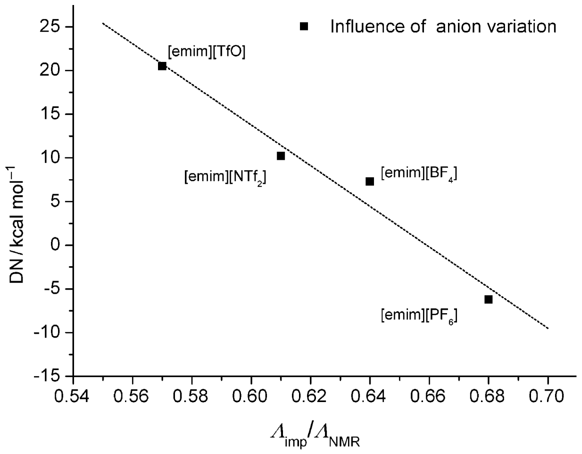

Figure 11. Correlation between the DNs and ionicity (values taken from ref. [49]) for different ILs: effect of the anion.

Values derived by XPS investigations: Steinrück et al.[53] recently reported X-ray photoelectron spectroscopic measurements (XPS) for ILs. They determined the bonding energies (BE) of certain core levels of the hetero-carbon atoms (C_{hetero}) of the imidazolium moiety referenced to the BE of the carbon atoms located in the alkyl chain (C_{alkyl}) of the 1-methyl-3-octylimidazolium cation, and found them to depend strongly on the appropriate anion of the IL (Figure 12). The authors ascribed this influence to a charge transfer from the anion to the imidazolium cation via a hydrogen bond with the proton at C2 of the $[omim]^+$ cation.

Stronger interacting anions like Cl^- lead to a lower core level BE because of electron density transferred to the head group carbon atoms. Imidazolium cations in IL with non-coordinating or weakly interacting anions like NTf_2^-, show higher core level BEs due to a reduced transfer of electron density. Since an interaction of this type should be linked to

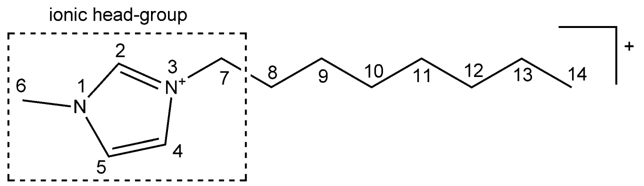

Figure 12. Labeled structure of the $[omim]^+$ cation according to Hunt et al.[54] The carbon atoms attached to the ring of the ionic head-group (C2, C4, C5, C6, C7) are referred to in the text as "C_{hetero}" and the atoms of the "tail" (C8–C14) as "C_{alkyl}".

the donicity of the anions, we expected a direct correlation between the DNs of the anions of the ILs and the core binding energy measured by XPS (Figure 13).

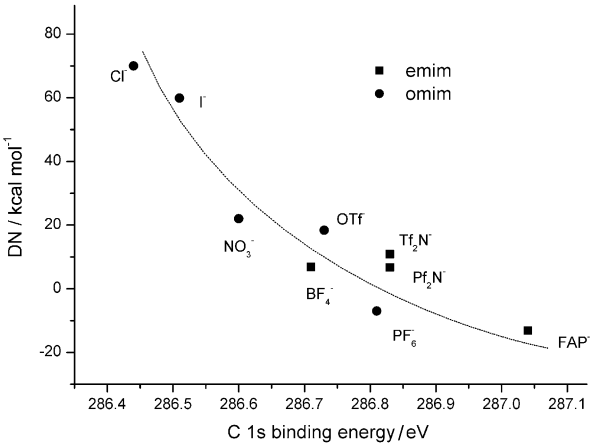

Figure 13. Correlation of C1s binding energy with $DN_{this work}$.

As expected a good correlation between the two values could be found. A larger DN, and thus a more effective transfer of electron density via the C2 positioned proton to the imidazolium carbon atom, results in a lower core level BE as this value is directly influenced by the local electron density at the particular atom. Despite the fact that our DNs were derived either from $[emim]^+$ or $[omim]^+$ containing ILs, whereas Steinrück et al. only used $[omim]^+$ containing ILs, the data correlate rather well. The "cation effect" on the DN is not so pronounced because only the alkyl chain of the cation was elongated. For different cations (quaternary amines or pyridinium cations), however, the effect may be much more distinct. Thus, the DN can be used to approximately estimate the influence that results from electron density transfer from the IL anions to the core level BE, or in more general terms, the electronic properties of charge accepting atoms/molecules.

Acceptor number (AN): The acceptor number was originally introduced by Gutmann et al.[13] to establish a method for quantifying the electrophilic or electron accepting properties of a solvent. Since the alternative methods to determine this parameter are quite complicated and the available data sets are rather scarce, only available for a limited number of solvents,[55–57] Gutmann et al. devised a more advanced technique. According to the DNs that turned out to be easily determined by NMR measurements on several probe molecules,[14,58,59] they searched for a counterpart to quantify electrophilic interactions. They selected triethylphosphine oxide as probe molecule and ^{31}P NMR spectroscopy as method of choice (Figure S5 in the Supporting Information), because of several advantages: 1) due to the high natural abundance and high NMR sensitivity of the ^{31}P nucleus, NMR measurements are very suitable; 2) triethylphosphine oxide exhibits a high solubility in many different solvents, and 3) has a high chemical stability. However, the molecular structure that assures an efficient electronic shielding of the ^{31}P nucleus without steric hindrance proved to be more important and leaves the oxygen atom as the only interaction possibility, excluding an interference of the probe nucleus by other interactions, such as contact contributions or multidentate coordination. Gutmann et al. used $(C_6H_5)_2POCl$ as reference substance and measured the chemical shift of the ^{31}P nucleus of Et_3PO for 4 to 6 different concentrations, to facilitate the extrapolation of the chemical shift to infinite dilution (δ_∞). They measured the ^{31}P signals of Et_3PO for more than 30 different organic solvents and found the chemical shift to vary within in a range of about 50 ppm. 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. This value was chosen in reference to the definition of the DN, and its original measurement procedure.[12] In order 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. In contrast to Gutmann's approach, we simply used the values of the chemical shift extrapolated to infinite dilution (δ_∞), without factorization of the magnetic susceptibility, as this physical property of ILs, as far as we know, has not been measured for the complete set of ILs investigated in this study. However, the average deviation between the ANs calculated from Gutmann's non-corrected values (Figure S6 and Table S4 in the Supporting Information) and the ANs obtained by using Gutmann's corrected values, is only about ± 0.3. This simplification should be unproblematic and the derived ANs sufficient for qualitative comparisons.

For the determination of 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. With increasing concentration the ^{31}P signal shifted to higher field in all ILs. As already reported by Gutmann, the dependence of the chemical shift on the concentration varies extremely for the different solvents. In some cases the correlations are 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 4.

These values clearly show that most ILs have an AN between 25 and 33, and thus an electron accepting ability like

Table 4. The ^{31}P chemical shifts and ANs for the ILs under investigation

Solvent	^{31}P NMR δ_{∞} [ppm]	AN
[emim][EtOSO$_3$]	−9.067	25.0
[C$_{12}$mim][NTf$_2$]	−9.081	25.0
[C$_8$mim][NTf$_2$]	−9.322	25.6
[emim][NTf$_2$]	−10.107	27.4
[emim][FAP]	−10.904	29.3
[emim][TCM]	−10.943	29.4
[emim][dca]	−11.939	31.7
[emim][SCN]	−12.211	32.4
[emim][BF$_4$]	−12.688	33.5
[emim][OTf]	−14.218	37.1
[emim][ClO$_4$]	−21.458	54.0
[emim][SnCl$_3$]	−30.593	75.4

aliphatic alcohols, namely AN(*tert*-butanol) = 27.1 and AN(*iso*-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 (see above) and can be explained in terms of increasing steric hindrance of the cation–anion interactions on increasing the chain length, and the aggregation of the long chain imidazolium cations via van der Waals forces, thus impeding the solvent–solute interactions.

Similar results for ILs containing BF_4^- and NTf_2^- anions were reported by Katoh,[60] who investigated imidazolium-based ILs by photoelectron emission spectroscopy (PEES). On comparing the obtained data with other PEES studies performed by Watanabe et al.,[61] they were able to assign AN values of around 25 to the liquids [bmim][BF$_4$] and [bmim][NTf$_2$], which is in quite good agreement with our results.

Kimura et al.[62] 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. Similar to their earlier work,[63] they found a linear correlation between the AN and these frequencies, and were able to assign ANs to the ILs under investigation. 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. The [emim][OTf] IL (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,[64] despite the low DN (only 7.6 kcal mol^{-1}) of this solvent. 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 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 good miscibility in water could also be facilitated by the chaotropic effect (Hofmeister effect)[65] of the perchlorate anion. On addition of [emim][ClO$_4$] to water, perchlorate is dissolved and destabilizes hydrogen bonding in the water phase, lowers the hydrophobicity and thus increases the solubility of the IL. The perchlorate anion seems to act as its own phase transfer catalyst. This effect could also enable the dissolvation of hydrophobic substances in polar solvents, like water, and thus the employment of [emim][ClO$_4$] as phase transfer catalyst.

The IL with the highest AN measured in our study belongs to [emim][SnCl$_3$] (1:1 mixture of [emim]Cl and SnCl$_2$; AN = 75.4), thus being 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.,[66] 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, namely 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. 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.

Similarly high ANs were already reported by Osteryoung et al., who also investigated the AN of differently composed chloroaluminate melts, namely [BuPy][AlCl$_4$] and [emim]-[AlCl$_4$].[36] 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).

Comparison with Kamlet–Taft α-parameters: According to the observations by Marcus in terms of DNs, he also found an interrelation between Gutmann's ANs and the Kamlet–Taft α-parameters. For more than 50 organic solvents he was able to show that the ANs depend linearly on the appropriate α-values.[8]

Although literature data are rather scarce, we tried to correlate our ANs with the already published α-values for these ILs (Table 3 and Table 4). 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-donation values (HBD value) reported by Lungwitz et al.[10] However, a clear correlation between their parameters and our ANs was again not apparent (Figure S7 in the Supporting Information).

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. As stated by Seddon et al. in a recent paper,[66] "*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 complete and 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 a closer insight into the cation dependence of the AN and α, and also the DN and β.

Conclusion

In this work we measured Gutmann donor and acceptor numbers for a large selection of ionic liquids composed of 26 different anions and imidazolium cations of varying chain length. We found a very distinct dependence of the measured DN on the anionic component of the IL, generating liquids with DNs covering the complete range of molecular solvents and even beyond. Some ILs showed a pronounced temperature dependence of their DN, possibly enabling future temperature controlled applications.

The DN values of the ILs were compared with those of molecular solvents and those determined by other groups with identical or different measuring methods, and showed a very good agreement with these results. The DNs could also be correlated with other physicochemical parameters that describe solvent–solute interactions like the β-parameter or the "ionicity", and we found good correlations, which underlined the validity of our findings. With the help of DFT calculations to investigate the cation–anion interactions, we were able to qualitatively reproduce and confirm our findings.

The measured ANs are mainly controlled by the electrophilic properties of the imidazolium cations used, and resulted in ANs similar to those of aliphatic alcohols for most of the ILs under investigation. The ANs could also be verified with findings of other groups, and were found to be much less anion dependent than the DNs, as expected. The comparison of the ANs with α-values showed no reasonable correlation, probably originating from the different measuring techniques. This has to be studied further for a larger set of data that contain ILs with different cations.

Experimental Section

Materials: All chemicals used were of analytical reagent grade and of the highest purity commercially available. The organic solvents used for the preparation of the ILs were dried as described in the literature.[67] NaCl, $NaClO_4$, DMF, diphenylphosphorus oxychloride (Ph_2POCl) and $POEt_3$ were purchased from Acros Organics. $POEt_3$ had to be dried prior to use by dissolving it in CH_2Cl_2, addition of dry $MgSO_4$, followed by filtration and evaporation of the solvent. $POEt_3$ was obtained as white crystals. The other chemicals were used as received. [D$_6$]DMSO was purchased from Eurisotop GmbH (Saarbrücken).

Ionic liquids: All operations were performed under nitrogen atmosphere. The [emim][Cl], [emim][Br], [emim][OTf] and [emim][DCA] ILs were obtained from Solvent Innovation; [emim][OTf] and [emim][DCA] were purified before use by treating them with activated charcoal, drying under vacuum for 3–4 days, and finally storing them over molecular sieve; [emim][NTf$_2$] and [bmim][NTf$_2$] were synthesized according to an anion metathesis procedure described in the literature;[68] [emim][SnCl$_3$] was synthesized analogous to a published procedure.[69]

The [emim][NO$_3$] and [emim][NO$_2$] ILs were synthesized by ion exchange. A chromatography column was filled with Dowex-ion exchange resin (1×8 200–400 mesh) and loaded with NO_2^-, or NO_3^-, by using saturated solutions of $NaNO_2$ or $NaNO_3$, respectively. To exchange the anion, [emim]Br dissolved in a small amount of water was passed through the column until no Br^- could be detected in the eluate by addition of $AgNO_3$. The volume of the solvent was reduced and the residue was recrystallized twice from an acetone/methanol mixture (10:1). The solids were obtained as white crystals.

The [emim][ClO$_4$] IL was synthesized by a direct metathesis route (see the Supporting Information); [emim][MeOAc] was synthesized by ion exchange. A chromatography column was filled with Dowex-ion exchange resin (1×8 200–400 mesh) and loaded with OH^- by using an aqueous NaOH solution (10%). To exchange the anion, a solution of [emim]Br (1 M) was added to the column. The volume of the eluate containing [emim]OH was reduced and added drop-wise to an equimolar aqueous solution of 2-methoxyacetic acid (MeOAcH). The [emim][MeOAc] IL was obtained as a pale yellow viscous liquid by removal of water under ultrahigh vacuum (see elemental analysis and NMR spectroscopy data reported in the Supporting Information).

ILs [C$_6$mim][NTf$_2$], [C$_8$mim][NTf$_2$], [C$_{10}$mim][NTf$_2$], [C$_{12}$mim][NTf$_2$], [C$_{14}$mim][NTf$_2$], [C$_{16}$mim][NTf$_2$], [C$_{10}$mim][Cl], [emim][PF$_6$], [emim]-[Pf$_2$N], [emim][SCN], [emim][POEtHex$_2$], [emim][OcOSO$_3$], [emim]-[HexOSO$_3$], [emim][BuOSO$_3$], [emim][SbF$_6$], [emim][BF$_4$], [bmim]-[OTf], [omim][OTf], [emim][TCM], [emim][EtO$_2$PO$_2$] and [emim][Ac] were provided by courtesy of the group of Prof. Peter Wasserscheid (Chair of Chemical Engineering I, Erlangen, Germany). ILs [omim]I, [omim][NO$_3$] and [omim]Cl were provided by courtesy of the group of Prof. Hans-Peter Steinrück (Chair of Physical Chemistry II, Erlangen, Germany). A sample of [emim][FAP] was supplied by the Deutsche Forschungsgemeinschaft through SPP1191 on Ionic Liquids.

Instrumentation and measurements: Karl–Fischer titrations were done on a 756 KF Coulometer. Elemental analyses (Euro EA 3000 (Euro Vector) and EA 1108 (Carlo Erba)), and NMR spectroscopy (Bruker Avance DRX 400WB FT-spectrometer) were used for chemical analysis and compound characterization, respectively. The ^{23}Na NMR measurements were performed on a Bruker Avance DRX 400WB FT spectrometer and the ^{31}P NMR measurements on a Bruker Avance DPX 300 FT spectrometer equipped with an automatic sample changer.

Preparation of solutions and analysis of data: All IL test solutions were dried under high vacuum, overnight, prior to the measurements and were always kept under dry N_2 atmosphere. The probe substances ($NaClO_4$ and Et_3PO) were also stored and added to the IL under N_2 atmosphere. An appropriate amount of $NaClO_4$ was added to the IL samples to give 0.2 M solutions. In polar ILs with high DN it dissolved readily, but in less polar ILs a residue persisted. The IL samples were then transferred to NMR spectroscopy tubes containing sealed reference capillaries. The ^{23}Na NMR investigations were referenced to an NaCl (3 M) solution contained in the capillary. For the ^{31}P NMR measurements two capillaries had to be used, namely one filled with Ph_2POCl as pure ^{31}P reference and the other with [D$_6$]DMSO for the deuterium field lock. The recorded spectra were evaluated by using MestReC 4.9.9.3 and Win-NMR. The ^{23}Na signals had in some cases to be fitted (by using Origin 7) with Lorentz functions in order to determine the correct NMR shift values because of extreme line broadening effects.

The DN values were assigned to the ILs by using a linear calibration line consisting of values for 16 different organic solvents taken from several literature sources.[8,12] For most of the ILs these values were remeasured and compared to the literature values to verify the feasibility of our method. The calibration line had a fit coefficient of about 0.95. This divergence originated from the different analytical methods used to ascertain the DNs. Some were determined by Gutmann's original method (calorimetrically with $SbCl_5$ in dichloroethane), others by ^{23}Na NMR[14] and some were calculated by using correlations with other solvent parameters.[8] The calibration line, the employed equation and the NMR values are given in the Supporting Information.

The ANs were determined by using a linear calibration line consisting of values for 35 different organic solvents taken from Gutmann's original paper that introduced the acceptor number concept.[13] The values taken for the calibration line were the uncorrected values of the chemical shift extrapolated to infinite dilution (δ_∞), without factorization of the magnetic susceptibility, as this physical property of the ILs was, as far as we know, not measured for the complete set of ILs investigated in this study. Therefore, the NMR spectroscopy data obtained for the ILs were also used without factorization of the magnetic susceptibility for correction. Since the average deviation of the ANs calculated from δ_∞ and our calibration line compared to the ANs calculated with the corrected values (δ_{corr}) and Gutmann's original corrected calibration line, is only about ± 0.3, this simplification seems to be rather unproblematic as long as it is kept in mind. The calibration line (δ_∞) had a fit coefficient of about 0.999. The acceptor values were calculated according to the equation $\mathrm{AN}=3.76112+-2.34326\times\delta_\infty$ [ppm]. The calibration line, the employed solvents and their NMR spectroscopy data used for the calibration, are given in the Supporting Information.

DFT calculations: All structures were fully optimized by using the B3LYP hybrid density functional[70–72] and the LANL2DZ basis set augmented with polarization functions further denoted as LANL2DZp,[73–78] and characterized as minima structures by computation of vibrational frequencies (for minima, all frequencies are positive, NImag = 0). All energies were corrected for zero point energies. The Gaussian 03 suite of programs was used throughout.[79]

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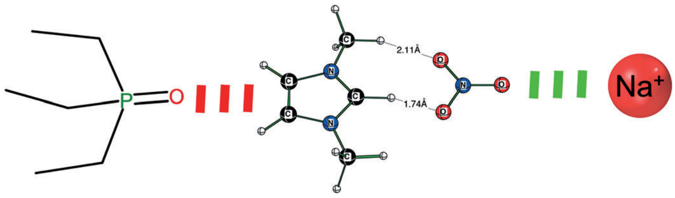
Ionic Liquids

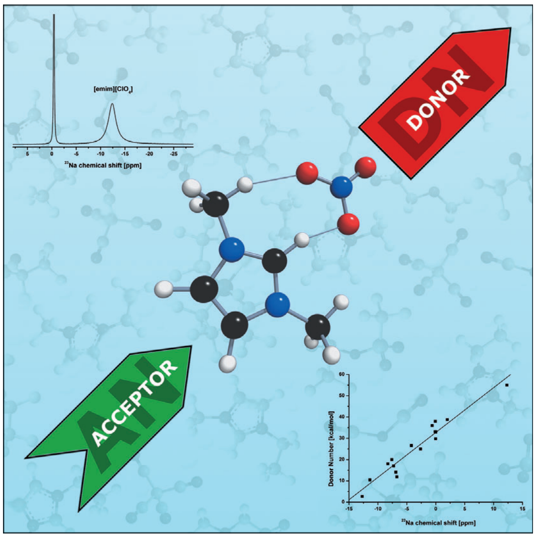
*M. Schmeisser, P. Illner, R. Puchta, A. Zahl, R. van Eldik** …… ■■■■–■■■■

Gutmann Donor and Acceptor Numbers for Ionic Liquids



Give and you shall receive: The Gutmann donor and acceptor numbers for a series of 36 different ionic liquids that include 26 distinct anions are presented. The DNs and ANs were obtained by ^{23}Na and ^{31}P NMR spectroscopy, respectively. Both values showed a strong dependence on the anionic and cationic components of the ionic liquid. The data are presented and correlated with other solvent parameters and compared to donor numbers reported by other groups.

The quantification of solvent effects…



…is an important tool to understand physicochemical phenomena in solution. According to Gutmanns' "donor–acceptor concept", the donor number is a measure for the tendency to donate electron pairs to acceptors, and the acceptor number a measure for the electrophilic properties of a solvent. To achieve a better understanding of the complex solvent–solute relationship in ionic liquids, donor and acceptor numbers for a series of 36 imidazolium based ionic liquids have been determined by using ^{23}Na and ^{31}P NMR spectroscopy. For more details see the Full Paper by R. van Eldik et al. on page ■■ ff.