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Article

A Metallacage Encapsulating Chloride as a Probe for a Solvation Scale in Ionic Liquids

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With the purpose of assessing the reactivity of chloride ions dissolved in ionic liquids (ILs), a relative scale for the solvation of chloride is given for a series of ILs based on the bis(trifluoromethane)sulfonimide ([Tf_2N]) anion and different cations, 1-butyl-3-methylimidazolium ([bmim]), 1-butyl-2,3-dimethylimidazolium ([bdmim]), 1-butyl-1-methylpyrrolidinium ([bmpy]), 1-butylpyridinium ([bpy]), 1-pentyl-1,1,1-triethylammonium ([C_5e_3am]), and 1-(2-hydroxy)-ethyl-3-methylimidazolium ([mimeOH]). Insights into the solvation of chloride are achieved by the thermodynamic study of the reaction of dissociation of a chloride-templated nickel(II) metallacage performed at various temperatures by UV–visible spectroscopy in each IL. The order of chloride solvation [C_5e_3am][Tf_2N] < [bmpy][Tf_2N] < [bmim][Tf_2N] $\leq$ [bdmim][Tf_2N] < [bpy][Tf_2N] $\ll$ [mimeOH][Tf_2N] was ascertained from the reaction enthalpies determined in the different ILs. The reaction entropies display a concentration-dependent behavior, which has highlighted a correlated motion of the ions in these ILs.

Introduction

During the last 2 decades, the number of catalyzed reactions performed in ionic liquids (ILs) has been increasing at an incredible rate.[1] Although these solvents are widely used in catalysis, their microscopic physical properties such as solvent−solute interactions remain poorly understood despite the critical role they play in the reactivity of the solutes.[2] Various methods for the estimation of the polarity of ILs have been developed using dyes[3] or more recently using an electron donor−acceptor complex,[4] fluorescent probes,[5] magnetic and paramagnetic probes,[6] or retention times of selected compounds migrating on an IL stationary phase.[7] These techniques provide polarity scales based on solvent−solute interactions that occur with the specific probe(s). However, because each solute behaves differently in a given solvent, these scales cannot be universally applied to any dissolved species.

One commonly encountered solute in ILs is chloride, often present as an impurity by virtue of the synthetic route most frequently used in their preparation, viz., chloride (or halide) metathesis.[8] It is generally accepted that chloride can poison reactions catalyzed by transition-metal complexes in ILs.[9] Moreover, the solvation of chloride in 1-butyl-3-methylimidazolium-based ILs has been related to the thermodynamics of chloride dissociation from a ruthenium(II) complex, which was directly associated with the feasibility of a catalytic hydrogenation reaction involving dissociation of chloride as the rate-determining step.[10] A better understanding of how

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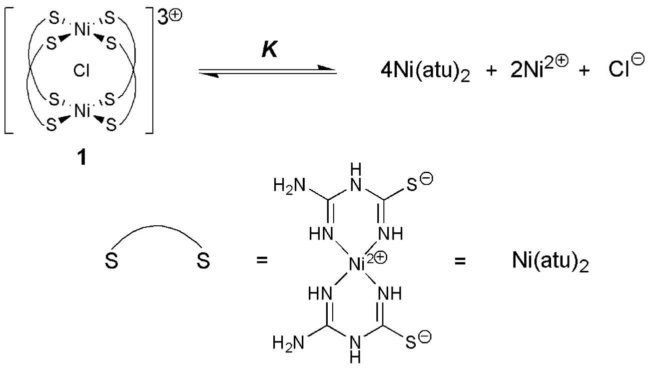
Scheme 1



efficiently an IL can solvate chloride would therefore give an appreciable insight into its reactivity in a particular IL.

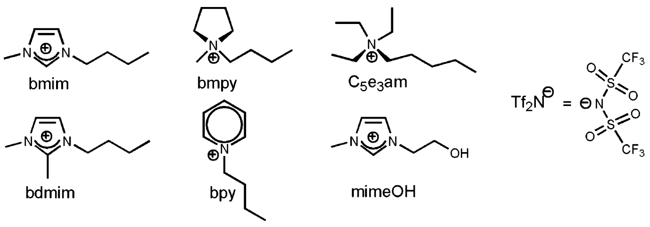
Solvent effects have often been evaluated through thermodynamic studies of a given equilibrium, mostly in organic solvents[11] but also in ILs.[12] The equilibrium constant of a keto−enol tautomerism has been determined in five ILs as well as in organic solvents by UV−visible spectrophotometry and ^{1}H NMR spectroscopy in order to assess the solvent polarity. Using a multiparameter approach describing different aspects of polarity, it was possible to estimate the dielectric constant of the ILs.

Herein, the thermodynamics for the destruction of a chloride-templated nickel(II) cage dissolved in several different ILs based on the bis(trifluoromethane)sulfonimide (Tf_2N^-) anion is evaluated. The reaction enthalpies, obtained by variable-temperature UV−visible measurements, provide a relative scale for the solvation of chloride by ILs containing different cations.

Results and Discussion

Recently, Vilar and co-workers reported the chloride-templated nickel(II) metallacage $[(Ni(atu)_2)_4Ni_2Cl][X_3]$ (**1**·X_3; Hatu = aminidothiourea, X = ClO_4), illustrated in Scheme 1.[13] Because of the strong color change that takes place upon the formation of **1** in methanol, they used it as a colorimetric sensor for quantitative chloride analysis. Besides, they have observed that dissolution of **1** in methanol leads to partial dissociation of the cage according to the equilibrium depicted in Scheme 1. Because of the release of the chloride ion into the solvent bulk, the equilibrium is strongly influenced by the solvation of chloride. Thus, the investigation of this equilibrium represents an ideal probe to evaluate the ability of a solvent (in this work an IL) to solvate chloride ions. As a result of the potentially explosive nature of perchlorate salts, the tetrafluoroborate analogue of **1** was prepared. Provided that the counteranion cannot compete with chloride in terms of its templating ability in the formation of **1**, it should not influence the equilibrium shown in Scheme 1 and consequently should not affect the outcome of this study.

Chart 1



The thermodynamics for the destruction of the cage **1** (Scheme 1) was studied in a range of ILs, [Cation][Tf_2N], where Cation = bmim, bdmim, bmpy, bpy, C_5e_3am, or mimeOH (see Chart 1). It is assumed that the nature of the IL cation affects more significantly the solvation of the negatively charged species involved in the equilibrium. A molecular dynamics study has shown that only cations are present in the first solvation shell around halides in [bmim]-[PF_6].[14] The reaction parameters, ΔH and ΔS, can be divided into two components, one of which is an intrinsic contribution strictly related to the equilibrium and one associated with the solvation of the species.[15] Consequently, a comparison of the reaction enthalpies determined in each IL provides a relative scale for the solvation of chloride in these ILs.

Solutions of **1** in [Cation][Tf_2N], where Cation = bmim, bdmim, bmpy, bpy, or C_5e_3am, were prepared, and the analytical concentration of **1**, c_0, was determined by inductively coupled plasma (ICP). Then, for each of these ILs, two more solutions were made by dilution. The analytical concentration of **1** in each solution, c, corresponds to c_0d, where d is the dilution factor. The absorption spectrum of **1** in [Cation][Tf_2N] was recorded between 450 and 800 nm at variable temperature for all sets of solutions. Figure 1 shows the temperature dependence of the absorbance of **1** in [C_5e_3-am][Tf_2N]. All of the spectra display an absorption band for **1** at 638 nm, the wavelength at which all of the absorbances, A, were measured and used for subsequent calculations. All spectra and data used for the calculations are given in the Supporting Information.

The equilibrium constant, K, can be expressed as follows, where $[c]$ is the concentration of **1** at equilibrium.

$$K = \frac{1024(c - [c])^7}{[c]} \qquad (1)$$

Equation 3 is then obtained by combining Lambert−Beer's law, eq 2, with eq 1, in which the optical pathway is 1 cm

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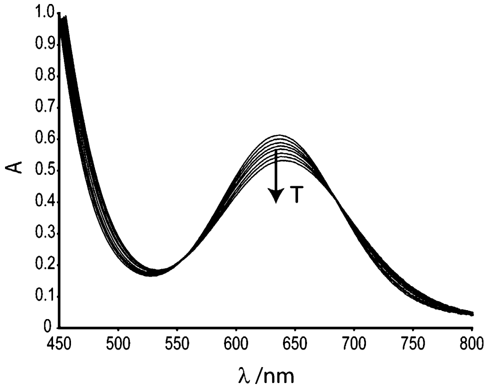

Figure 1. Absorption spectra of **1** dissolved in [C_5e_3am][Tf_2N] (0.37 mM) at different temperatures. From top to bottom (at 638 nm): 9.9, 19.4, 28.9, 38.7, 48.2, 57.8, 67.3, and 76.9 °C.

and ϵ is the molar extinction coefficient of **1** at 638 nm.

$$A = [c]\epsilon l \qquad (2)$$

$$\ln K = 7 \ln(c\epsilon - A) - \ln A + \ln 1024 - 6 \ln \epsilon \qquad (3)$$

The temperature dependence of the equilibrium constant was treated using the van't Hoff equation (eq 4), and by combination with eq 3, the inverse of the temperature can be expressed as a function of the absorbance at 638 nm according to eq 5 and is illustrated in Figure 2. These data were treated using a simultaneous least-squares-fitting procedure. The reaction enthalpy, ΔH, and the molar extinction coefficient, ϵ, were fitted with a common value for the three solutions of the same IL. The reaction entropies, ΔS_i (i = 1−3), needed to be fitted distinctly for each dilution and IL (see Figure 2). The fitted enthalpies and ϵ's are collected in Table 1.

$$\ln K = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} \qquad (4)$$

$$\frac{1}{T_i} = -\frac{R}{\Delta H}\left[7 \ln(c_0 d_i \epsilon - A_i) - \ln A_i + \ln 1024 - 6 \ln \epsilon - \frac{\Delta S_i}{R}\right] \qquad (5)$$

An independent determination of ϵ would be feasible if the solubilization of **1**·X_3 is fast compared to the dissociation that takes place to reach the equilibrium, as is the case in methanol. Unfortunately, in the ILs under study this requirement is not fulfilled; the sample preparation method prevents such measurements from being performed (see the Experimental Section).

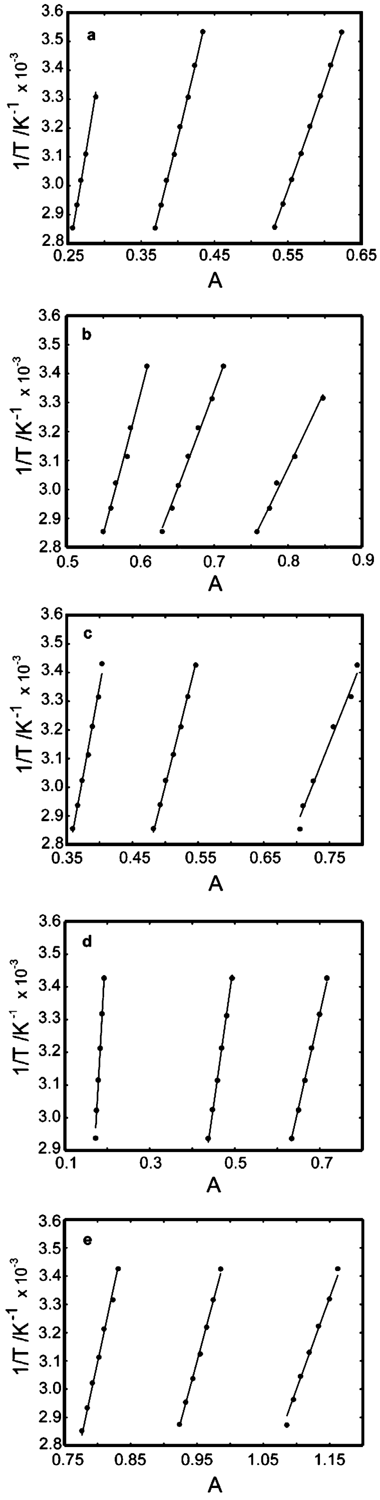

Figure 2. Temperature dependence of the absorbance of **1** at 638 nm in [Cation][Tf_2N] for three dilutions. The lines represent the calculated temperatures using the best-fitted parameters. Cation = C_5e_3am (a), bmpy (b), bmim (c), bdmim (d), and bpy (e).

Enthalpic Contribution. The reaction enthalpies vary from 4.3 kJ·mol^{-1} for [bpy][Tf_2N] to 16.8 kJ·mol^{-1} for [C_5e_3am][Tf_2N], which demonstrates a significant change with the cation. Therefore, according to the assumptions made, the influence of solvent (IL cation) is quantitatively measurable. The effect of solvent on ΔH values has often been related to the solvent polarity using different approaches for the description of polarity.[11c−e] Solvent polarity is a concept that expresses solvent properties at a molecular level, including specific and nonspecific solvent−solute and solvent−solvent interactions, and has been defined by Reichardt as *the overall solvation capability*.[16] Because of its complexity, the solvent polarity is usually not well described by macroscopic parameters such as the dielectric constant, which does not consider all of the interactions involved in the solvation

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Table 1. Best-Fit Parameters for the Temperature Dependence of the Absorbance of **1** at 638 nm in [Cation][Tf_2N] and Polarity Scales for the Selected ILs

Cation	ΔH/kJ·mol^{-1}	molar extinction coefficient/M^{-1}·cm^{-1}	dielectric constant (ϵ_r)^a	$(\epsilon_r - 1)/(\epsilon_r + 2)$	α^b	π^{*b}	E_T^N (lit.)
C_5e_3am	16.8 ± 0.1	3010 ± 13	10.0	0.750			0.764
bmpy	12.3 ± 0.3	3210 ± 50	11.9	0.784	0.427	0.954	0.617 (0.544^b)
bmim	8.6 ± 0.2	5030 ± 100	11.7	0.780	0.617	0.984	0.650 (0.644^b)
bdmim	8.2 ± 0.1	5020 ± 80	11.5	0.778	0.381	1.010	0.549 (0.541^b)
bpy	4.32 ± 0.08	10100 ± 170	11.5	0.778			0.597 (0.648^c)

^{a} Reference 19. ^{b} Reference 3c. ^{c} Reference 21.

process.[16] However, in some cases, by application of Onsager's reaction field theory,[17] the reaction enthalpy measured in various solvents has been successfully related to the dielectric constant (ϵ_r); i.e., ΔH plotted against $(\epsilon_r - 1)/(\epsilon_r + 2)$ displays a linear relationship.[11e,18] Dielectric constants of a series of ILs have been reported lately, and the values for the ILs under investigation herein are shown in Table 1.[19] In fact, no such correlation is observed between the reaction enthalpies and the dielectric constants of the ILs [Cation][Tf_2N] (see Table 1). In this situation, the solvation cannot be adequately evaluated by this parameter alone.

A polarity scale, which takes the specific solvent−solute interactions into account, should be a more appropriate way to consider the solvation of chloride in the various ILs. Among the empirical scales of solvent polarity, Dimroth−Reichardt's $E_T(30)$ (or E_T^N) scale,[20] based on solvatochromic pyridinium *N*-phenolate betaine dyes, has emerged as a good indicator of the hydrogen-bond-donor (HBD) properties of solvents[16] and is probably the most widely studied polarity scale in the IL literature.[21] Multiparameter polarity scales, such as the linear solvation energy relationships proposed by Kamlet, Abboud, and Taft (KAT), are better suited for the description of several types of solvent properties (hydrogen-bond-acceptor basicities, β, HBD acidities, α, and dipolarity/polarizability, π^*).[22] The KAT scale has been investigated by Welton and co-workers for a range of ILs.[3c] Nevertheless, we were only aware of three sets of KAT parameters corresponding to the ILs employed in this work (Table 1).[3c] E_T^N values from this work and other studies are collected in Table 1. The somewhat higher value obtained for the pentyltriethylammonium [C_5e_3am] IL is probably due to the occurrence of a Hofmann elimination reaction catalyzed by the pyridinium phenolate, which would lead to the formation of pentyldiethylammonium, which can hydrogen-bond to the dye and cause an overestimation of E_T^N. Besides the fact that the E_T^N values are more easily accessible, this scale is likely to be adequate for this study because the hydrogen-bond-acceptor ability of the IL is not relevant for the series of [Tf_2N]-based ILs under investigation. In a review, Marcus has studied the possible correlations between parameters resulting from the various polarity scales and found that the $E_T(30)$ (or E_T^N) values can be expressed as a linear combination of α and π^*.[23] However, no correlation is observed between the reaction enthalpies and E_T^N, which shows that chloride solvation in the [Cation][Tf_2N] ILs cannot be explained by this polarity scale. The HBD ability (α value) must certainly have an influence on the solvation of chloride, but it is not the only factor improving solvation. Indeed, [bmim][Tf_2N] and [bdmim][Tf_2N] display the same chloride solvation ability, although they have very different α values.[3c] Moreover, despite the lack of KAT parameters available, it is reasonable to propose that the HBD ability of [bpy][Tf_2N] is lower than that of [bmim][Tf_2N], but nevertheless [bpy][Tf_2N] solvates chloride more efficiently. The dipolarity/polarizability contribution, π^*, which increases slightly in the order [bmpy][Tf_2N] < [bmim][Tf_2N] < [bdmim][Tf_2N],[3c] may have an effect on the stabilization of the solvated chloride. Furthermore, a higher π^* value is expected for the pyridinium IL and possibly the lowest π^* value for the alkylammonium IL, which is consistent with the ΔH trend. Accordingly, the HBD ability and the dipolarity/polarizability must both contribute to the enhanced solvation of chloride in the ILs but with relative proportions that are different from the ones taking part in E_T^N.[23] The higher ΔH obtained in [bpy][Tf_2N] could also be attributed to specific anion−π interactions, which have been previously identified between halides and neutral aromatic compounds.[24]

Dissolution of **1** in [mimeOH][Tf_2N] led to a yellow solution with no observable absorption band corresponding to **1** in the UV−visible spectrum, indicating that **1** is completely dissociated in this IL because of a more efficient solvation of the chloride ion by the mimeOH cation. The higher solvation capability of the mimeOH cation was expected from its chemical structure, allowing a greater HBD ability, as further evidenced by the large E_T^N value of 0.934 (0.948[25]). Polar protic solvents are known to destabilize the chloride-templated metallacage because of the competing solvation of chloride;[13] in water, for instance, the assembly is immediately dismantled. This observation, together with the fitted reaction enthalpies, give the following trend for chloride solvation in the [Cation][Tf_2N] ILs:

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$$[C_5e_3am] < [bmpy] < [bmim] \leq [bdmim] < [bpy] << [mimeOH]$$

In a study on cation effects on halide nucleophilicity in [Tf_2N]-based ILs, the activation enthalpies for a S_N2 reaction revealed similar enthalpic costs associated with the breaking of a chloride−cation association in [bmim][Tf_2N] and [bdmim][Tf_2N] with a lower one in [bmpy][Tf_2N],[26] which is consistent with the solvation trend established here.

The molar extinction coefficients of **1** at 638 nm in the studied ILs are larger than those in methanol (417 $M^{-1}\cdot cm^{-1}$ at 643 nm)[13] and appear to be dependent on the nature of the IL cation. In the case of the imidazolium-based ILs, [bmim][Tf_2N] and [bdmim][Tf_2N], the ϵ values are about the same. Similar ϵ values are also observed for the related ammonium- and pyrrolidinium-based ILs, [C_5e_3am][Tf_2N] and [bmpy][Tf_2N]. In the pyridinium IL, [bpy][Tf_2N], the structure of which notably differs from the other ILs, **1** displays a different and higher molar extinction coefficient.

The small variations in λ_{max} indicate that the solvation of **1** is weakly affected by the type of IL. However, the larger differences in the molar extinction coefficients might result from variations in the size of the metallacage arising from different liquid structures (different packing of the ions) within the ILs. For example, a particular structure of a solute can be induced by the IL, which acts as a template.[27]

Entropic Contribution. The necessity of using three distinct reaction entropies to simultaneously fit a set of data for a given IL is a consequence of the significant dependence of ΔS on the concentration of **1**. The reaction entropy, expressed per mole of **1**, is not expected to vary with the analytical concentration of **1**. Interestingly, a linear trend is obtained when ΔS, determined in all ILs, is plotted against the molar fraction of the IL, as shown in Figure 3. According to this graph, ΔS is affected by the molar fraction of the IL but is independent of the chemical nature of the IL. Therefore, it suggests that, irrespective of the IL, a similar structural reorganization is required upon dissociation of **1**.

As mentioned above, the reaction entropy can be divided into two parts:

$$\Delta S = \Delta S_{eq} + \Delta S_{solv} \tag{6}$$

where ΔS_{eq} represents the intrinsic reaction entropy and ΔS_{solv} is the difference in entropy, per mole of **1**, due to solvation of all of the species.

The solvation contribution to ΔS depends on the solvation number of each species and is roughly proportional to the difference in solvation numbers, δN, between the products and reactants of the equilibrium. Equation 6 can then be expressed as follows:

$$\Delta S = \Delta S_{eq} + \delta S_{solv}\,\delta N \tag{7}$$

where δS_{solv} is the difference in the solvation entropy of 1 mol of solvating molecule (cation, anion, or ion pair of the IL) per 1 mol of **1**. Using a simple model, δN is a parameter that does not depend on the concentration of **1** or on the molar fraction of the solvent (IL). However, in this system, the reaction entropy is a function of the molar fraction of the IL, x(IL), according to eq 8. The intercept, B, in eq 8 does not equal ΔS_{eq} and has no physical meaning because the reaction takes place in a solution. The molar fraction of a solvent in a solution remains close to 1.

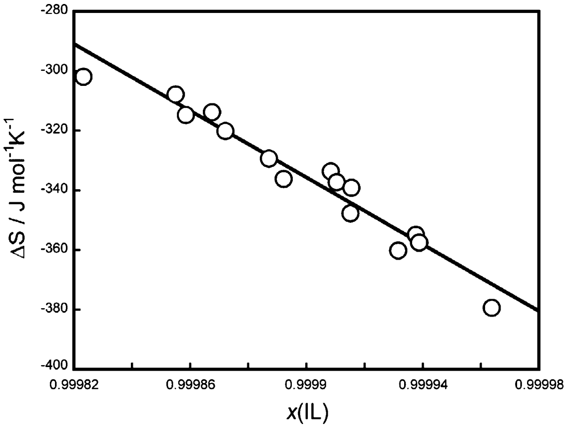

Figure 3. Linear dependence of the reaction entropy on the molar fraction of the IL. A least-squares fit of the data gives slope = $(-5.5 \pm 0.4) \times 10^5$ $J\cdot mol^{-1}\cdot K^{-1}$ and intercept = $(+5.5 \pm 0.4) \times 10^5$ $J\cdot mol^{-1}\cdot K^{-1}$ ($R^2 = 0.95$).

$$\Delta S = B + Ax(\mathrm{IL}) \tag{8}$$

The implication from eq 8 is that δN (or each individual solvation number) is not a constant but varies with x(IL), which consequently means that the solvation sphere around each species is not finite but is intimately connected to the whole bulk of IL. Our results provide evidence that rearrangement of the entire IL takes place when **1** decomposes into its components. This notion involves a correlated motion of the ions (or ion pairs) in the IL, which is supported by previously reported conductivity and diffusion measurements.[28] In these studies, it has been shown that the diffusive ions do not fully contribute to the observed conductivity. This phenomenon was attributed to the correlated motion of species of opposite charges.[28] The behavior of ILs as organized networks in the solid state as well as in the liquid state has been recently highlighted.[29] Polymeric supramolecules involving hydrogen bonding in 1,3-dialkylimidazolium salts were evidenced in the solid state by X-ray diffraction crystallography analysis, and this organized structure appears to be substantially maintained in solution, as revealed by ^1H NMR spectroscopy, conductometry, and microcalorimetry measurements.

Conclusions

A thermodynamic study for the dissociation of a nickel(II) metallacage encapsulating a chloride anion was conducted in a range of ILs in order to provide insights into the

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solvation of chloride. The determination of the reaction enthalpies provide a relative scale for chloride solvation in the [Cation][Tf_2N] set of ILs, according to the following trend: [C_5e_3am] < [bmpy] < [bmim] ≤ [bdmim] < [bpy] ≪ [mimeOH], which was not explicitly described by the conventional empirical polarity scales. The solvation capability toward chloride is the lowest in the tetraalkylammonium IL and the highest in the functionalized imidazolium IL that contains a hydroxyl group. These results indicate that it is important to select the most appropriate IL for a specific purpose where chloride ions play an important role, e.g., in catalysis (see the Introduction). A particular application may require the stabilization of the chloride ion provided by a reasonably high solvation or, conversely, a rather low solvation, which will enhances its reactivity. The solvation of chloride by [bmim] cations has been recently illustrated with a substitution reaction, in a 1:1 mixture of [bmim][Cl]/[bmim][Tf_2N], in which the "nonnucleophilic" [Tf_2N] anion was able to compete with chloride.[30] The reaction entropy was shown to be concentration-dependent, but it was not affected by the change of the IL cation and the correlation of ΔS with the molar fraction of the IL reiterates the correlated motion of ions within the IL. As far as we know, this represents a rare example of a supramolecular assembly reported in ILs.

Experimental Section

Nickel tetrafluoroborate hexahydrate (Acros, 99%), aminidothiourea (Hatu; Acros, >99%), tetrabutylammonium chloride (Fluka, >97%), 1-chlorobutane (Acros, >99%), 1-bromopentane (Acros, 98%), 2-chloroethanol (Acros, 99%), 1-methylpyrrolidine (Acros, 98%), pyridine (Acros, >99%), triethylamine (Merck, for synthesis), and $LiTf_2N$ (Fluka, >99%) were used as received, apart from 1-methylimidazole (Lancaster, 99%) and 1,2-dimethylimidazole (Acros, 98%), which were distilled from KOH prior to use. The synthesis of the metallacage [$Ni_6(atu)_8Cl$][BF_4]$_3$ (**1**) was carried out as previously described by Vilar with minor modifications.[13] The complex Ni(atu)$_2$ was first isolated from $Ni(BF_4)_2 \cdot 6H_2O$ and Hatu in methanol according to the published method,[31] then reacted with 0.5 equiv of $Ni(BF_4)_2 \cdot 6H_2O$ and 0.25 equiv of tetrabutylammonium chloride in methanol/acetone (3:1), and recrystallized from the same solvent mixture. The formation of the nickel metallacage **1** was confirmed by the presence of a characteristic absorption band at 643 nm in the UV−visible spectrum recorded in methanol.[13] The halide salts of imidazolium, pyrrolidinium, pyridinium, and ammonium cations were prepared by adapting the literature procedures.[26,32] NMR spectra were recorded on a Bruker Avance 400 spectrometer, and ^1H NMR chemical shifts were referenced to a residual solvent.

Synthesis of [Cation][Tf_2N]. The hydrophobic Tf_2N^--based ILs were synthesized via metathesis in water at room temperature with $LiTf_2N$, according to published methods.[33,34] All of these ILs were carefully washed with water to avoid the presence of halide impurities and then dried under vacuum at 70 °C for ca. 1 day. The UV−visible measurements were performed at an ambient atmosphere without precautions taken to exclude moisture. The water content in each IL was determined by Karl Fischer titration and varies between 400 ([bpy][Tf_2N]) and 1800 ([bdmim][Tf_2N]) ppm. However, it represents extremely low molar fractions of water ($5.3 \times 10^{-8}-2.3 \times 10^{-7}$) that are unlikely to modify the solvation. Moreover, the reaction enthalpies display no correlation with the water content.

Preparation of the Solutions of [$Ni_6(atu)_8Cl$][BF_4]$_3$ (1) in [Cation][Tf_2N] IL (Cation = bmim, bdmim, bpy, bmpy, C_5NEt_3, or mimeOH). A solution of **1** (5−10 mg) in methanol/acetone (3:1, ca. 1 mL) was loaded in [Cation][Tf_2N] (5−6 mL). After evaporation of the organic solvents under reduced pressure, partial precipitation of the metallacage was observed. The suspension was then centrifuged and the supernatant collected. The nickel concentration of the resulting clear green solution was determined by ICP analysis using the following procedure for the sample preparation. Aliquots of this solution were digested in 96% H_2SO_4 at 140 °C for 4 h, followed by the addition of 30% H_2O_2 at 100 °C, stirred for 2 h, and diluted to a known mass with 2% HNO_3. Two diluted solutions were prepared by weight from the stock solution of **1** in [Cation][Tf_2N].

UV−Visible Measurements. Absorbance spectra of **1**, dissolved in the various ILs, were recorded between 450 and 800 nm at variable temperature, between 10 and 80 °C, on a Perkin-Elmer Lambda 850 UV−visible spectrometer. The measurements were performed in a thermostated cuvette with an optical path length of 1 cm. After the temperature was set, the sample was allowed to reach equilibrium for ca. 30 min before acquisition was started. A blank spectrum was performed with each IL. The absorbances used in the data analysis and shown in the Supporting Information were obtained after subtraction of the blank values for each IL.

Data Analysis. The experimental data [$1/T$ vs $A(638)$] were fitted with a Levenberg−Marquardt algorithm using the *Visualiseur/Optimiseur* programs working on a *Matlab* platform.[35] The analytical concentrations of **1** were fixed to the values obtained by ICP, and the fitted parameters were the reaction enthalpies, reaction entropies, and molar extinction coefficients of **1** at 638 nm. The errors correspond to 1 standard deviation.

E_T^N Determination. A concentrated solution of Reichardt's dye (Fluka, 97%) in ethanol was micropipetted and loaded in the [Cation][Tf_2N] IL. The ethanol was then removed under vacuum at room temperature. The absorption spectrum was recorded, and the maximum absorption wavelength, λ_{max}, was determined with an absorbance between 0.4 and 1.8. The E_T^N value was calculated from λ_{max} using the standard procedure.[21]

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Supporting Information Available: UV−visible spectra of **1** in each IL at variable temperature for the different concentrations are shown in Figures S1−S15. Absorbances at 638 nm, temperature, and concentration are collected in Tables S1−S5. This material is available free of charge via the Internet at http://pubs.acs.org.

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