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Solubility of Alkali Metal Halides in the Ionic Liquid $[C_4C_1im][OTf]$

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The solubilities of the metal halides LiF, LiCl, LiBr, LiI, NaF, NaCl, NaBr, NaI, KF, KCl, KBr, KI, RbCl, CsCl, CsI, were measured at temperatures ranging from 298.15 to 378.15 K in the ionic liquid 1-butyl-3-methylimidazolium trifluoromethanesulfonate ($[C_4C_1im][OTf]$). Li^+, Na^+ and K^+ salts with anions matching the ionic liquid have been also investigated to determine how well these cations dissolve in $[C_4C_1im][OTf]$. This study compares the influence of metal cation and halide anion on the solubility of salts within this ionic liquid. The highest solubility found was for iodide salts and the lowest solubility, for the three fluoride salts. There is no outstanding difference in the solubility of salts with matching anions in comparison to halide salts. The experimental data were correlated employing several phase equilibria models, including ideal mixtures, van't Hoff, the λh (Buchowski) equation, the modified Apelblat equation, and the non-random two-liquid model (NRTL). It was found that the van't Hoff model gave the best correlation results. On the basis of the experimental data the thermodynamic dissolution parameters (ΔH, ΔS, and ΔG) were determined for the studied systems together with computed gas phase metathesis parameters. Dissolution depends on the energy difference between enthalpies of fusion and dissolution of the solute salt. This demonstrates that overcoming the lattice energy of the solid matrix is the key to the solubility of inorganic salts in ionic liquids.

Introduction

Alkali metals are elements from the first group of the periodic table of elements,[1] having one ns electron in the outer orbital and starting from Lithium (Li) to Francium (Fr). All alkali metals apart from Fr are widely used in many industrial sectors and can be found in our day to day life.

Solutions of alkali metal salts in ionic liquids have become of interest for several potential applications. The ability of ionic liquids to process metals, ionometallurgy, is an area of growing interest because of the ability to control speciation and redox properties[2] of solute salts. Most studies have concentrated on the extraction of metals from aqueous solution using ionic liquids (ILs) with different cations and anions in liquid-liquid extraction.[3,4] Other approaches for metal extraction include the use of deep eutectic solvents (DESs), which are mixtures of hydrogen bond donors with quaternary ammonium salts, to extract metals from complex matrices and metal salts.[5–8] ILs are widely used to separate metal ions through extraction, membrane, and adsorption systems.[3] ILs yield solutions that are completely different from those of salts in either traditional organic solvents or water.[9] ILs favour the extraction of charged species, and therefore, most metal ions are preferentially transported to the IL phase based on cation- or anion- exchange mechanisms.[10] There is also substantial current research into the use of ionic liquids as non-flammable electrolytes for lithium ion batteries.[11–13] The most studied ILs in this regard include tetraalkylammonium, pyridinium, piperidinium, pyrrolidinium and imidazolium cations with trifluoromethanesulfonate or bis(trifluoromethanesulfonyl)-imide imide organic anions or inorganic anions, such as $[BF_4^-]$, $[PF_6^-]$, and $[AsF_6^-]$. Another challenge in this area is the increased viscosity and insufficient conductivity of binary systems $[Li^+]_m[A^+]_n[X^-]_{(m+n)}$ formed as a result of dissolution of the LiX salt in the $[A^+][X^-]$ ionic liquid.[11]

A study of Li^+, Na^+, Cs^+, Ca^{2+}, Sr^{2+}, and La^{3+} extraction confirmed that imidazolium ILs with nonafluorobutanesulfonate ions ($[NfO]^-$) exhibit good extraction abilities from aqueous solutions.[3] The IL anion was reported to be the most important factor affecting the solubility of metal ions in ILs. However, imidazolium-based ILs have been found to be better solvents than pyridinium-, ammonium-, sulfonium- or phosphonium-based ILs for metal extraction.[10] It was also reported that there is a poor solubility of metal salts in imidazolium ILs with non-matching anions.[14] Other research groups have found that $LiNTf_2$ is more soluble than $NaNTf_2$ in $[C_2C_1im][NTf_2]$.[15]

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Recently Lui *et. al.,* using Kosower's salt, suggested that a salt dissolved in an ionic liquid can be so disassociated as to be made into an ideal solution.[9] It was found that the anion to cation charge-transfer behaviour of Kosower's salt in several ionic liquids followed a pseudo-lattice model and the solute behaved as two distinct species, a cation and an anion, completely divorced from each other (i.e. highly screened) and capable of independently interacting with the solvent ions or other solute ions. Thus, it was concluded that ionic liquids appear to form ideal mixtures of ions with the dissolved Kosower's salt. However, there are also examples of solutions of other salts in ionic liquids that do and do not show such ideal behaviour.[16] Arene halides, aprotic weakly polar solvents, were recently studied in several trifluoromethanesulfonate 1-alkyl-3-methyl imidazolium ionic liquids. The substantial difference in phase behaviour of salts in comparison to other solvents in this ILs was found.[17]

In this study, the solubilities of alkali metal halides LiF, LiCl, LiBr, LiI, NaF, NaCl, NaBr, NaI, KF, KCl, KBr, KI, RbCl, CsCl, CsI and the commercially available alkali metal trifluoromethanesulfonates (Li[OTf], K[OTf] and Na[OTf]) were measured at temperatures ranging from 298.15K (25°C) to 378.15K (105°C) in the ionic liquid 1-butyl-3-methylimidazolium trifluoromethanesulfonate ($[C_4C_1im][OTf]$). This study compares the influence of the metal cation and halide anion on the solubility of simple salts in ILs. The experimental data were correlated with the modified Apelblat, Buchowski λh, and van't Hoff equations, the ideal model, and non-random two-liquid (NRTL) model. By using the van't Hoff equation, the dissolution enthalpy, entropy, and molar Gibbs free energy of these salts in the $[C_4C_1im][OTf]$ ionic liquid were calculated. In addition, the same parameters for NaCl in a range of other ionic liquids were calculated using recently reported solubility data.[10]

Materials and Methods

Materials. Lithium fluoride, lithium bromide, lithium iodide, lithium trifluoromethanesulfonate (99.995%), sodium fluoride, sodium chloride, sodium bromide, sodium iodide, potassium fluoride, potassium bromide, potassium iodide, caesium iodide, rubidium chloride, 1-methyl imidazole and 1-chlorobutane were supplied by Sigma-Aldrich. Potassium chloride, caesium chloride and sodium bromide were purchased from Acros Organics. Sodium iodide and lithium chloride were supplied by Alfa Aesar. All salts were of 99+% purity, however they were dried before every dissolution experiment at 105 °C for 24 h *in vacuo*.

The ionic liquid, 1-butyl-3-methylimidazolium trifluoromethanesulfonate ($[C_4C_1im][OTf]$) was synthesised in two steps, as previously reported[18] and characterisations of the ionic liquid is given in the SI. The purity of the lithium salt used for this reaction played a significant role in the ionic liquid's water solubility and it is necessary to use the highest purity Li[OTf] available. $[C_4C_1im][OTf]$ was dried under vacuum at elevated temperature prior to every measurement until it had water content less than 0.01%, as determined by Karl-Fischer titration. Enthalphy of fusion was possible to determine only for K[OTf] by means of DCS analysis.

Solubility Measurements. A solubility measurement requires a pure solvent and solute, reliable and satisfactory separation of the undissolved solute from a saturated solution, and precise temperature control. Each salt was added to the ionic liquid and stirred for at least 24 h. Saturation was confirmed by observing the presence of undissolved material. Obtained saturated solutions were filtered using 0.2 µm syringe filters and glass syringes, which had been preheated to the temperature of the experiment – to ensure no precipitation would occur with a temperature change. Dissolution and filtration were performed in a glovebox under a dry nitrogen atmosphere. All samples were diluted with distilled water after filtration to prevent crystallization at room temperature and analysed using inductively coupled plasma atomic emission spectroscopy (ICP-OES). Each analysis was repeated five times, and the average recorded. Differences in the sampling method could result in slightly different results obtained which is discussed at the end of the results section. It is worth mentioning that the intensities of the spectra for Cs^+ were very low, which may result in certain errors in the determination of Cs content at low concentrations (concentrations lower than 5ppm).

Computational Details. DFT calculations have been carried out with Gaussian 09,[19] at the B3LYP/6-311+G(d,p) level.[20,21] To account for dispersion interactions Grimme's –D3 dispersion correction with the Becke and Johnson damping (BJ-damping) function has been added to the B3LYP functional.[22,23] In order to account for relativistic effects, LanL2DZ pseudo-potentials and the associated basis sets have been employed for the heavy atoms (Cs, I).[24] All structures have been optimised under no symmetry constraints and have been confirmed as minima by vibrational analysis. Optimisation convergence criteria employed are 10^{-9} on the root-mean-square density matrix and 10^{-7} on the energy matrix. The numerical integration grid was improved from the default to a pruned (optimised) grid of 99 radial shells and 590 angular points per shell. The dispersion correction combined with the diffuse nature of some of the ions (Cs and I) made convergence difficult in some cases. We report some structures which retain a single small imaginary frequency due to very low energy torsion motion of the cluster.

Results and Discussion

Solubility data modelling

A number of thermodynamic models can be used for solubility prediction; ideal mixing, van't Hoff, the λh (Buchowski) equation, the modified Apelblat equation, and the non-random two-liquid model (NRTL). Each model has been briefly described in the supplementary information.

Solubilities of the studied salts in $[C_4C_1im][OTf]$, in molar fractions, are presented in Table 1 for a range of tested temperatures. The mole fraction solubility of the salt (χ) in the solvent can be calculated by eq. 1:

Table 1. Experimental molar fractions, χ, of studied salts in [C4C1im][OTf] at T = 298.15 to 378.15 K.

Salt	χ*10^4 at temperatures, K				
	298.15	318.15	338.15	358.15	378.15
LiF	1.9	2.0	2.1	2.2	2.4
LiCl	299.1	413.8	693.0	1028.9	1143.7
LiBr	690.5	962.3	2150.0	2231.1	2611.1
LiI	2209.2	2714.3	3142.4	3328.6	4492.3
Li[OTf]	754.9	825.5	1255.2	1487.5	1526.6
NaF	0.6	0.9	1.0	1.2	1.3
NaCl	9.5	19.9	20.2	22.7	27.8
NaBr	22.0	26.8	27.4	28.8	29.8
NaI	140.4	210.8	220.1	226.1	275.2
Na[OTf]	979.6	1041.1	1156.1	2613.4	2844.3
KF	8.3	8.9	9.3	11.4	14.3
KCl	49.9	74.5	82.3	122.8	127.8
KBr	162.6	165.7	176.0	204.7	208.0
KI	1945.7	2241.7	2632.2	3004.4	3165.7
K[OTf]	1645.8	1748.4	1868.4	1967.7	2251.1
RbCl	3.7	4.4	4.7	4.8	4.9
CsCl	56.1	67.3	113.0	118.5	175.8
CsI	2414.2	2717.0	3218.0	3917.3	4032.0

$$\chi = \frac{m_1/M_1}{m_1/M_1 + m_2/M_2} \qquad \text{Eq. 1}$$

where, m_1 and m_2 represent the mass of salt and ionic liquid, respectively, and M_1 and M_2 are their respective molecular weights.

The overall average relative deviations (ARDs) of the five models were found to be 0.34% for van Hoff, 0.38% for Ideal model, 0.44% for Buchowski, 0.61% for Apelblat and 2.81% for the NRTL model. Hence, the van Hoff is the most suitable model for the description of these salts solubility behaviour. Model parameters are listed in supplementary material, Table S1.

Solubility trends

The obtained solubility data allows calculation of the thermodynamic characteristics of the studied systems. Using van't Hoff plots of the logarithm of mole fraction solubility versus the reciprocal of the absolute temperature allows for the determination of the thermodynamic parameters enthalpy (ΔH_{sol}) and entropy (ΔS_{sol}) of dissolution from the slope and the intercept, respectively (see examples of NaF and CsI at the Fig . S1).

The Gibbs free energy of solution can then be calculated employing the following equation (Eq. 2):

$$\Delta G_{sol} = \Delta H_{sol} - T\Delta S_{sol} \qquad \text{Eq. 2}$$

The calculated dissolution enthalpy, entropy, and the Gibbs free energy are presented in the Table 2.

Table 2. Thermodynamic parameters of salt solubility in [C_4C_1im][OTf] at 298,15K.

Salt	ΔH, kJ/mol	ΔS, J/mol	ΔG, kJ/mol
LiF	2.79	-62.14	21.31
LiCl	16.94	27.49	8.74
LiBr	16.62	33.85	6.53
LiI	7.57	12.77	3.76
Li[OTf]	9.43	9.89	6.48
NaF	8.09	-52.61	23.77
NaCl	10.90	-19.67	16.77
NaBr	3.27	-39.49	15.04
NaI	6.74	-12.04	10.34
Na[OTf]	14.04	26.28	6.20
KF	6.19	-38.82	17.77
KCl	11.24	-6.04	13.04
KBr	3.26	-23.57	10.29
KI	5.97	6.44	4.05
K[OTf]	3.44	-3.61	4.52
RbCl	3.25	-54.47	19.49
CsCl	13.34	1.23	12.97
CsI	6.54	10.00	3.56

The results show that the ΔH_{sol} of all the studied salts in [C_4C_1im][OTf], within the experimental temperature range examined, are endothermic ($\Delta H_{sol} > 0$), indicating that the ionic interactions for the solute salts in the ionic liquid are less favourable than sum of those within the solid inorganic salt lattice and pure ionic liquid solvent. Values of ΔH_{sol} close to zero indicate nearly athermal mixtures, in which the sum of specific interactions in the mixtures is equal to the sum of the interactions in the separated salt and ionic liquid and the solubility of the salt is being dominated by the entropy of dissolution.[25]

Thus, LiF, NaBr, KBr, RbCl and KOTf salts showing low and high solubility in [C_4C_1im][OTf] may all be considered as close-to-athermal solutions.

A number of the salts examined have negative entropy contributions. Positive values of the entropy of dissolution lead to increasing solubility with increasing temperature and suggest that the solute ions are well dissociated in the ionic liquid and that ion pairing is minimal. Very negative values of the entropy of dissolution lead to low solubilities at all temperatures and indicate increased ordering in the mixture.

Based on the calculated data, the values of the Gibbs energy of solution are positive and indicate that some (very little) external energy is needed to dissolve the studied salts in [C_4C_1im][OTf]. The negative entropies determined for these salts are interesting; many (but not all) salts exhibit increased entropy on dissolution.

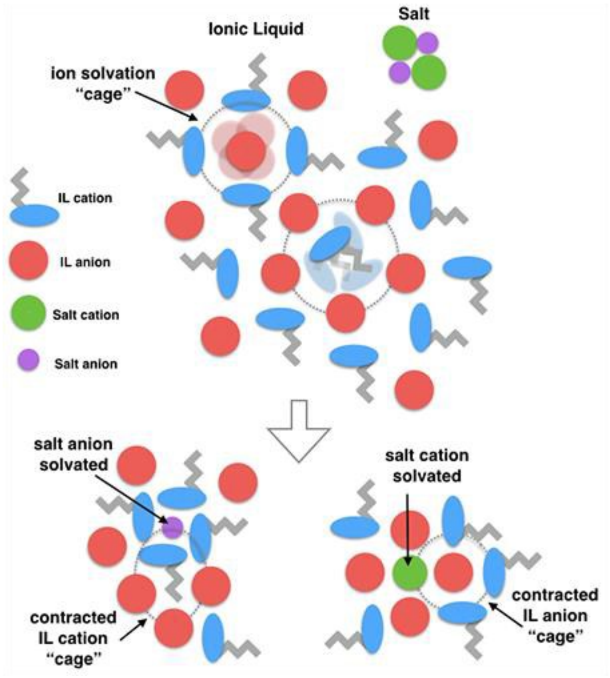

Fig. 1. Schematic representation of the solvation of salt within IL "cage" (low salt concentration).

It is difficult to be definitive about the causes for negative entropy changes, however we can comment on the potential reasons, their likelihood and consequences. Negative entropy of the addition of a solute to a solvent is not unknown, examples include dissolving hydrophobic solutes in water,[26] dissolving highly charged salts in water[27] or small solutes in polymer solutions.[28] The mechanisms promoted to explain the negative entropy are typically couched in terms of a decrease in the number of available thermodynamic states and the loss of some of its configurational entropy by the solvent. Entropy loss can take the form of a loss of possible exchange options, a restriction in movement (translation, rotation, vibration), or a restriction of dynamic features such as a loss of dynamics within a H-bond network, i.e. the solvent has become more structured. In complex solvents, structuring can occur at one level while configurational freedom is increased in another, such as self-associating solvents (i.e. the formation of carboxylic acid dimers, where the dimers remain capable of accessing a large number of microstates).

The negative entropy is for the system as a whole thus the salt in IL mixture must have less entropy than the salt and IL solution. While a definite explanation for this phenomena is not possible with the current levels of information available, we can propose a potential rationalization. The salts all have a low solubility and thus, if the bulk of the solute is unaffected, there may be a substantial loss of freedom associated with the local solute environment. For example, a small salt anion could be surrounded by strongly interacting IL-cations producing an "electrostriction" effect. The cations are pulled in towards the anion, but they are also large and thus experience mutual repulsive ionic and steric interactions.

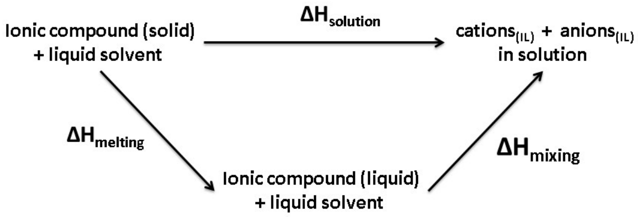

Fig. 2. Adapted Hess's Law cycle of the energy changes when a solid dissolves.

Table 3. The energy difference between fusion and dissolution (solvation) of studied salts (ΔHmix) and the molar fraction of salts that can be achieved at 298,15K.

Salt	$\chi*10^4$	ΔH_{mix}, kJ/mol
NaF	1	-25.27
LiF	2	-24.26
RbCl	4	-15.16
KF	8	-21.01
NaCl	10	-17.25
NaBr	22	-22.84
KCl	50	-15.29
CsCl	56	-2.56
NaI	140	-16.85
KBr	163	-22.24
LiCl	299	-2.96
LiBr	690	-0.98
K[OTf]	1646	-39
KI	1946	-18.03
LiI	2209	-7.04

Overall this could result in little change in the overall enthalpy, while affecting the entropy. This confinement will affect ion-exchange, translation, rotation and vibration. In ILs ions are generally considered as "caged" but with relatively facile rotational and vibrational motion within the cage.[29] The smaller cage volume due to increased local density and potentially slightly stronger (H-bonding and ionic) interactions between the ions and solute are expected to impact significantly restricting rotation. As the cations are charge balanced by anions, the local anions will become more structured, which in turn will lead to structuring of the next shell of cations.

Moreover, the IL ions are large (very large compared to water), and these effects may extend well into the solvent. Long range Coulomb effects leading to over compensation, and thus extended ordering have been noted for ILs at interfaces. Thus, the local density of ions is increased and ion motion (exchange, translation, rotation, vibration) is more limited, potentially leading to a decrease in entropy for the whole salt in IL mixture.

From the enthalpy change cycle (Fig. 2) it is clear that the melting and mixing energies of the salts need to be overcome before dissolution can occur.

The energy difference between the standard enthalpy of melting and the heat of dissolution (calculated from our experimental data) should be equal to the mixing energy and explain the different dissolution ability of salts in the IL. However, no dependence of solubility on the value of enthalpy of mixing (ΔH_{sol}-ΔH_{melt}) was found (Table 3). For example, KI and K[OTf] show quite high solubility and very negative enthalpies of mixing, which is comparable to the poorly soluble fluorides.

In an attempt to discover whether the solubilities of the alkali metal salts could be better understood and/or predicted, we compared the ΔG of dissolution to a number of different parameters. No dependence was found that encompassed all of the salts studied, but some correlations were found for subsets of the studied salts. Some linear dependencies were found for ΔG of dissolution and standard parameters of alkali halide salts, such as melting point, dissociation energy, bond length, ΔG_f, C_p, lattice energy, lattice constant and electronegativity difference (See supplementary information Fig. S2). The trend is always the same for anions of salts and correlation is in the order I-Br-Cl-F. However, no correlations with the cations were found.

It is worth noting that alkali salts with anions matching the anion of the ILs deviate from the linear trend for the salts with halide anions. This can be seen from the Fig. 3, which shows the correlation of ΔG of dissolution to melting point of salts.

The greatest solubility was shown by iodides and the poorest by fluorides. Solubility follows standard solid–liquid equilibrium (SLE) theory stating that the ideal solubility increases as T_m decreases. Knowing these dependencies for the studied alkali halides, thermodynamic parameters and solubilities can be predicted for other alkali halides that are not commercially available, such as some Rb and Cs salts.

Following recent studies of the dissolution of metal salts with matching anion as in weakly coordinating [NTf_2]-based ionic liquids,[14,30] K[OTf], Na[OTf] and Li[OTf] were studied in [C_4C_1im][OTf]. Due to the matching anion, it can be assumed that the solubility represents the dissolution affinity of the metal cation toward the ionic liquid anion. Chiappe et. al found, that when a salt anion is matched to the IL anion, the solubility increases in order Li-Na-K, which is the opposite a finding of other researchers where Li[NTf_2] was found to have greater solubility than Na[NTf_2] in [C_2C_1im][NTf_2].[31]

Thermodynamics of NaCl dissolution in other ionic liquids

Using recently published data on the dissolution of NaCl in a number of ionic liquids,[10] it was possible to calculate the thermodynamic parameters of NaCl dissolution in a these ILs, Table 4. No correlation was found between the obtained ΔG of dissolution and the standard parameters (melting point and lattice energy), Fig. S3.

Values for the thermodynamic parameters calculated from the reported solubility data[10] are very close to those obtained with solubility data in this study for the same system of NaCl in [C_4C_1im][OTf], which reassures us of the comparability of these results with those we report here.

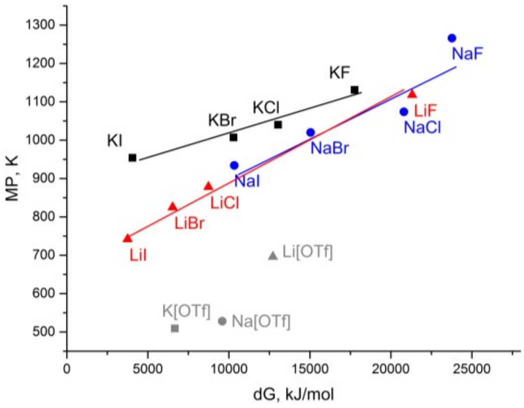

Fig. 3. Linear correlations of melting point and ΔG of dissolution for alkali metal salts. Salts with anions matching the ionic liquid anion do not fit this correlation.

Computational Studies

Our aim was to sample a range of structures for a subset of the simple ion systems.

IL ion pairs for [C_4C_1im]Cl, [C_4C_1im]I and [C_4C_1im][OTf] were generated based on the six key lowest energy structures established for [C_4C_1im]Cl; front-but, front-meth, top, bottom, side-but and side-meth.[32,33] The potential energy surface for alkyl chain rotation (all other coordinates optimised) was investigated and multiple local minima identified for each ion-pairing, SI Figures S4-S6. Relative conformer energies are reported in SI Tables S3-S5. In addition, simple ion-pairs were computed for the salts MX and M[OTf], M=Li, Na, K and Cs, X=Cl or I, SI Figure S7-S8 and Table S6.

Table 4. Thermodynamic parameters of NaCl dissolution in ILs calculated using literature solubility data [10].

IL	ΔH, kJ/mol	ΔS, J/mol*K	ΔG, kJ/mol
[C_2C_1im][C_2SO_4]	9.65	0.41	9.53
[C_2C_1im][C_1SO_3]	20.33	29.3	11.6
[C_2C_1im][DMP]	20.38	40.78	8.22
[$C_2C_1C_1$im]Cl	21.29	12.65	17.52
[C_4C_1im]Cl	19.65	3.91	18.48
[C_4C_1im][DCA]	2.63	-27.87	10.94
[C_4C_1im][OTf]	9.63	-24.68	16.99
[C_4C_1im][BF_4]	9.23	-21.92	15.77
[C_4C_1im][NTf_2]	6.05	-34.13	16.23
[C_8C_1im]Cl	31.86	63.21	13.01
[C_4C_1pyr][DCA]	5.85	-20.81	12.06
[C_4C_1pyr][TfA]	2.05	-23.87	9.17
[C_4C_1pyr][OTf]	1.39	-41.85	13.87
[C_4C_1py][DCA]	2.13	-23.52	9.14
[C_4C_1py][C_1SO_4]	8.04	-9.72	10.93
[$EtOHNMe_3$][$C_1C_1PO_4$]	9.42	6.2	7.57

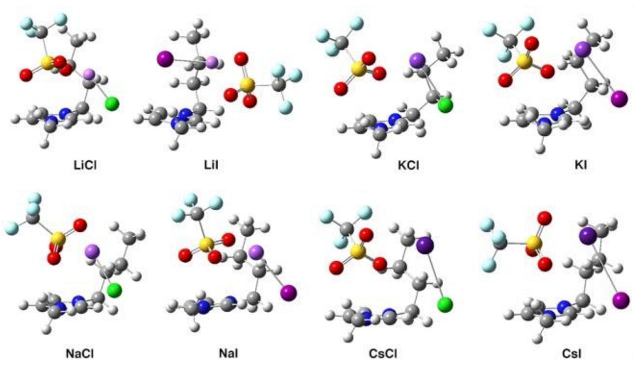

Fig. 4. Lowest energy structures obtained for the clusters of [C4C1im][OTf]MX.

Possible cluster structures (containing an IL ion-pair and salt ion pair $[C_4C_1im][OTf]MX$) were then generated using three separate approaches:

(a) the salts MX were placed in one of the 5 remaining "open" key positions around the optimised IL ion-pair $[C_4C_1im][OTf]$ and the structure optimised. This represents a salt pair interacting with an IL pair, i.e. there is no dissociation of pre-existing pairs.

(b) only the salt anion X was placed in one of the 5 remaining "open" key positions around the optimised IL ion-pairs $[C_4C_1im][OTf]$, the salt cation was then placed close to the oxygen atoms of the $[OTf]^-$ anion. Thus, in this case the salt was not added as an ion-pair but as well separated individual ions. This approach represents dissociation of MX ion pairs.

(c) starting from an optimised IL ion-pair $[C_4C_1im]X$ X=Cl, I, the salt cation was located near the salt anion, and the $[OTf]^-$ anion was placed in one of the 5 remaining key positions around the cation. In each case three orientations of the $[OTf]^-$ anion where investigated, the SO_3 group of the anion orientated up, down or with the C-S bond parallel to the imidazolium ring. This arrangement represents preferable pairing of the X anion with IL cation.

Final optimised structures are depicted in Figures S9-S16, and relative energies are reported in Tables S6-S13. The lowest energy structure obtained for each cluster type is shown in Figure 4. The most stable conformers in each case consisted of an anion in the front and top positions around the $[C_4C_1im]^+$. There was no strong preference for the larger $[OTf]^-$ anion to take the top (anion-π) position and the smaller salt anion to take the front (H-bonding) position. The salt cation, in all of the most stable structures, was positioned between the oxygen atoms of the $[OTf]^-$ anion and the salt anion. The $[OTf]^-$ anion exists on a very shallow potential energy surface with respect to rotation and reorientation of the SO_3 group, giving rise to many local minima. The alkyl chain also exhibited rotation and reorientation, leading to numerous local minima in which different CH_2 groups could interact with the anion. We have not attempted to locate all of the possible minima, but to sample a sufficient range of low energy minima.

A wide range of low energy conformers is possible < 25kJ/mol, Figure 5, these include the salt occupying the side-meth and side-but positions while the $[OTf]^-$ anion takes a top position. Both anions can take on "top" positions, and the salt or $[OTf]^-$ anions can take on a bottom position. In general, conformers with the triflate oxygen atoms directed towards the imidazolium ring are lower in energy.

The low energy conformers of the mixed IL-salt clusters are very similar and do not offer insight into the differing solubility of the salts. Conformers in which the salt cation was separated from the salt anion were ≈100 kJ/mol higher in energy. These structures are therefore significantly less stable potentially indicating that even on dissolution the salt may prefer to remain as ion-pairs rather than individually solvated ions.

We might expect to find the greatest differences between salts LiCl (two smallest ions) and CsI (two largest ions). In $[C_4C_1im][OTf]CsI$ there are low energy conformers where the $[OTf]^-$ oxygen atoms interact with Cs^+ rather than $[C_4C_1im]^+$.

Table 5. Computed metathesis ΔE_{gp}, ΔH_{gp}, $T\Delta S_{gp}$ and ΔG_{gp} (kJ/mol) in the gas-phase at the B3LYP-D3BJ/6-311+G(d,p) level relative to the experimentally determined solubility χ for salts in $[C_4C_1im][OTf]$ at T = 298.15

Salt	$\chi*10^4$	ΔE_{gp}	ΔH_{gp}	$T\Delta S_{gp}$	ΔG_{gp}	ΔH_{mix}
NaCl	9.5	15.1	-12.1	5.7	-6.4	-17.25
KCl	49.9	5.3	-2.1	6.7	4.6	-15.29
CsCl	**56.1**	**-12.1**	**15.6**	**5.2**	**20.8**	**-2.56**
NaI	140.4	0.7	2.6	5.2	7.7	-16.85
LiCl	**299.1**	**17.2**	**-14.6**	**4.5**	**-10.1**	**-2.96**
KI	1945.7	-14.8	18.3	6.2	24.5	-18.03
LiI	2209.2	-16.2	18.5	4.0	22.5	-7.04
CsI	2414.2	-29.4	33.2	4.8	38.0	-

In contrast for $[C_4C_1im][OTf]LiCl$ the O-Li interaction is much shorter and the Li^+ tends to interact with an individual oxygen atom rather than two as Cs^+ does.

We have computed (gas phase, gp) energy parameters for a metathesis reaction of reactants MX + $[C_4C_1im][OTf]$ going to products $[C_4C_1im]X$ + M[OTf] for X=Cl and I and M=Li, Na, K and Cs, Table 5 (Eq. 3):

$$\Delta E_{gp} = E_{products} - E_{reactants} \quad \text{Eq. 3}$$

A negative value indicates that products are more stable and metathesis (and hence dissolution) is favoured. In general, the

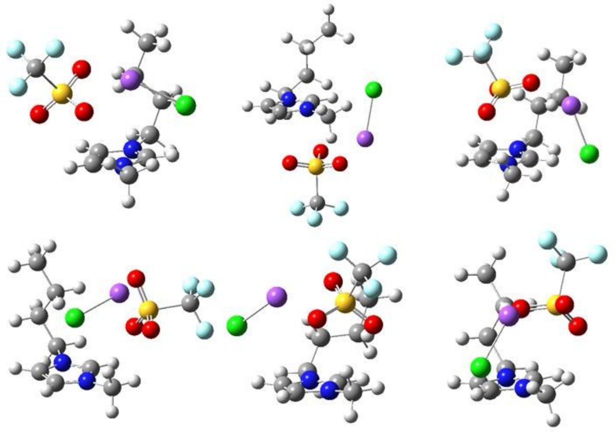

Fig. 5. Variety of structures for clusters of [C4C1im][OTf]NaCl.

lower values (or even negative values) of ΔE_{gp} are for the least soluble salts, i.e. increasing solubility correlates to increasing ΔE_{gp} in the order NaCl<KCl<NaI<KI<LiI<CsI. However, there are two clear outliers, LiCl and CsCl, which do not match the trend. Experimentally LiCl is far more soluble, and CsCl is far less soluble than is predicted based on the trend observed with ΔE_{gp}.. These two salts, LiCl and CsCl, were also found to possess the lowest energy of mixing ($\Delta H_{mix} = \Delta H_{sol} - \Delta H_{melt}$) and the highest ΔH of dissolution (Table 2) for the salts examined computationally. The deviation between the measured solubilities and predicted thermodynamic parameters could be due to more significant solvation effects for these particular chloride salts, kinetic influences on the dissolution process, or more complex speciation (i.e. dimerization) in solution.

Conclusion

The solubilities of LiF, LiCl, LiBr, LiI, NaF, NaCl, NaBr, NaI, KF, KCl, KBr, KI, RbCl, CsCl, and CsI and Li[OTf], Na[OTf] and K[OTf] were measured at temperatures ranging from 298.15 to 378.15 K in the ionic liquid, $[C_4C_1im][OTf]$. The solubility of the halide salts increases in the order of (298.15 K): F<Cl<Br<I. Solubility does not depend on the ionic radii of salts and generally increases with temperature.

The van Hoff equation appears to be the most precise model to describe the solubility of metal salts in $[C_4C_1im][OTf]$ and the correlation fit order of the models is: van't Hoff > Ideal > Buchowski > Apelblat > NRTL. This modeling data is especially important for the prediction of the dissolution behavior of the studied salts at other temperatures. Despite the ideal solubility model giving good correlations for the studied solutions, metal alkali salts do not form ideal mixtures with $[C_4C_1im][OTf]$, as was previously found for Kosower's salt in several ionic liquids.[9] Hence, in parallel with molecular systems, the degree of deviation from ideal mixing is related to the degree of similarity of the salts that are being mixed. Kosower's salt, with its large organic cation is much more similar in structure to room temperature ionic liquids than the alkali metal salts studied here.

On the basis of the experimental data the thermodynamic dissolution parameters (ΔH, ΔS, and ΔG) were determined for the studied systems. It appears that all studied dissolution processes are endothermic ($\Delta H_{sol} > 0$), and dissolution is limited by the different energies of mixing, such as the lattice energy inherent to the solid solute salts, which must be overcome during dissolution. There are some significant differences in the mechanisms of dissolution, as highlighted by the values of the dissolution entropy. Linear correlations of the free energy of dissolution and standard parameters of salts were found and could be useful for predicting dissolution of other alkali halides that were not studied in this work.

Ion pair - salt calculations were carried out and a wide range of similar low energy structures was identified for all the cluster systems studied. Subtle differences such as more directional interactions and tighter clusters for the smaller salt ions, and less directional interactions in looser cluster for the larger salt ions are evident. Nevertheless, the overall impression is that solubility differences are not related to differences in structural arrangements. Analysis of the energies for a metathesis reaction mimicking solvation found a loose trend, however LiCl and CsCl act as outliers. The negative entropy determined experimentally is not found for the simple clusters, indicating that entropic contributions from the solvent environment are important.

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