Investigations of structure property relationships of highly hygroscopic Imidazolium and Choline based ILs for the prediction of thermodynamic trends

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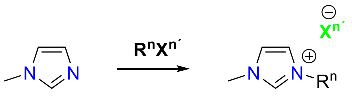
Abstract:

1,3-alkyl-imidazolium-based ionic liquids show a wide range of applications from use as a "designer solvent", in catalysis[1-3] up to material science[4-6]. The interaction between cation and anion can be investigated by analyzing the crystal structure.[7] In our work, we synthesized various 1,3-functionalized imidazolium and choline based Ils for the use as drying agent in sorption systems. Here especially substances with organic anion such as acetate, lactate and formate were quiet interesting because they expected, among other beneficial properties, a low melting point and a strongly pronounced hygroscopic behavior. However, the purification of the synthesized compounds showed a number of previously unknown crystal structures, which allowed to examine the interaction of cations and anions could be examined. In addition, the crystal structure data provided the molecular volume of the ions, which is used to predict thermodynamic aspects.

Synthesis:



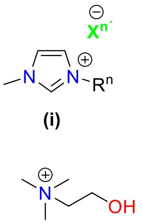
(1)

(i)

R^1 = Me ; X = I (3)
R^2 = Et ; X = Br (4)
R^3 = Pr ; X = Br (5)
R^4 = Iso ; X = Br (6)
R^5 = CH_2CH_2OH ; X = Br (7)
R^6 = CH_2COOH ; X = Cl (8)

Scheme 1

For the use in our systems, it is necessary to have liquid media, which can be pumped and preferably does not crystallize during regeneration. As a result, especially RTILs are an interesting approach to avoid this problem. The known requirements reduce the possible anions mainly to the organic ones, esp. formate, acetate, lactate and oxalate. It is understandable, that the choice of the cations results from the same considerations as for the anions. This means a relative short alkyl chain length or hydrophilic groups like alcohols or carboxylic acids attached to the 3-position in 1-methyimidazole (***Scheme 1***).



(i)

R^1 ; X = Br (10); Cl (11); Ac (12); Form (13); Lac (14); NO_3) (15)
R^2 ; X = Cl (16); I (17); Ac (18); Form (19); Lac (20); NO_3) (21)
R^3 ; X = Ac (22); Form (23); Lac (24); HCO_3) (25)
R^4 ; X = HCO_3 (26)
R^5 ; X = Ac (27); Form (28)

(i) X = Cl (2); Ac (29); Form (30)

Chart 1

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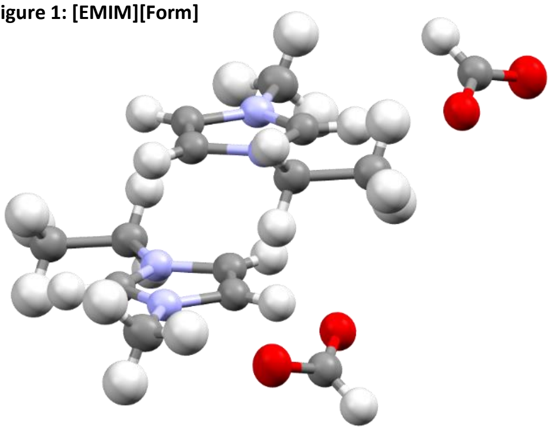
The first step to synthesize the ILs is a quarternization reaction to the imidazolium salt.[8-14] Subsequently the anion can be changed by an ion exchange column according to Alcalde et al. (***Chart 1***).[15] To verify the completeness of the exchange we analyzed the NMR Spectra and do a silver test. The high purity of these procedure is evidenced by the crystal structures of the compounds **3, 7, 8, 12, 13, 19, 25-30.**[7]

Determination of Molecular Structures:

The investigations of the crystal structures showed some interesting aspects regarding the spatial orientation of the cations to the anions. Especially the three structures **12**, **13** and **19**, which are shown in the figures below differ from each other.

Figure 1: [EMIM][Form]



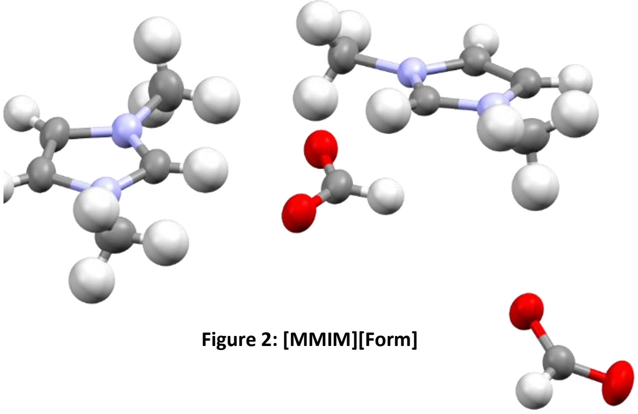


Figure 2: [MMIM][Form]

It is obvious that both formate anions are oriented with the carboxylic acid group toward the cation. In comparison, the acetate anion is arranged perpendicular to the cations in the crystal. It thus occupies a special status, since the formate and acetate variety of the alcohol-substituted imidazole also show an orientation similar to the two formate ILs.

Furthermore, some hydrogen bonds have been found in the structures, which have an influence on the packing of the ions, even if they are partly weak (**27**, **28**). Here, the bonds are electrostatically stabilized and form a bond between the anions and cations. A detailed discussion of all structures can be taken from Brünig et al. [7]

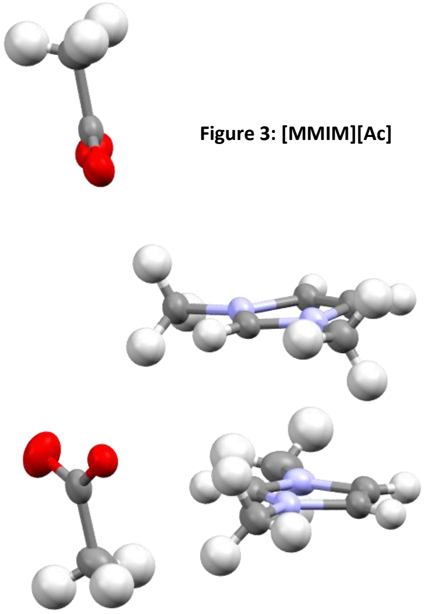


Figure 3: [MMIM][Ac]

Thermodynamic measurements:

The ITC allows an investigation of the solution process of ILs and thus a comparison with the dilution process of the salts, which are liquid at RT. By an addition of a defined amount of water, the energy of the hydration process can be recorded.

During ITC measurements the substances **12** and **13** show a transition from an initial endothermic to a subsequent exothermic process. For this transition, which give an indication of the solubility behavior, both substances require very different amounts of water. The substances [MMIM][Ac] **12** show a transition from endothermic to an exothermic signal at a ratio of about 14:1 (a mole fraction of 93.28 %) At this extremely high concentration, this process corresponds rather to a solution of the water in the ionic liquid.[16]

While the solution process of conventional salts such as LiCl or NaOH is usually strongly exothermic, the ILs investigated in our experiments (solid at RT) show an endothermic behavior. This process can be assigned to the cleavage of the lattice. The subsequent dilution, however, is strongly exothermic and is based on the formation of hydrogen bonds.

As already mentioned, for ILs the state of matter depends on the combination of cation and anion. Thus (for the [MMIM] cation), the transition from an endothermic to an exothermic signal takes place at an IL:H_2O ratio of 2:1, by changing the acetate anion to the formate one. The titration curve is shown in the lower diagram.

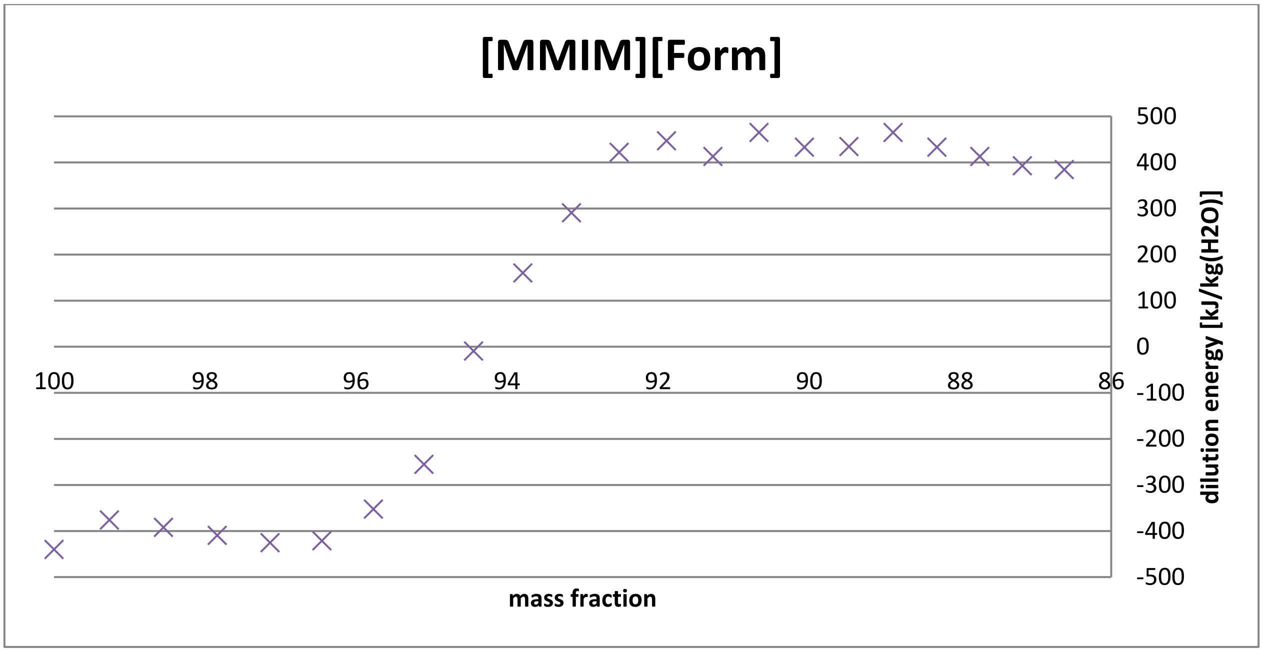


Diagram 1: A similar solution behavior in the titration analysis was found for the alcohol substituted imidazolium salts **27** and **28**.

Table 3. The table shows the different ratios for the maximum exothermic dilution enthalpy (ΔH^{dil}_{max}) and the ratio for the transition from an endothermic to an exothermic titration signal.

Ratio IL:H_2O	**[12]**	**[13]**	**[29]**	**[30]**
ΔH^{dil}_{max}	**3:1**	**3:2**	**5:2**	**5:1**
endotherm-exotherm	14:1	2:1	3:1	4:1
Ratio IL:H_2O	**[27]**	**[28]**	**[7]**	
ΔH^{dil}_{max}	**4:1**	**2:1**	**1:1**	
endotherm-exotherm	16:1	4:1	6:5	

Conclusion:

Through the use of an ITC as well as the analysis of the crystal structures, the solution process of some ILs could be elucidated and discussed. It was shown that the solution process depends thermodynamically on the combination of cation and anion. In addition, a strong endothermic behavior of some solid ILs was observed before they entered the liquid state. This endothermic dissolution process is followed by a strongly exothermic process, which usually exceeds the dilution heat of conventional salts.

Acknowledgements:

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