1. Introduction

Ionic liquids (ILs) are molecules composed of anions and cations in which at least one component is an organic molecular structure that hinders efficient close packing. Thus, their melting point temperatures are below 100 °C which differentiate them from typical inorganic salts.

ILs can have useful physical properties, such as low volatility, and are often used as solvents and electrolytes. As suitable systems for a wide range of applications they attracted the attention of many researchers.1 It turned out2 that ILs are more complex than molecular solvents and thus their bulk and interfacial structures are markedly different. They show rich structural diversity both in the nature of ions that can be employed as well as in the organization of these ions in the liquid phase. A sample of representative popular anions and cations chemical structures usually used in ILs is presented in Figure 1.2

By increasing the cationic alkyl side-chain length even the transition from the known spatially heterogeneous structure to a liquid crystal-like phase was observed.3

However, the growing number of reviews dealing with the physicochemical properties of ILs in their pure state has been extended to investigations of their mixtures with molecular cosolvents. It has been shown that ILs in solutions can serve as excellent model (electrolyte) systems, because they exist in diverse structures and the hydrophobic part of the cation can be varied almost optionally. Investigations of ion association of ILs in diverse organic solvents reveal namely that their ion pairing is entropy-driven and thus associated with cation desolvation, in line with the only moderate strength of cation-solvent interactions.4,5 The association of imidazolium based ILs as model 1,1-electrolytes in water solutions is weak but evidently dependent on the molecular structure (alkyl chain length), which also strongly affects the mobility of imidazolium cations.6 According to experimental and computational results, hydrophobic hydration of the side chain on the imidazolium ring is most responsible for structure making/breaking properties of investigated imidazolium salts.7 Ionic liquids with long alkyl chains behave similar to conventional surfactants forming aggregates in water,8 but due to possible variations in the chain length and counter-ions they are extremely appropriate for studying self-assembly processes in solutions.

Thus, ILs exhibit properties from simple salts to liquid crystal-like structures and there are still many unex-
explored opportunities for manipulating their structure to control their functions and applications.

2. Ionic Liquids in Their Pure State

The large number of cation-anion combinations and the tunability of the cation and/or the anion structure offer possibility to synthesize ILs with targeted properties. In Figure 2 a schematic representation of the different types of possible interactions in an imidazolium-based ionic liquid is presented.\(^9\) In addition, the hydrophobicity of cation can be varied by the length of side alkyl chains.

Consequently, ILs in their pure state exist in very different structures. Figure 3 shows an example for the structures in the bulk phase of imidazolium hexafluorophosphate ([C\(_n\)mim]PF\(_6\)), where the increase in the length of side chain from 2 to 12 carbon atoms leads from globular to sponge-like structure.

On the whole – dependent on the composition and building elements of an ionic liquid there are diverse possibilities for structuring – from ion pairs, hydrogen bond networking to ion clusters and – as seen already before – to self-assembled structures (Figure 4).

Thus, ILs even in their pure state form rather complicated and complex structures, whereas for example in sodium chloride, as the simplest electrolyte, the single unit has completely known and unique properties. Sodium and chloride ions have ascribed defined positions and so the structure of the NaCl crystal has no diversity,
should be easily understood and thus it is simple in comparison to different structures of ionic liquids. Therefore, ionic liquids can without doubt be judged as complex electrolytes in their pure state. The reason for this complexity is – as already mentioned – mainly in the structure of cations.

### 3. Ionic Liquids in Solutions

Whereas understanding the properties of pure ILs is of fundamental interest, the practical applications generally require the admixture of other compounds, acting either as a reactant or product or as a cosolvent required for process optimization. Some earlier investigations reveal that addition of an IL in an organic solvent enhances the electrochemical and thermal stability of IL/organic solvent binary mixtures which often reflects in higher electrical conductivity and better device performances at low temperature than comparable mixtures of salts with high melting point temperatures.

Recently, it has been demonstrated that ILs can serve as an excellent model system for investigating the influence of the ion structure on the mobility and ion pairing even in aqueous solutions, where the interionic interactions are weak. It turned out that due to possible variations in the structure of chain length and counter-ions the surface active ionic liquids (SAILs) have a great potential for investigation of micellization process in aqueous solutions. Even more, SAILs were used in investigations of aggregation behavior in non-aqueous solvents where solvophobic effect and the hydrogen-bonding interactions were found as the main factors controlling the aggregates formation.

### 3.1. Ionic Liquids in Aqueous Solutions

**Ion Mobility.** Recently, the mobility and the mechanism of ion pairing in aqueous solutions were investigated systematically on nine imidazolium based ILs from 1-methylimidazolium chloride, [mim]Cl, to 1-dodecyl-3-methylimidazolium chloride, [C12mim]Cl, with two isomers 1,2-dimethylimidazolium chloride, [1,2-mim]Cl, and 1,3-dimethylimidazolium chloride, [1,3-mim]Cl in the line. The values of their molar electric conductivity – as still one of the most suitable quantity for investigation of electrolyte solutions – for diluted solutions of the studied ILs at 298.15 K are presented on Figure 5 together with the data for NaCl aqueous solution for comparison.

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**Figure 3.** Snapshots of the bulk structure of [Cnmim][PF6] ILs for n = 2−12. Each box shows 700 IL ion pairs at equilibrium with polar domains (red, anion + cation imidazolium ring) and nonpolar domains (green, cation alkyl chain) observed. Note that the box dimensions are not of the same length due to differences in ion size and box density. Reprinted with permission from ref.2 https://pubs.acs.org/doi/10.1021/cr500411q. Further permissions related to the material excerpted should be directed to the ACS.

**Figure 4.** Different models for the bulk structure of ILs. See text for details. Reprinted with permission from ref.2 https://pubs.acs.org/doi/10.1021/cr500411q. Further permissions related to the material excerpted should be directed to the ACS.
As one can see here, the values for NaCl are only slightly higher than those for [mim]Cl. So it can be assumed that studied ILs in diluted water solution behave like simple 1,1-electrolytes – molar conductivity is linear dependent on the square root of concentration.

The experimental molar conductivity of diluted IL solutions (c ≤ 0.005 M) were analyzed in the framework of Barthel’s low-concentration chemical model (lcCM) which describes successfully thermodynamic and transport properties of diluted solutions, yielding the molar conductivity of the solute at infinite dilution, Λ∞, and the standard-state (infinite dilution) ion association constant, K_A (details are given in ref.23). By using the literature value λ∞_Cl⁻(298.15K) = 76.35 S · cm² · mol⁻¹, the limiting molar conductivity was split into separate ionic contributions, λ_i∞, and then the values of limiting ionic conductivity were estimated for all cations. Consequently, the diffusion coefficients, D_i∞, as the characteristic properties of ionic transport, which are not affected by inter ionic interactions, were calculated by using the relation

\[
D_i^\infty = \frac{k \cdot T}{e_i |z_i|^2 F^2 \Lambda_i^\infty}
\]  

(1)

Values of D_i∞ for ILs cations, studied in at 298.15 K are presented in Figure 6 as a function of the number of C atoms in the alkyl side chain, together with the values that were obtained from MD simulations that were carried out at the same temperature.6

Again, the diffusion coefficient of [mim]^+ is only slightly lower from that for Na^+, D_Na^+, (298.15 K) = 13.3 · 10⁻¹⁰ m² · s⁻¹, and D_i∞ is decreasing with increasing length...
of alkyl chain (Figure 6), but not linearly with the growing number of C atoms in the side alkyl chain as it has been also obtained by MD simulations.\(^6,24\) In addition, it was found that the aggregation tendency of cations with long alkyl chains at higher IL concentrations impedes their diffusivity.

This assumption was confirmed by the results of MD simulations at high concentrations. It was observed that within less than 1 ns \([\text{C}12\text{mim}]^+\) cations formed micelles that remained stable throughout the rest of the simulations as expected. In contrast, \([\text{mim}]^+\) cations remained dispersed in water and did not show any signs of aggregation. The cation distribution in water is visualized for these two cases in Figure 7.\(^6\) The reduction of \([\text{C}12\text{mim}]^+\) diffusivity is thus also a result of the cation aggregation. \([\text{C}12\text{mim}]^+\) cations diffuse as members of these micelle aggregates, which move much slower through the solvent than single cations because of the large aggregate sizes.

Recently, for \([\text{C}n\text{mim}]\text{Cl}\), \([\text{C}n\text{mim}]\text{Cl}\), \([\text{C}n\text{mim}]\text{Cl}\) and \([\text{C}n\text{mim}]\text{Cl}\) the data on conductivity of concentrated aqueous solutions at 298.15 K, presented in Figure 8, were published.\(^25\) To reproduce this type of concentration dependence, the empirical Casteel-Amis four-parameter equation\(^26\) is widely used. Generally, data fitting is carried out on the molality scale. For the present systems, Casteel-Amis equation can be reasonably applied in the mole-fraction scale of IL, \(x_{IL}\), that is

\[
\kappa = \kappa_{\text{max}} \left( \frac{x_{IL}}{x_{IL,\text{max}}} \right)^n \exp \left[ m \left( x_{IL} - x_{IL,\text{max}} \right)^2 \right] - n \left( \frac{x_{IL} - x_{IL,\text{max}}}{x_{IL,\text{max}}} \right)
\]  

where, \(\kappa_{\text{max}}\) is the highest electrical conductance for a given mixture, \(x_{IL,\text{max}}\) is the mole fraction of IL in which the electrical conductivity of the mixture at a given temperature shows a maximum, and \(n\) and \(m\) are parameters of the fit. Casteel-Amis parameters are given in Table S1 in the Supplementary data and fitted conductivity values are graphically presented in Figure 8. In the inset of Figure 8, the values for NaCl solutions are added for comparison.

Evidently, in all the here presented systems, conductivity increases sharply in dilute region, due to the increased number of free ions in solutions. But with the addition of ILs, it reaches maximum at nearly the same mole fraction, i.e. at around \(x_{IL} \approx 0.05\), and then it decreases. This trend is assumed to be the result of the competition between the increasing number of free ions available to contribute to the conductivity and the increasing system viscosity, impeding ion mobility. And here, the conductivity decreases also with the increasing alkyl chain length of the cation, whereas the viscosity is higher for ILs with a longer side chain. As ions are added to the system ion diffusion is hindered by increased viscous forces, resulting in a decrease in ion mobility and, thus, diffusion.

Actually, this behavior is not new – the same was observed for “common simple” electrolytes, where the maximum often was not reached due to limited solubility, as it is demonstrated here for NaCl in water (inset in Figure 8). And thus, ILs could be very helpful at studying the concentrated electrolyte solutions, where the reliable theories are still lacking.

Ion association. For in the ref.\(^6\) studied imidazolium based ILs in water it was found, that \(K_A\) values are small (~2.5 ≤ \(K_A\) ≤ ~6) but distinctly higher than obtained with the same model recently for alkali metal halides in water.\(^28\) For \([\text{C}n\text{mim}]^+\), \([\text{C}n\text{mim}]^+\) and \([\text{C}12\text{mim}]^+\), the binding free energies with \(\text{Cl}^-\), \(\Delta G_{\text{bind}}^{\text{MD}}\) and \(\Delta G_{\text{bind}}^{\text{MD}}\) were obtained also from...
MD simulations, using thermodynamic integration as specified in ref.6 From the measured values of $K_A$, binding free energies were calculated using the relation $\Delta G_{\text{bind}}^{\text{exp}} = -RT \cdot \ln K_A$. In Figure 9, the comparison of $\Delta G_{\text{bind}}^{\text{exp}}$ and $\Delta G_{\text{bind}}^{\text{MD}}$ is shown. Evidently, results from MD simulations are in reasonable agreement with the experiment.

Despite the fact that the fact that conductivity measurements of dilute electrolyte solutions are probably still the most accurate route to ion-pair association constant, $K_A$, at least for symmetrical electrolytes,23 such studies can determine only the overall association and thus yield little information on the nature of the aggregate(s) formed, while conventional spectroscopic techniques, like NMR or Raman spectroscopy, generally detect only contact CIPs.29 On the other hand, dielectric relaxation spectroscopy (DRS) is sensitive to all ion-pair types and allows their identification and quantification provided reasonably accurate dipole moments, $\mu_i$, of the species formed are available or can be calculated.30,31 Having a look on DRS spectra for $[C_4\text{mim}]\text{Cl}$ solution in water (Figure 10) we can see an area, which corresponds to ion pairs (IP).32

Thus, MD simulations and experiments reveal that the association of investigated ILs as model 1,1 electrolytes in water solutions is weak but evidently dependent on the molecular structure (alkyl chain length), which also strongly affects the mobility of cations.

3.2. Ionic liquids in Non-aqueous Solutions

Pure ILs are usually quite viscous and less conductive, whereas the mixing of ILs with molecular liquids (co-solvents) causes a significant decrease of viscosity and a sharp increase of conductivity.11–14 A huge number of investigations on conductivity of mixtures of ILs with molecular solvents is available in the literature. Surprisingly, despite the large practical interest for such systems, systematic studies of the transport properties of binary mixtures of ILs and cosolvents in a broad concentration range – from diluted solutions to pure ILs – are still scarce. Thus, in this paper we will focus our attention mainly on those imidazolium based ILs, which are also well investigated in a broader concentration range in aqueous and non-aqueous solutions and thus the comparison of their properties is possible.

Diluted solutions. In Figure 11 a) the molar conductivity of $[C_4\text{mim}]\text{Cl}$ in acetonitrile (AN),32 methanol (MeOH)5 and dimethyl sulfoxide (DMSO)5 are presented together with values in water.6 Evidently, the mobility of $[C_4\text{mim}]^+$, as indicated by the ionic limiting conductivity $\lambda_{[C_4\text{mim}]^+}$ and the diffusion coefficients $D_{[C_4\text{mim}]^+}$, is decreasing with increasing viscosity of the solvents (Table 1).

In Figure 11 b), the molar conductivity of $[C_4\text{mim}]\text{Cl}$,32 $[C_4\text{mim}]\text{BF}_4$ and – for comparison – tetra-

---

**Figure 10.** Relative permittivity, $\varepsilon'(v)$ (■) and dielectric loss, $\varepsilon''(v)$ (●) spectrum of a representative $[C_4\text{mim}]\text{Cl}$ solution in water ($c = 0.4618$ mol dm$^{-3}$) at 298.15 K. Symbols represent experimental data, lines show the corresponding fit, and the shaded areas indicate the contributions of the individual processes to $\varepsilon''(v)$. Adopted from ref.32 with permission from PCCP Owner Societies.

**Figure 11.** Molar conductivity of a) $[C_4\text{mim}]\text{Cl}$ in AN,32 water,6 MeOH5 and DMSO5 and b) $[C_4\text{mim}]\text{Cl}$,32 $[C_4\text{mim}]\text{BF}_4$ and TBABr in AN33 at 298.15 K; symbols denote experiment and lines lcCM calculations.
butylammonium bromide (TBABr)\textsuperscript{33} as “classical” electrolyte in AN are shown. While in water only weak association was observed (\(K_A \cong 5–6\)) for \([\text{C}_4\text{mim}]\text{Cl}\), it is expectedly more expressed in solvents with lower dielectric constants, but evidently depends strongly also on the anion as can be seen in Table 1, where literature data of molar limiting conductivity, \(\Lambda^\infty\), and association constants, \(K_A\), for \([\text{C}_4\text{mim}]\text{Cl}\) and \([\text{C}_4\text{mim}]\text{BF}_4\) in water, DMSO, AN, DMF, MetOH and DCM at 298.15 K are gathered, as obtained from lcCM model. Where the value of the ionic limiting conductivity \(\lambda^\infty\text{[C}_4\text{mim}\text{]+}\) is available, also the (average) values of the diffusion coefficient \(D^\infty\text{[C}_4\text{mim}\text{]+}\) are listed.

Whereas values of \(\Lambda^\infty\) are not very “sensitive” on the applied model for the analysis of conductivity data, the opposite is true for \(K_A\). Even more, \(K_A\) values are also slightly dependent on the set upper distance limit at which the ions are still treated as ion pairs. However, the abundant different interactions acting together in ILs make them very complex (Figure 2), so that it is not surprising that the dielectric constant is incapable to adequately model the solvent–solute interactions and has often failed in correlating solvent effects qualitatively and quantitatively. It is namely rather surprising, that \(K_A\) values for \([\text{C}_4\text{mim}]\text{Cl}\) and \([\text{C}_4\text{mim}]\text{BF}_4\) in AN and MetOH are different despite very similar dielectric constants of these two solvents. However, the obtained \(K_A\) values obtained from conductivity data using lcCM model make sense. It could be again concluded that ILs in solutions behave as common (“classical”) simple electrolytes, with more expressed ion association in solvents with lower dielectric constants.

### Table 1. Literature data on molar limiting conductivity, \(\Lambda^\infty\), and association constants, \(K_A\), for \([\text{C}_4\text{mim}]\text{Cl}\) and \([\text{C}_4\text{mim}]\text{BF}_4\) in water, DMSO, AN, DMF, MetOH and DCM at 298.15 K as obtained from lcCM model. Where possible, ionic limiting conductivity \(\lambda^\infty\text{[C}_4\text{mim}\text{]+}\) and the (average) values of the diffusion coefficients \(D^\infty\text{[C}_4\text{mim}\text{]+}\) are given. \(\varepsilon\) and \(\eta\) denote dielectric constant and viscosity of solvents, respectively.\textsuperscript{a}

| Solvent  | \(\varepsilon\) | \(\eta\) | \(\Lambda^\infty\text{[Cl]}\) | \(\Lambda^\infty\text{[BF}_4\text{]}\) | \(K_A\text{[Cl]}\) | \(K_A\text{[BF}_4\text{]}\) | \(\lambda^\infty\text{[C}_4\text{mim}\text{]+}\) | \(D^\infty\text{[C}_4\text{mim}\text{]+}\) |
|----------|----------------|--------|------------------|------------------|----------------|------------------|------------------|------------------|
| H\(_2\)O  | 78.36          | 0.8903 | 109.34\textsuperscript{b} | 108.64\textsuperscript{e} | 5.2\textsuperscript{d} | 6.2\textsuperscript{e} | 32.99\textsuperscript{b} | 32.29\textsuperscript{e} | 8.69            |
| DMSO     | 46.52          | 1.9946 | 38.53\textsuperscript{d} | 41.51\textsuperscript{d} | 13.4\textsuperscript{d} | 14.89\textsuperscript{d} | 14.53\textsuperscript{d} | 3.92            |
| DMF      | 36.81          | 0.845  | 89.83\textsuperscript{c} | 10.6\textsuperscript{c}  | 35.96          | 15.7\textsuperscript{c} | 17.8\textsuperscript{c} | 81.55          |
| AN       | 35.96          | 0.3413 | 173.91\textsuperscript{c} | 189.29\textsuperscript{d} | 63.7\textsuperscript{c} | 17.8\textsuperscript{c} | 81.55          | 81.81\textsuperscript{f} | 21.75          |
| MetOH    | 32.63          | 0.5438 | 108.64\textsuperscript{d} | 121.84\textsuperscript{d} | 15.5\textsuperscript{d} | 37.7\textsuperscript{d} | 57.5\textsuperscript{d} | 56.25\textsuperscript{d} | 14.98          |
| DCM      | 8.82           | 0.415  | 161.08\textsuperscript{1} | 161.08\textsuperscript{1} | 161.08\textsuperscript{1} | 161.08\textsuperscript{1} | 161.08\textsuperscript{1} | 161.08\textsuperscript{1} | 479\textsuperscript{i} |

\(\text{aUnits: } \eta, \text{ mPa} \cdot \text{s}; \Lambda^\infty, \lambda^\infty\text{[C}_4\text{mim}\text{]+}, \text{S} \cdot \text{cm}^2 \cdot \text{mol}^{-1}; D^\infty\text{[C}_4\text{mim}\text{]+}, 10^{-10} \text{m}^2 \cdot \text{s}^{-1}; \text{bref.32, cref.32, dref.34, cref.35, cref.4, cref.16, cref.17, cref.35, cref.35}\)

Concentrated solutions. Despite still growing number of studies and reviews dealing with physicochemical properties of ILs in the pure state and of their mixtures with cosolvents, the systematic studies on transport properties covering entire miscibility range are still scarce. In Figure 13 a) some literature data on conductivity of concentrated solutions of \([\text{C}_4\text{mim}]\text{BF}_4\) in AN, MetOH, DMSO, DCM, and propylene carbonate (PC, \(\eta = 2.512 \text{ mPa} \cdot \text{s}, \varepsilon = 64.96\)
at 298.15 K) are presented as determined by Stoppa et al.\textsuperscript{37} Conductivity of three imidazolium based tetrafluoroborate salts in AN from the same paper are shown in Figure 13 b) together with data on TBABr in AN\textsuperscript{38} for comparisons.

From Figure 13 it is evident that conductivity follows the typical pattern of concentrated electrolyte solutions, discussed already in paragraph 3.1. and presented in Figure 8 for aqueous solutions.\textsuperscript{6} After a rapid rise in the low concentration region, $\kappa$ passes through a well-defined maximum. As it follows from the data, presented in Figure 13 b) and table S1 in Supplementary data, $\kappa$ for ILs in AN decreases with increasing alkyl chain length of the cation, as it has been observed also for the aqueous solutions of ILs, presented in Figure 8. Whereas in water solution the position of the conductivity maximum was more or less close to the $x_{\text{IL}} \approx 0.05$, here the maximum is reached at higher concentration and it moves toward lower $x_{\text{IL}}$ with increasing length of the side alkyl chain of cation.

Figure 13 a) reveals clearly that $\kappa$ for $[\text{C}_4\text{mim}]\text{BF}_4$ depends strongly on the solvent: when the viscosity increases (AN < MetOH < DMSO < PC), $\kappa$ decreases. But DCM does not follow this order: despite the fact that its viscosity is very low (0.415 mPa s at 298.15 K), the conductivity of $[\text{C}_4\text{mim}]\text{BF}_4$ solutions in DCM is close to that in DMSO and PC with much higher solvent viscosity (Table 1). This behavior can be ascribed to higher ion association in DCM due to the lower dielectric constant. The value, obtained in diluted solutions by Borun and Bald\textsuperscript{35} ($K_A = 479$ at 298.15 K, Table 1) confirms strongly this assumption. Even more – also in other solvents the decrease of conductivity after the maximum could be ascribed to stronger ion association. Unfortunately, there is no theory to describe this behavior.

3. 3. Surface Active Ionic Liquids

Aggregation/micellization in aqueous solutions. As it is already presented in Figure 7, it was confirmed by MD simulations that $[\text{C}_{12}\text{mim}]\text{Cl}$ forms micelles at higher concentrations. Even more, the great potential of surface active ionic liquids (SAILs) at investigating the thermodynamics of micellization process in solutions due to possible variations in the structure of cations, side chain length and counter ions has been demonstrated recently.\textsuperscript{8,18,19} The systems studied recently by Šarac et al.\textsuperscript{8} are presented in Figure 14.

It was found that in many ways the behavior of SAILs is identical to that observed for “classical” cationic surfactants: the critical micelle concentration is decreasing with the length of the hydrophobic chain (Figure 15) and ex-
presses a minimum in the temperature dependence, but depends strongly also on the counter ion.\(^8\)

In general, the micellization process for SAILs is as usual endothermic at low temperatures and exothermic at high temperatures, but it was verified that counter ions play an extremely important role.\(^8\) Even more, it was confirmed, that the hydrophobicity of counter ions evidently contributes to the heat capacity change and the water accessible surface area removal upon burial of non-polar group from the contact with water during the micellization process.

The main driving force for the formation of micelles is presumably the apparent disaffinity of water for the non-polar (interacting) surfaces known as the hydrophobic effect. The parameter that illustrates this effect is the heat capacity of micellization, \(\Delta_M^C_{0p}\) which is always highly negative and can be ascribed to the removal of water molecules from contact with nonpolar surface area upon micelle formation.\(^39\) By modeling the micellization processes as a transfer of surfactant molecules into the micellar phase, the heat capacity can be expressed in terms of the change of water accessible nonpolar and polar surface areas, as derived by Spolar et al.\(^40\) from the protein folding studies:

\[
\Delta_M^C(J \cdot K^{-1} \cdot mol^{-1}) = -1.34(\pm 0.33) \cdot \Delta A_{np}^{0}(A^2) + \\
+ 0.59(\pm 0.17) \cdot \Delta A_{p}^{0}(A^2)
\]

where \(\Delta A_{np}\) stands for the loss of water accessible polar and \(\Delta A_{np}\) for nonpolar surface area upon protein folding. Because the hydrophobic head groups of non-ionic surfactants remain hydrated upon micelle formation, the “theoretical” contribution of water accessible nonpolar surface area change to the heat capacity change upon micelle formation, \(\Delta_M^C_{0p}(th_{np})\), can be assumed to reflect only the change in exposure of the hydrophobic tails to water. Consequently, the Eq. (3) is reduced to

\[
\Delta_M^C_{0p}(th_{np})(J \cdot K^{-1} \cdot mol^{-1}) = -1.34(\pm 0.33) \cdot \Delta A_{np}^{0}(A^2)
\]

This approach turned out as useful for a series of non-ionic surfactants.\(^41,42\)

According to Richards,\(^43\) water accessible surface area of a methylene group is 30 Å\(^2\) and 88 Å\(^2\) for a methyl group. Thus, \(\Delta A_{np}\) of the hydrophobic tails of the surfactants investigated in ref.\(^8\) is 358, 418, 478 and 538 Å\(^2\) for the C\(_{10}\), C\(_{12}\), C\(_{14}\) and C\(_{16}\) alkyl chain, respectively, giving the values of \(\Delta_M^C_{0p}(th_{np})\) = -479, -560, -640 and -720 J \cdot K\(^{-1}\) \cdot mol\(^{-1}\) for the same order of alkyl chains. Comparison of \(\Delta_M^C_{0p}(th_{np})\), estimated by Eq. (4) with \(\Delta_M^C_{0p}(exp)\), as illustrated in Figure 16 a), reveals that there is an evident discrepancy between \(\Delta_M^C_{0p}(th_{np})\) and \(\Delta_M^C_{0p}(exp)\). This discrepancy was explained in two ways:
a) It can be assumed that there are still water molecules in the interior of the micelle upon micellization and thus the $\Delta A_{np}$ estimated by the approach of Richards mentioned above is overestimated. That is, the "real" $\Delta A_{np}$ is smaller than according to Richards.
b) The Eq. (4) holds well for non-ionic surfactants, but it probably is not valid for ionic surfactants. Positive contribution of the removal of water accessible polar surface area to the heat capacity change of micellization should also be considered and cannot be neglected, consistent with the findings for the heat capacity change upon protein folding.

The influence of counterion on $\Delta M^c_{cp}$ for $[C_{12}mim]X$ systems is illustrated in Figure 16 b). For $[C_{12}mim]Cl$, $[C_{12}mim]Br$ and $[C_{12}mim]I$ it is obvious that the difference between $\Delta M^c_{cp} (\text{exp})$ and $\Delta M^c_{cp} (\text{thnp})$ increases along with an increase in the size of the anion. It is plausible to conjecture that the removal of water accessible polar surface area also increases along with an increase in the size of counter ion binding onto the micelle but it can be concluded that the $\Delta A_{np}$ part here cannot be neglected or/and that the hydrophobic parts of counter ions are incorporated in the micelles. In this case the contribution to the $\Delta M^c_{cp}$ of the removal of the hydrophobic part of counterion from the contact with water after micellization can be assumed. Thus, the "hydrophobic" anions (OTs$^-$, OTf$^-$, TFA$^-$ and Sal$^-$) can be partially incorporated in the micelle and the hydrophobic part of the anion can contribute to the $\Delta A_{np}$. The incorporation of counterions was already confirmed for $[C_{12}mim]OTs$ by Singh et al. using various methods and for $[C_{12}mim]OTf$ by DRS.

Recently, it was demonstrated on the dodecyltrimethylammonium chloride (DTACl) in the 0.01 M solutions of sodium ortho- ($o$-HBz$^-$), denoted previously as Sal$^-$), meta- ($m$-HBz$^-$), and para- hydroxybenzoate ($p$-HBz$^-$) that even small changes in the structure of anion of the added salt, such as the position of the substituent on an aromatic ring, considerably influence the micellization process. However, it should be kept in mind, that the micellization of DTACl in that case was studied in the presence of NaCl, which also considerably affects the self-aggregation process. To prove the influence of isomerism of counterions on micellization of surfactant in water without any added compound the study of micellization of $[C_{12}mim]o$-HBz, $[C_{12}mim]m$-HBz, $[C_{12}mim]p$-HBz together with the benzoate salt ($[C_{12}mim]HBz$) (Figure 17) was carried out recently.

It was found that the temperature dependence of cmc shows a nearly U-shaped form (Figure 18 a)) but is strongly dependent on the presence and position of the -OH group in the counterion. The micellization process is endothermic at low temperatures and becomes exothermic at higher temperatures – a phenomenon usual for ionic surfactants – for all here investigated systems, only for $[C_{12}mim]o$-HB it turned out that the micellization is exothermic in the whole investigated temperature range. It is namely well-known that $o$-HBz$^-$ provokes the formation of more compact elongated micelles by stronger interaction of $o$-HBz$^-$ with surfactant molecule and its subsequent incorporation resulting in the highest exothermicity of micellization process in the case of $o$-HBz$^-$. More details are available in ref.19

**Aggregation in non-aqueous solutions.** Whereas the aggregation behavior of SAILs in aqueous solutions is relatively well investigated and understood, studies on the aggregation of SAILs in non-aqueous solvents are scarce although they are very important in many applications. Recently, the aggregation behavior and related physicochemical properties of $[C_{12}mim]Br$ in DMSO, AN, DMF and formamide (FA) were investigated by conductivity and density measurements. It turned out that the aggregate formation in non-aqueous solutions is not as favored as in water, which is actually similar to the behavior observed for some conventional ionic surfactants by Ray. The critical aggregation concentration, cac, as a function of the empirical parameters of solvent polarity $E^\gamma N_T (30)^{49}$ is presented in Figure 19.

![Figure 17. Structures of investigated systems: a) $[C_{12}mim]^+$; b) Bz$^-$; c) $o$-HBz$^-$; d) $m$-HBz$^-$ e) $p$-HBz$^-$]
A larger \( E_N^{(30)} \) value reflects weaker interaction between hydrocarbon and the solvents. Thus, interactions of the SAILs alkyl chain with organic solvents increase with decreasing \( E_N^{(30)} \) values of the solvents. This reduces the tendency of the SAILs aggregation and increases its cac value, which should increase with decreasing \( E_N^{(30)} \) values of the solvents. Obviously, the reported data for DMF, AN and DMSO are in line with this prediction, but for FA this is not valid.\(^{20}\) Thus, despite the fact, that “solvophobic effect” of the solvents plays an important role in the aggregation of the classical surfactants\(^{20,51}\) and SAILs in non-aqueous solvents, also other factors may be important, as it is demonstrated here for the case of FA.

It is necessary to stress that DMSO, DMF and AN are aprotic solvents, while FA is a protic solvent and capable of forming hydrogen-bonds. Based on molecular dynamics simulations, Hanke et al.\(^{52}\) reported that ionic liquids are strongly solvated by the hydrogen-bonding solvents, principally by forming hydrogen bonds with the anions. This indicates that the stronger hydrogen-bonding interactions of the SAILs anions with protic solvents would result in a decrease of the binding degree of the anions at the aggregates surface. In such a case, the electrostatic repulsion between the head groups of the SAIL cannot be decreased effectively, thus weakening the tendency towards aggregation. Therefore, it seems quite likely that the solvophobic effect and the hydrogen-bonding interactions of the SAIL anions with the solvents are the main factors controlling the aggregates formation of SAILs in non-aqueous solvents. Anyway, the work of Feng and coworkers\(^{20}\) provides some very important new insight into the roles of solvophobic effect and hydrogen-bonding of non-aqueous solvents in the SAILs aggregation and supplies helpful guide how the aggregation of SAILs could be controlled and regulated by solvent properties.

4. Concluding Remarks

It can be concluded that ILs are complex in their pure state, where the structure is strongly dependent on the structures of cations and anions enabling and/or hindering the packaging and/or arrangement of IL molecules. In solutions, ILs behave like simple (“classical”) electrolytes and/or common (“classical”) surfactants, thus they are sharing the “complexity” of electrolyte solutions. But also in solutions, the structures of the ions play a very important role due to the possibility of diverse ion-ion and ion-solvent interactions. Let me mention only two fields, where the great potential of ILs due to their “tunability” of structures and properties can be used:

a) There is still a lack of theories for concentrated electrolyte solutions. Whereas for “classical” electrolytes the limited solubility could be the reason for less effort in...
studying concentrated solutions, by applying ILs the whole concentration range from pure solvent to pure electrolyte can be covered. Despite many studies, the observed maximum in the electrical conductivity (Figures 8 and 13) is still not described well and remains the challenge for the theoreticians.

b) With their wide possibilities of structures in hydrophobic part and counterions, SAILs are promising systems to study the aggregation processes in non-aqueous solutions.

Therefore, ILs can serve as excellent model systems for studying ionic interactions, hydrophobic effect, and specific ion effect to help us at broadening and deepening the knowledge on electrolyte and surfactant aqueous and non-aqueous solutions.

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**Povzetek**

Ionske tekočine sodijo med najbolj pogosto preučevane sisteme v zadnjih letih in zanimanje zanje – s poudarkom na razvoju ionskih tekočin za posebne namene kot tudi za temeljne raziskave – še vedno narašča. V tem prispevku so opisane podobnosti in razlike med običajnimi, »klasičnimi« elektroliti ter površinsko aktivnimi snovmi (surfaktanti) in ionskimi tekočinami ter površinsko aktivnimi ionskimi tekočinami. Pregled literaturnih podatkov razkrije, da se ionske tekočine v raztopinah obnašajo kot »klasični« elektroliti in jih lahko opišemo z obstoječimi modeli v območju njihove veljavnosti. Še vedno pa nimamo modelov za opis koncentriranih raztopin elektrolitov in tu lahko ionske tekočine, ki so manj omejene s topnostjo kot običajni elektroliti, služijo kot odlični modelni sistemi. Tudi micelizacijo površinsko aktivnih ionskih tekočin v vodnih raztopinah je mogoče opisati na enak način kot za običajne surfaktante, vendar površinsko aktivne ionske tekočine ponujajo več možnosti za proučevanje vpliva specifičnih ionskih in izomernih efektov na proces micelizacije. Prav tako so ionske tekočine zelo obetavni sistemi za preučevanje agregacijskih procesov v nevodnih raztopinah.