In the frame of the present project we investigated problems related to fluid interfaces, adsorption processes related to solid interfaces of atmospheric relevance, and problems related to bulk phase liquid mixtures. The main results are summarized as follows.

1. Investigation of problems related to fluid interfaces

In this part of the project we investigated fundamental problems and methodological issues related to the fluid interface, problems related to the surface of water, problems related to the surface of binary liquid mixtures, investigation of surfactants at the free water surface, and investigation of anesthetics in lipid membranes. The main results are summarized as follows.

Fundamental problems and methodological issues

As a generalization of the Identification of the Truly Interfacial Molecules (ITIM) method, developed earlier in our group for detecting the intrinsic (i.e., capillary wave corrugated) surface of condensed phases seen at atomistic resolution, we developed a new method, based on the so-called α-shapes, that is able to detect the intrinsic surface of a disordered phase even if this surface is macroscopically not planar. We developed a method of reasonable computational cost to calculate the intrinsic (i.e., relative to the capillary wave-corrugated interface) solvation free energy profile of penetrants across fluid interfaces. We found a relation between the amplitude of the molecular scale roughness of fluid interface and the surface tension. We also addressed the fluidity of the opposite phase determines the properties of a liquid surface. We described how the thermodynamic properties of fluid surfaces can be characterized by non-intrinsic and intrinsic profiles and in a layer-by-layer manner. We applied it to various profiles of the Lennard-Jones surface.

The generalized version of the ITIM method (GITIM) is based on the following principles. We determine the Delaunay triangulation of the particles (represented by points) that constitute the phase of interest, and find those elements (i.e., segments, triangles, tetrahedra) of this Delaunay triangulation that have a circumscribed sphere of a radius smaller than a pre-defined α value. These elements together form the so-called α-complex, the shape of which, called the α-shape, constitutes the boundary of the phase. We demonstrated that for macroscopically planar surfaces the GITIM method reproduces well the results of an ITIM analysis. We have also investigated the relation between the value α and the radius of the probe sphere used in the ITIM method. Through this relation we also proposed an optimal choice of the value of α. We applied the GITIM method to analyze the surface of a porous soot particle, a spherical micelle of dodecylphosphocholine, and an aggregate of bile acids.

The solvation free energy profile represents the thermodynamic driving force of a penetrants moving from one phase to another. Having the intrinsic surface of a fluid phase determined the question whether this profile can be calculated relative to this intrinsic surface can be raised naturally. However, the large computational cost of a free energy profile calculation is exacerbated here by the need of determining the intrinsic surface in every single snapshot of the trajectory, which makes this kind of calculations computationally unaccessible. The method developed by us is based on the idea that the intrinsic surface does not have to be fully determined; it is enough to know it around the projection of the penetrant. This way the computational cost of this calculation can be substantially decreased, making is computationally feasible. We applied this method for calculating the free energy profile of the Cl^- ion and the CH_4 molecule at the water-dichloroethane (DCE) liquid-liquid interface.

The profile obtained for the chloride ion was compared to its non-intrinsic version. Both profiles reached the same bulk phase values, confirming the consistency of the calculations. At the interfacial region the two profiles exhibited several important differences. Perhaps the most important of them is that in an about 0.5 nm wide region at the organic side of the interface the intrinsic profile could have not been detected due to the lack of sample points/ This finding clearly reveals that the chloride ion penetrating from the polar aqueous to the apolar organic phase brings also its hydrate shell to the apolar phase. During the transfer the “bottleneck” connecting the hydrated ion with the aqueous phase becomes gradually narrower, and finally breaks up. Just before this breakup the hydrate shell, and thus also the ion is in the aqueous phase, i.e., at the aqueous sine of the intrinsic surface. However, right after this breakup the hydrated ion is no longer part of the aqueous phase, it is in the organic phase, and the distance of the ion itself from the intrinsic surface is equal to the radius of its hydrate shell (~0.5 nm). The presence of the non-sampled region of the profile is thus a direct consequence of the co-extraction of the hydrate shell. The narrowing of the aforementioned bottleneck increases the number of water-apolar contacts, i.e., the area of the surface itself, which thus has a free energy cost. As a consequence, the intrinsic solvation free energy profile, in contrast with the non-intrinsic one, exhibits a clear maximum just before the transition of the ion to the other phase, demonstrating that the ion transport is an activated process.

The intrinsic free energy profile obtained for CH_4 turned out to be different from that of the chloride ion in several respects. First of all, the slope of the two profiles has an opposite sign as a result of the substantial difference in the solubilities of the two species in the aqueous and organic medium. Secondly, no pronounced local maximum is seen in the profile of methane, which is due to the fact that, contrary to the chloride ion, it does not pull either a water finger out of the aqueous, or a DCE finger out of the organic phase. The third main difference is the lack of an under-sampled region in the profile of methane, which is the consequence of the fact that, unlike in the case of the chloride ion, methane is transported to the apolar phase without its first hydration shell.

We found a relation between the amplitude parameter characterizing the molecular scale roughness of a liquid surface, a, introduced earlier by us, and the surface tension, γ, for a large and rather diverse group of fluids (ionic liquids, aqueous solutions, neat liquids, water containing adsorbed amphiphiles). This relation can be summarized by the equation $a^{-1} = A + B \ln(\gamma + C)$, A, B and C being tuneable parameters.

To investigate the role of fluidity of the opposite phase on the properties of the liquid surface we simulated the water-CCl4 liquid-liquid interface in two different ways. In the first simulation the CCl_4 phase has been frozen in an equilibrium configuration, and only the water molecules have been allowed to move, whilst in the other one no such artificial freezing has been done. The obtained results revealed that the rigidity of the opposite phase introduces an ordering both in the layering structure and orientation of the surface water molecules. The enhanced orientational ordering leads to a stronger lateral hydrogen bonding structure of the molecules within the subsequent molecular layers beneath the surface, and hence also to a slower exchange of the water molecules between the surface and the bulk aqueous phase.

Finally, we showed how the excess of various thermodynamic properties, such as density, energy, free energy, pressure, and surface tension can be determined at the liquid surface by calculating the (intrinsic or non-intrinsic) profiles given by the subsequent subsurface molecular layers, and also by calculating the total contribution of these layers. This result is particularly important for the pressure (and, as a consequence, for the surface tension), because of its computational burden as well as of its importance in a number of phenomena. We also shown that about 80% of the surface tension of the Lennard-Jones fluid comes from the first atomic layer at the surface, while from th ethird layer on the surface tension contribution is already negligible.

Problems related to the free water surface

In this part of the project we investigated the surface tension anomaly of water, and provided, for the first time, a molecular level explanation of it, and investigated the dynamics of the water molecules at the intrinsic water surface.

Water exhibits a number of anomalous properties, among which the surface tension anomaly, namely that the surface tension of water exhibits an inflection as a function of temperature at 530 K (and, hence, its surface entropy goes through a maximum) has never been explained. To understand the molecular level origin of this anomaly we performed a set of simulations with 6 different water models at 10-15 different temperatures around the surface tension inflection point each, and, by means of intrinsic surface analyis, determined the temperature at which the two-dimensional, lateral hydrogen bonding network of the surface molecules, being infinite at room temperature, breaks down. This percolation temperature turned out to be identical with the surface tension inflection temperature for all the six models within ±5 K. Thus, the anomalous temperature dependence of the water surface tension was explained by this percolation transition. Further, hydrogen bonding at the water surface can be well described in terms of the random bond percolation model, namely, by the assumptions that (i) every surface water molecule can form up to 3 hydrogen bonds with its lateral neighbors, and (ii) that the formation of these hydrogen bonds occurs independently from each other. It was also found that the hydrogen bonding structure of the water surface is largely model-independent at the percolation threshold; the molecules have, on average, 1.90 ± 0.07 hydrogen bonded surface neighbors. This value leads to the bonding probability of 0.633 ± 0.023 at the percolation threshold, in an excellent agreement with the value of 0.653 characteristic to the honeycomb lattice of hexagonally arranged points. This finding revealed that the water molecules at the liquid surface are forming a distorted honeycomb-like lattice, similarly to the distorted tetrahedral arrangement of the water molecules in the bulk phase.

In investigating the dynamical properties at the surface of water we found that surface molecules have a non-negligible diffusion component along the surface normal, although this component is limited in time to 7-15 ps, a value comparable with the mean surface residence time. We also found that interfacial molecules move considerably faster, and their H-bonds live shorter than in the bulk liquid phase. This finding was explained by the relation between the number of H-bonded neighbors and mobility, namely that molecules being tethered by more H-bonds move slower, and their H-bonds live longer than in the case of molecules of less extensive H-bonding. Finally, it was also found that molecules residing long at the surface are clustering around each other, forming more and longer living H-bonds within the surface layer, but much less outside this layer than other interfacial molecules, indicating that longer surface residence is related to weaker interaction with the subsurface region.

Investigation of the free surface of binary liquid mixtures

In the frame of this project we investigated the intrinsic surface of neat acetone as well as that of its mixtures with water and methanol, and that of the aqueous solutions of HCN and dimethylsulfoxide (DMSO).

In neat acetone we found that the vicinity of the vapor phase affects only the first molecular layer of the liquid phase, and its effect vanishes in every respect already in the second molecular layer. The surface acetone molecules exhibit a dual orientational preference. In their dominant orientation the molecules stay perpendicular to the macroscopic plane of the liquid surface, the C=O bond lying almost parallel with it. Besides, another alignment is also found to be preferred, in particular, at the tips of the crests of the molecularly wavy liquid surface. In this orientation, the acetone molecule lays almost parallel with the surface plane.

We have found that acetone molecules are strongly adsorbed at the surface of their aqueous solutions, and this adsorption extends to several molecular layers. The composition of the intrinsic subsurface molecular layers were found to change monotonously as moving from the bulk vapor to the bulk liquid phase. In particular, the intrinsic surface layer corresponds to an intermediate composition between the two bulk phases. On the other hand, in acetone-methanol mixtures the two molecules are distributed uniformly along the macroscopic surface normal axis, as no strong preference for surface adsorption is shown by any of them. Further, in such systems the proximity of the interface influences the properties of only the first molecular layer of the liquid phase, while the second layer already turned out to be bulk-like in every respect. Similarly to the bulk liquid phases, like molecules were found to exhibit a marked tendency for self-association within the surface layer in both types of mixtures, resulting in relatively large lateral patches of like molecules at the liquid surface. In acetone-water mixtures the orientational preferences of the surface molecules were found to be governed primarily by the dipole-dipole interaction of the neighboring acetone molecules, and hydrogen bonding interaction of the neighboring acetone-water pairs. On the other hand, in acetone-methanol mixtures surface orientations were found to be composition independent; all the preferred orientations of both molecules correspond to the same alignment of the molecular dipole vector, which is nearly parallel with the macroscopic surface plane. Thus, in these systems the surface properties are governed primarily by dipolar interactions, whereas hydrogen bonding within the surface layer, which decreases steadily with increasing acetone mole fraction, plays only a minor role in this respect.

HCN is supposed to be a key molecule of prebiotic formation of peptides, nucleotides and several other elements and precursors of bio(macro)molecules. The weak point of this assumption, known as the ‘HCN World’ hypothesis is that the HCN concentration in prebiotic times was far from being enough for providing such molecules in a sufficient rate. The HCN World hypothesis thus requires the assumption of a HCN concentrating mechanism, such as surface adsorption, to be plausible. Our results showed that although HCN is fully miscible with water, it shows strong adsorption at the surface of its aqueous solutions, and, at the liquid surface, the HCN molecules tend to be located even at the outer edge of the surface layer. It turned out that in dilute systems the HCN concentration can be about an order of magnitude larger in the surface layer than in the bulk liquid phase. Furthermore, HCN molecules show a strong lateral self-association behavior at the liquid surface, forming thus floating HCN patches at the surface of their aqueous solutions. Moreover, HCN molecules are staying, on average, an order of magnitude longer at the liquid surface than water molecules, and this behavior is more pronounced at smaller HCN concentrations. Due to this enhanced dynamic stability, the floating HCN patches can provide excellent spots for polymerization of HCN, which can be the key step in the prebiotic synthesis of, e.g., partially water soluble adenine. All these findings make the hypothesis of ‘HCN World’ more plausible.

In investigating the surface layer of water-DMSO mixtures of different compositions we found that both molecules prefer to be in mixed local environment, which consists of both kinds of molecules, and this preference is even stronger here than in the bulk liquid phase. Neat-like patches, in which a molecule is surrounded by like neighbors, are not found, however, vacancies that are surrounded solely by water molecules are observed at the liquid surface. Our results show that strongly hydrogen bonded DMSO·H_2O complexes, known to exist in the bulk phase of these mixtures, are absent from the liquid surface.

Investigation of surfactants at the free water surface

To understand the role of the headgroup charge and tail length, we analyzed the properties of the adsorption layer of five surfactant molecules at the free water surface at two different surface densities, corresponding to unsaturated and saturated adsorption layers, respectively. The surfactants were chosen in such a way that three of them have the same (alcoholic) headgroup and differ from each other only in their apolar chain lengths, while three of them have the same (dodecyl) tail, but differ in their headgroups, belonging to non-ionic, cationic and anionic surfactants, respectively. Our results showed that all surfactants prefer to point straight away from the aqueous phase by the apolar tail in the case of the saturated adsorption layer, and this preference is stronger if the headgroup of the surfactant bears a net charge. On the other hand, when the adsorption layer is unsaturated, the apolar tails prefer tilted alignment relative to the surface plane, and this tilt angle is smaller if the tail is shorter or the headgroup is charged. Apolar tails prefer rather elongated conformations, in which only a few dihedrals are *gauche*-aligned. The *gauche*/*trans* ratio turned out to be about 0.5, independently from the tail length, headgroup type, and position of the given dihedral along the tail. Unlike its orientation, the conformation of the apolar tail was found to be independent from the headgroup type. We found that in the case of the unsaturated layer the counterions prefer to stay somewhat farther away from the vapor phase than the charged headgroups, while in saturated layers this difference is washed out by the dominance of the energetic over the entropic factor in determining the counterion distribution. We also found that in the case of the saturated adsorption layer charged surfactants result in a much rougher aqueous surface (at least, in terms of its amplitude) than non-ionic ones. Concerning the immersion depth of the headgroup into the aqueous phase (in terms of molecular layers) we found a marked contrast between the behavior of the ionic and non-ionic surfactants. Thus, alcoholic surfactants are found to be located right at the water surface, their apolar tails not being considerably immersed into the aqueous phase, and the alcoholic headgroups being preferentially located in the surface layer of water. On the other hand, ionic surfactants are immersed several layers deep into the aqueous phase, headgroup atoms reaching the sixth-eighth, and tail carbon atoms the third-fourth subsurface layer in several cases. The observed difference is related, on one hand, to the ability of the alcoholic surfactants of substituting surface water molecules in their lateral hydrogen bonding network at the water surface, and that of their apolar tails for replacing dangling hydrogens, and, on the other hand, to the energetic gain of the ionic headgroups if they are fully hydrated rather than being in contact with hydrocarbon tail groups.

Investigation of anesthetics in lipid membranes

We investigated neat DPPC membrane as well as DPPC bilayers containing four different general anesthetics, i.e., chloroform, halothane, diethyl ether and enflurane at two different pressures, i.e., at 1 bar and 1000 bar. To find out which properties of the membrane might possibly be related to the molecular mechanism of anesthesia and its pressure reversal, we have been looking for properties that change in the same way in the presence of any anesthetic, and change in the opposite way by the increase of the pressure. This way, we have ruled out the density distribution of various groups along the membrane normal axis, orientation of the lipid heads and tails, self-association of the anesthetics, as well as the local order of the lipid tails as possible molecular reasons of anesthesia. We have found that the molecular surface area, and hence also the molecular volume of the membrane is increased by the presence of any anesthetic molecule, and decreased by the pressure, in accordance with the more than 50 years old critical volume hypothesis. We also found that anesthetic molecules prefer two different positions along the membrane normal axis, the middle of the membrane and the outer edge of the hydrocarbon region, close to the polar headgroups. The increase of the pressure is found to decrease the former, and increase the latter preference, and hence it might also be related to the pressure reversal of anesthesia.

2. Investigation of adsorption processes of atmospherical importance at solid interfaces

In this part of the project we investigated problems related to the adsorption of water at aerosol grains formed by various mono- and dicarboxylic acids, and the adsorption of various atmospheric pollutants at the surface of ice. The main results are summarized as follows.

Adsorption of water on aerosol grains of carboxylic acids

In the frame of this project we investigated the adsorption of water on aerosol grains built up by a dicarboxilyc acid, namely malonic acid molecules, and by two small monocarboxylic acid molecules, namely acetic and propionic acid. Particular attention was paid to the size of the neat acid aggregates as well as the temperature and pressure dependence of the adsorption, including the phase diagram of the systems studied.

In studying malonic acid aerosols we found that the equilibrium size of the neat malonic acid grains is larger than what we could reach in the simulation, thus, we could only provide a lower boundary for this value. This finding also implies that the neat malonic acid aerosol grains must be at least an order of magnitude larger than those of oxalic acid. In the presence of water the molecular structure of the system was found to be independent both from the pressure and the composition of the system; thus, temperature turned out to be the only important thermodynamic parameter concerning the behavior of the system. Below 175 K water molecules were adsorbed at the surface of the larger malonic acid grains, whereas at higher temperatures the two components formed a liquid-like mixture. These findings are in a clear contrast with our earlier results concerning oxalic acid grains, where the phase behavior of the system was also sensitive to the molar ratio of the components.

We found that aerosols of acetic and propionic acid behave similarly as water adsorbents, and both the temperature and the water content have a strong influence on the behavior of the systems. Two situations have been evidenced for the acid–water aggregates, corresponding either to water adsorption on large acid grains at very low temperatures, or to the formation of demixed droplets consisting of acid molecules adsorbed at the surface of water aggregates at higher temperatures and high water content. At low water content and high temperature, only a partial mixing between water and acid molecules was observed, in particular, at the surface of the aggregate. At moderate temperatures, an intermediate situation is obtained, which is characterized by a partial deliquescence of the acid aggregate.

Our investigations confirmed and explained the recent experimental claim that aerosols of more hydrophilic molecules (e.g., those having more carboxylic groups or shorter hydrocarbon chains) can act as more efficient cloud condensation nuclei than those of less hydrophilic molecules.

Adsorption of atmospheric pollutants at the surface of ice

In the frame of the project we investigated the adsorption of several common tropospheric compounds, namely various aromatic hydrocarbons, HCN, H_2O_2, as well as methylene fluoride and methylene chloride at the surface of I_h ice under tropospheric conditions by means of Grand Canonical Monte Carlo simulations. Besides determining the adsorption isotherms we have also analyzed the layering, orientation and energetics of the adsorption layer in every case.

Concerning the adsorption of aromatic hydrocarbons, we determined the adsorption isotherm of benzene, naphtalene, anthracene, and phenantrene at the surface of ice. We found that the adsorption follows the Langmuir mechanism only up to a rather low relative pressure value in every case. In this range specific surface sites, called α sites, to which adsorbate molecules can particularly strongly be bound in specific orientation, are occupied. In these α sites presumably the dangling OH bonds of the ice surface form O-H$\cdots\pi$ type hydrogen bonds with the delocalized π electrons of the adsorbed aromatic molecule lying parallel with the ice surface. Once these α sites are saturated, lateral interactions become increasingly important, leading to large fluctuations of the lateral density of the adsorption layer, and an increasing deviation of the adsorption isotherm from the Langmuir shape. The adsorption layer is found to be strictly monomolecular and even unsaturated in every case, as condensation well precedes the saturation of this monolayer for all the four aromatic adsorbates considered in this study.

In the case of HCN the adsorption isotherm turned out to be of Langmuir shape, and the saturated adsorption layer was found to be practically monomolecular, however, lateral interactions were found to have a non-negligible effect on the adsorption. The Langmuir shape of the isotherm can be rationalized by the fact that the interaction energy for HCN-water and HCN-HCN pairs is rather close to each other, and hence monomolecular adsorption even in the presence of lateral interactions turns into a special case. At low surface coverages the HCN molecules prefer a tilted orientation, pointing by the N atom flatly toward the ice surface, in which they can form a strong O-H$\cdots$N type hydrogen bond with the surface water molecules. At high surface coverages, an opposite tilted orientation is preferred, in which the H atom points toward the ice phase and the HCN molecule can form only a weak C-H$\cdots$O type hydrogen bond with a surface water molecule. This orientational change is dictated by the smaller surface area occupied by a H than a N atom, and the corresponding energy loss is (over)compensated by the formation of C-H$\cdots$N type hydrogen bonds between neighboring HCN molecules.

In the case of H_2O_2 the obtained results, in qualitative agreement with available experimental data, revealed that the main driving force of the adsorption is the formation of new H_2O_2-H_2O_2 rather than H_2O_2-water H-bonds. The adsorption isotherm belongs to class III, and not even its low pressure part can be described by the Langmuir formalism. At low coverages H_2O_2 prefers perpendicular alignment to the surface, in which they can form three H-bonds with surface waters. At higher coverages parallel alignment, stabilized by H-bonds between neighbouring H_2O_2 molecules becomes increasingly preferred.

We found that while methylene fluoride exhibits multilayer adsorption, and its adsorption isotherm belongs to class II according to the IUPAC convention, methylene chloride does not show considerable adsorption. Both the surface orientation and the binding energy of the two molecules turned out to be rather similar to each other; first layer molecules form one single hydrogen bond with the dangling OH groups of the ice surface. A much stronger difference is seen, however, in the magnitude of the lateral interactions, in particular, in multilayer systems. This energy reflects the cohesion of the molecules in the condensed phase rather than the energetics of the adsorption. The average lateral binding energy contribution in condensed methylene chloride is almost twice as large in magnitude then in methylene fluoride. This difference, which is also reflected in the markedly different boiling points, is responsible for the different adsorption behavior of the two molecules. Namely, methylene chloride does not adsorb considerably at the surface of ice because, unlike methylene fluoride, it condenses well before the building up of even the first adsorbed molecular layer.

3. Investigation of bulk phase liquid mixtures

In this part of the project we studied the thermodynamics of mixing acetone with methanol and that of water with DMSO by means of thermodynamic integration, investigated the local environment of the molecules in bulk water-DMSO mixtures of various compositions through the properties of the Voronoi polyhedra of the molecules, and investigated the local microscopic structure in ionic liquids using a nearest neighbor approach.

We investigated in the entire composition range at the thermodynamic properties accompanying the mixing (i.e., Helmholtz free energy, energy and entropy of mixing) of methanol and acetone using three methanol and two acetone models, and that of water and DMSO using four conventional water and eight DMSO models. For methanol-acetone mixtures we found a model combination that not only reproduces qualitatively the full miscibility of the two components, but also reproduces very accurately (i.e., within 0.3 kJ/mol) the change of the thermodynamic quantities (i.e., nergy, free energy, TS) upon mixing. For water-DMSO mixtures all the 32 model combinations turned out to be able to reproduce the experimental values rather well, within RT (free energy and energy) and R (entropy) at any composition, and quite often the deviation from the experimental data is even smaller, being in the order of the uncertainty of the calculated free energy or energy, and entropy values of 0.1 kJ/mol and 0.1 J/mol K, respectively. On the other hand, none of the model combinations considered can accurately reproduce all the three experimental functions simultaneously. Furthermore, the fact that the entropy of mixing changes sign with increasing DMSO mole fraction is only reproduced by a handful of model pairs. Model combinations that (i) give the best reproduction of the experimental free energy, while still reasonably well reproducing the experimental energy and entropy of mixing; and (ii) that give the best reproduction of the experimental energy and entropy, while still reasonably well reproducing the experimental free energy of mixing are identified. We also found that the full miscibility of methanol and acetone is of entropic, while that of water and DMSO is of energetic origin. As a consequence, methanol-acetone mixtures are of microheterogeneous structure, while for water-DMSO mixtures no such microheterogeneities are expected.

Concerning the local structure of water-DMSO mixtures, our results showed that both molecules prefer to be in an environment consisting of both types of molecules, but the affinity of DMSO for mixing with water is clearly stronger than that of water for mixing with DMSO. As a consequence, the dilution of the two neat liquids by the other component has been found to follow different mechanisms: when DMSO is added to neat water small domains of neat-like water persist up to the equimolar composition, whereas no such domains are found when neat DMSO is diluted by water. The observed behavior is also in line with the fact that the main thermodynamic driving force behind the full miscibility of water and DMSO is the energy change accompanying their mixing, and that the entropy change accompanying this mixing is negative in systems of low, and positive in systems of high DMSO mole fractions. We have also found a direct evidence for the existence of strong hydrogen bonded complexes formed by one DMSO and two water molecules, but it has also been shown that these complexes are in equilibrium with single (monomeric) water and DMSO molecules in the mixed systems. These structural results are in full accordance with the expectations concerning the lack of microheterogeneities, based on the thermodynamic analysis of the mixing of these two components.

Concerning the ionic liquids, we studied in detail the spatial, radial, and orientational relative distribution of ions in a set of imidazolium-based liquids, in which the 1-butyl-3-methylimidazolium (C_4mim^+) cation is coupled with the acetate (OAc^-), chloride (Cl^-), tetrafluoroborate (BF_4^-), hexafluorophosphate (PF_6^-), trifluoromethanesulfonate (TfO^-), or bis(trifluoromethanesulfonyl)amide ($TFSA^-$) anion. It was established that several structural properties are strongly anion-specific, while some can be treated as universally applicable to ionic liquids, regardless of the nature of the anion. Namely, strongly basic anions, such as OAc^- and Cl^-, prefer to be located in the imidazolium ring plane next to the $C–H^{2/4–5}$ sites. By contrast, the other four bulky and weakly coordinating anions tend to occupy positions above/below the plane. Similarly, the H-bond-like interactions involving the H^2 site are found to be particularly enhanced in comparison with the ones at $H^{4–5}$ in the case of asymmetric and/or more basic anions (C_4mimOAc, C_4mimCl, C_4mimTfO, and C_4mimTFSA), in accordance with recent spectroscopic and theoretical findings. Other IL-specific details related to the multiple H-bond-like binding and cation stacking issues are also discussed in this paper. The secondary H-bonding of anions with the alkyl hydrogen atoms of cations as well as the cation–cation alkyl chain aggregation turned out to be poorly sensitive to the nature of the anion.