

Chasing Aqueous Biphasic Systems from simple salts by exploring the LiTFSI / LiCl / H₂O phase diagram

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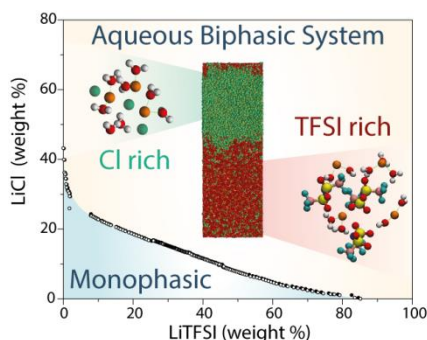
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The phase diagram of ternary LiTFSI / LiCl / H₂O mixtures reveals the possibility to form Aqueous Biphasic Systems with simple monovalent salts with a common cation.

Abstract: Aqueous Biphasic Systems (ABS), in which two aqueous phases with different compositions coexist as separate liquids, have first been reported over a century ago with polymer solutions. Recent observations of ABS forming from concentrated mixtures of inorganic salts and ionic liquids raise the fundamental question of how "different" the components of such mixtures should be for a liquid-liquid phase separation to occur. Here we show that even two monovalent salts sharing a common cation (lithium) but with different anions, namely LiCl and lithium bis(trifluoromethanesulfonyl)imide (LiTFSI), may result in the formation of ABSs over a wide range of compositions at room temperature. Using a combination of experimental techniques and molecular simulations, we analyze the coexistence diagram and the mechanism driving the phase separation, arising from the different anion sizes. The understanding and control of ABS may provide new avenues for aqueous-based battery systems.

The development of aqueous Li-ion batteries has recently led to the exploration of highly concentrated aqueous electrolyte solutions using organic lithium salts in order to slow down the kinetics of water splitting in the vicinity of the electrodes and therefore enable larger operating voltages.^[1-3] In an attempt to decrease the amount of expensive organic salt used in these aqueous electrolytes,^[4] we investigated mixtures with an inexpensive lithium salt and could observe an unusual phenomenon, namely the formation of an Aqueous Biphasic System (ABS). When two liquids with very different physicochemical properties, such as water and oil, are put in contact, they usually coexist as separate phases with a sharp interface. This fact has long been exploited e.g. for the separation of aqueous solutes via liquid-liquid extraction using organic phases or ionic liquids.^[5-7] While first ABS based on polymers were discovered in the late 19th century,^[8] the coexistence of two aqueous solutions of different salts has only been reported much more recently and the range of such ABS remains comparatively limited.^[9-11] Their composition usually involves a concentrated inorganic salt and an ionic liquid. The resulting phases both contain a sizeable amount of water (hence their name) and the origin of the phase separation is thought to result from the simultaneous presence of water hydrogen bond network structuring (kosmotropic) or disordering (chaotropic) ions.^[10] This raises the fundamental question: how "different" should the components of the mixture be for such a liquid-liquid phase separation to occur -- i.e. in the aqueous case, for an ABS to form? Here we show that even mixtures of two monovalent salts sharing a common simple cation (lithium, Li⁺) but with different anions result in the presence of water in the coexistence between two aqueous liquid phases over a wide range of compositions at room temperature.

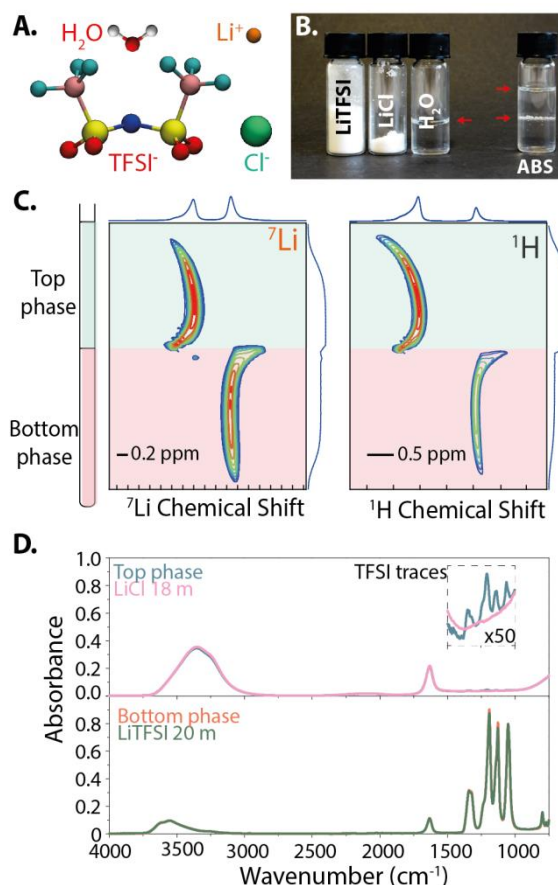


Figure 1. A. Constituents of the system: water molecule, Li⁺ cation, TFSI⁻ and Cl⁻ anions. B. Stoichiometric amount of LiTFSI, LiCl and water to prepare the 12m LiCl – 5m LiTFSI Aqueous Biphasic System (ABS). C. Chemical Shift Imaging (CSI) of an NMR tube containing the 12m LiCl – 5m LiTFSI ABS, revealing distinct local environments for Li⁺ cations and water in the two phases. The color indicates the intensity (from blue for low to red for high) as a function of chemical shift and position, while the shape of the peaks reflects the distortion of the magnetic field near the liquid-liquid and liquid-air interfaces. D. FTIR spectra of the top and bottom phases of the 12m LiCl – 5m LiTFSI ABS compared with those of a 18m LiCl solution and a 20m LiTFSI solution, respectively.

Specifically, we investigate aqueous mixtures of lithium bis(trifluoromethanesulfonyl)imide, LiTFSI, which can form so-called "water-in-salt"^[1] electrolytes (with a salt-to-solvent ratio larger than one in mass and volume) relevant e.g. for battery applications, and the more standard lithium chloride, LiCl, salt (see Fig. 1A). We show in Fig. 1B that a global composition of 12m (mol/kg of water) LiCl and 5m LiTFSI results in approximately equal volumes of two coexisting liquids with a sharp interface. The formation of an interface between these two liquids exchanging matter is further evidenced in the SI by images showing the evolution of a drop of 5m LiTFSI in a saturated (18m) LiCl solution, as well as by the measurement of a finite surface tension (5.7 mN/m for the 12m LiCl – 5m LiTFSI, approximately an order of magnitude smaller than the for the water-air interface).

Nuclear Magnetic Resonance (NMR) then provides spatially resolved specific information on the chemical environment of the various species. The evolution of the chemical shifts across the interface (Fig. 1C) indicates that both Li^+ cations and water molecules adopt distinct local environments in the two liquid phases, while the change of dielectric constant results in a distortion at the interface between the two phases. In addition, Fourier-Transform Infrared (FTIR) spectroscopy allows us to probe the local environment of water in both phases, which in turn provides indirect information on their composition. As shown in Fig 1D, water molecules from the top phase exhibit O-H bond stretching modes (broad signal around 3400 cm^{-1}) similar to those in an aqueous 18m LiCl solution, while weak absorbance peaks around 1250 cm^{-1} reveal traces of TFSI in solution.^[12] A similar resemblance between the bottom phase and aqueous 20m LiTFSI can also be deduced from their FTIR spectra.

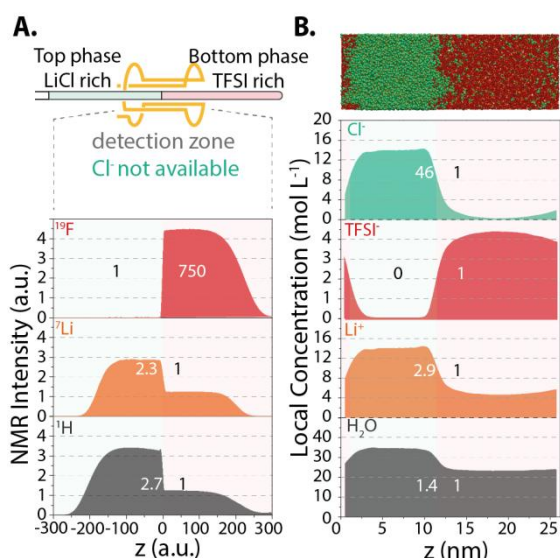


Figure 2. A. Density profiles for ^{19}F , ^7Li and ^1H obtained by NMR for the 12m LiCl – 5m LiCl ABS compared with B. those obtained by Molecular Dynamics simulations for Cl^- , TFSI $^-$, Li^+ and H_2O for the same system. On the top of panel B, a snapshot extracted from the simulation (Li^+ ions are in orange, Cl^- anions in green, TFSI $^-$ anions in red, and water molecules are not shown) illustrates the presence of a sharp interface.

The liquid-liquid phase separation is further quantitatively examined in Fig. 2, which compares the equilibrium density profiles for various elements probed by NMR imaging experiments and computed by molecular dynamics simulations (MD, see Methods). Despite the difference in length scales probed by both approaches ($\sim 1\text{cm}$ for NMR, $\sim 10\text{nm}$ for MD), they provide a consistent picture of a sharp interface between two coexisting liquids. The compositions are in good agreement for the species that we could probe

experimentally (all but Cl^- anions), which validates the MD simulations. In particular, MD simulations predict almost quantitatively the ratio of Li^+ concentration in both phases, as well as the virtual absence of TFSI $^-$ in the Cl-rich phase. The predicted water content in the TFSI-rich phase is smaller than in the other one, even though the ratio is slightly larger than the experimental one. The density profile for Cl^- is also readily available from MD (see Fig. S2 in SI) and indicates that its concentration in the TFSI-rich phase is larger than that of TFSI $^-$ in the Cl-rich phase.

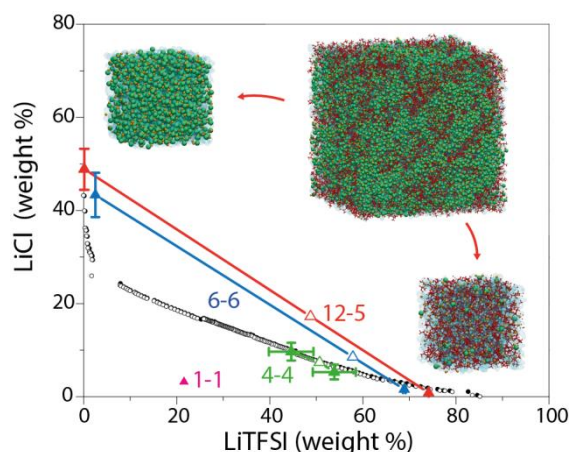


Figure 3. Phase diagram of the ternary LiCl-LiTFSI- H_2O mixture. The phase boundary is located by cloud point experiments between full black circles corresponding to a biphasic system and empty circles corresponding to a monophasic system. Tie lines are obtained by MD simulations for 12m-5m (red), 6m-6m (blue), 4m-4m (green) and 1m-1m (magenta) LiCl-LiTFSI systems and relate the global composition of the system (empty triangles) to that of the resulting phases (full triangles). MD simulation snapshots illustrate the initial system for the 12m LiCl – 5m LiTFSI composition and resulting LiCl and LiTFSI rich phases.

The formation of an ABS, *i.e.* phase separation between two liquid phases, depends on the global composition of the system. The boundary between the monophasic and biphasic regions of the phase diagram, determined by cloud point measurements (see Methods), is shown in Fig. 3. As for the above-mentioned system (12m LiCl + 5m LiTFSI), we also observe a phase separation in the MD simulations for a global composition of 6m+6m, while for a more dilute system (1m+1m) the system remains monophasic. At a global composition of 4m+4m, the system is close to the transition between the one- and two-phase behaviour (see density profiles for 4m+4m and 6m+6m in SI). The resulting compositions of the coexisting liquids in the phase-separating cases, obtained from the MD density profiles (see SI), are very close to the experimental phase boundaries. Such an agreement is remarkable considering the complexity of the system. This further supports the validity of the MD simulations, which in turn complements the experimental phase boundaries with the tie lines (which could in principle

be obtained by separating and weighting both phases, but would require larger volumes and therefore be much more expensive).

We finally turn to the physical origin of the phase separation. In contrast to previously reported ABS, in the present systems the salts share a common cation. In agreement with previous MD studies of bulk WiSEs,^[1] we find that in our case the relevant cationic species in both phases is the hydrated Li^+ , despite the observed partial desolvation in this high concentration regime (see Fig. S3 in SI), indicating that the phase separation is essentially driven by the different properties of the anions.

The driving force to form an ABS was previously proposed to result from the difference in interaction with water molecules between two salts: one structuring water (kosmotropic) and the other disordering the hydrogen bond network of water (chaotropic),^[10] a phenomenon classically evidenced by viscosity measurements.^[13] While TFSI^- was reported to be chaotropic, viscosity measurements carried out in this work (see Fig. S4 in SI) reveal that TFSI^- exhibits a positive Jones-Dole B-coefficient, which is usually observed for kosmotropic salts. This could result from the large size and hydrophobic character of TFSI^- anion.^[13,15] However the concept of chao/kosmotropicity, which underlines the effect of individual ions on water, should be taken with some caution at such high concentrations. This is particularly true for WiSEs where the salt-to-water ratio is larger than one, since in this regime the effects of ion-water interactions are not additive.^[16,17]

From a thermodynamic point of view, a mixture of a solvent with two salts sharing a common ion can be considered as a ternary mixture, due to the constraint of electroneutrality. Using integral equations, Lo Celso *et al.* analyzed the phase behaviour of such mixtures for neutral (solvent) and charged (ions) hard spheres^[18] and found that an asymmetry in the size of the counterions can be sufficient to induce a phase separation, for a range of compositions and temperatures. On the microscopic scale, this means that the liquid structures satisfying both the local electroneutrality and packing constraints with each counterion separately are more stable than for the case when all ions are mixed. This is not to say that water does not play a role in the mixing free energy, which determines whether or not the phase separation occurs: It does contribute both energetically (via ion solvation and screening of electrostatic interactions) and entropically (configurational entropy via the composition of each phase). However, this contribution may not be the dominant one. This claim is further supported by the low solubility of alkali halides in conventional ionic liquids.^[19]

In this work, we have shown the formation of ABS formed by mixing salts containing a common cation,

namely LiTFSI and LiCl. With the help of NMR and MD simulations, we demonstrated that for a large range of compositions, the system segregates into two phases, one being rich in LiTFSI and containing some LiCl and one containing almost exclusively LiCl at high concentration. While the chao/kosmotropic phenomenological effect of ions was previously suggested, our findings support the idea that the anion size asymmetry is the driving force for the formation of an ABS in this system. While the first ABS based flow cell battery was proposed recently,^[20] preliminary results indicate the possibility to make use of this ABS to develop aqueous dual-ion batteries (see Fig. S5 in SI). Furthermore, controlling this phase separation phenomenon could provide new avenues to recycle LiTFSI from aqueous solutions.

Methods

Experimental methods and details of the molecular dynamics (MD) computer simulation are described in the Supplementary Information.

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Keywords:

Aqueous Biphasic System • Concentrated Li-ion electrolytes • Molecular Dynamics • Phase diagrams • Water-in-Salt Electrolytes

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