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

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

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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.\(^1\text{-}^3\) In an attempt to decrease the amount of expensive organic solvent 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.\(^5\text{-}^7\) 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.\(^9\text{-}^{11}\) 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.

Fig. 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"\(^1\text{-}^3\) 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.\textsuperscript{12} A similar resemblance between the bottom phase and aqueous 20m LiTFSI can also be deduced from their FTIR spectra.

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 (~1cm for NMR, ~10nm 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.

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 LiCl ABS) 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 behavior (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, 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). This indicates 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 (chaotrophic), a phenomenon classically evidenced by viscosity measurements. While TFSI was reported to be chaotrophic, 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. However the concept of chaoko/motropicty, which underlines the effect of individual ionic 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.

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 behavior of such mixtures for neutral (solvent) and charged (ions) hard spheres 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.

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 chaoko/motropic 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, 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 Supporting Information. No unexpected or unusually high safety hazards were encountered.

Supporting Information

Experimental procedures and simulations details. Photography of drop of LiTFSI in LiCl aqueous solutions. Concentrated profiles calculated from MD simulations with different global compositions. Solution of Li+ cations in the LiCl and LiTFSI rich phases. Viscosity measurements and Jones-Dole coefficients for LiTFSI, LiCl and KCl aqueous solutions. Dual ion battery using the ABS as electrolyte.

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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.
Aqueous Biphasic System

LiCl (weight %)

Cl rich

TFSI rich

Monophasic

LiTFSI (weight %)
Supporting information for: Chasing Aqueous Biphasic Systems from simple salts by exploring the LiTFSI / LiCl / H₂O phase diagram

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**Experimental Procedures and Simulation Details**

**MD simulations**

All-atom molecular dynamics (MD) simulations are carried out with the GROMACS 5.1 simulation package. Initially, two independent simulation boxes for LiCl+water and LiTFSI+water are prepared with the PACKMOL package according to the concentrations of interest. The sizes of the simulation box and numbers of species are summarized in Table S1. The initial configurations in the simulation boxes are first relaxed by minimizing the potential energy using steepest descent and then the two independent simulation boxes are merged into a single simulation box. For the equilibration and production runs, the simulation boxes are maintained at an isotropic pressure of 1 bar with the Parrinello-Rahman barostat and the temperature at 298 K with a velocity rescaling thermostat. We monitor the density profiles for ions and water molecules until the profiles are converged (see Table S1 for the duration of the equilibration and production runs). The density profiles reported in the figures correspond only to the production runs. Periodic boundary conditions are applied in all three spatial directions. Non-bonded interatomic interactions are described by a 6–12 Lennard-Jones potential with a cut-off at 1.2 nm. The Particle-Mesh Ewald (PME) method with a Fourier spacing of 0.12 nm and a 1.2 nm real-space cut-off is used to calculate electrostatic interactions. The LINCS algorithm is employed for all bond constraints. The OPLS-AA force field is used for Li+, Cl− and the CL & P force field is employed for TFSI−. The SPC/E model is used for the water molecules.

| System | Equilibrium box lengths (nm) X x Y x Z | Equilibration & Production run (ns) | Number of ions/molecules |
|--------|---------------------------------------|-----------------------------------|-------------------------|
| 1m+1m  | 4.2 x 4.2 x 21.0                      | 100 & 400                         | Li⁺  400  Cl⁻  200  TFSI⁻  200  Water  10746 |
| 4m+4m  | 4.2 x 4.2 x 30.2                      | 500 & 230                         | Li⁺  1600  Cl⁻  800  TFSI⁻  800  Water  10746 |
| 6m+6m  | 4.2 x 4.2 x 35.9                      | 500 & 180                         | Li⁺  2340  Cl⁻  1170  TFSI⁻  1170  Water  10746 |
| 12m+5m | 9.1 x 9.0 x 26.2                      | 200 & 160                         | Li⁺  11137  Cl⁻  7937  TFSI⁻  3200  Water  35988 |

**Materials**

All the chemicals, such as lithium bistrifluoromethanesulphonimdate (Solvay), lithium chloride (Alfa Aesar, 98+%) are used as received. Ultrapure Milli-Q water is used in all the experiments.

**Solution preparation**

Solutions are prepared by mixing the two salts in a vial. The right amount of water is added to reach the target final composition.

**Optical Microscopy**

Movies of the drop of 5m LiTFSI in 18m LiCl were recorded by injecting with a syringe a drop of about 10 μL. The total magnification is x12.5.

**Liquid-state Nuclear Magnetic Resonance Imaging**

Liquid-sate NMR spectra are recorded on a Bruker 4.7 T Avance HD spectrometer mounted with a Diff-30 Z-gradient probehead. ¹H and ⁷Li mapping of the tubes are recorded using a 1D Chemical Shift Imaging (CSI) sequence with 4 transients and 128 gradient increments. The gradient pulse was 1 ms long, with a maximum gradient strength of 20.2 G/cm for ⁷Li and 7.9 G/cm for ¹H, corresponding to an overall field of view of 3 cm. The RF pulse strength was set to 6 kHz for ¹H and 15.6 kHz for ⁷Li, and the recycle delays were set to 1s in both cases. The concentration profiles for ¹H, ⁷Li
and $^{19}$F are obtained using a direct acquisition under a small constant gradient. The full echo signal is recorded with an echo sequence (‘improf’ in Bruker spectrometers), with a 90° pulse followed by a short gradient pulse during the first echo delay, and after a refocusing 180° pulse, the gradient is switched on and the full echo FID is recorded. The parameters used are shown in the table below for each nucleus:

Table S2: NMR parameters used for the concentration profiles.

| Nucleus | Transients number | Recovery delay | RF strength | Gradient strength |
|---------|-------------------|----------------|-------------|-------------------|
| $^1$H   | 32                | 3 s            | 6 kHz       | 12 G/cm           |
| $^{19}$F| 128               | 1 s            | 7.4 kHz     | 12 G/cm           |
| $^7$Li  | 16                | 10 s           | 15.6 kHz    | 12 G/cm           |

The excited zone corresponds to the liquid inside the NMR coil, which is roughly 2.5-3 cm high. The longitudinal relaxation times ($T_1$) of each species have been measured to ensure quantitative measurements.

Table S3: Longitudinal relaxation times ($T_1$) measured for the different species in the 12m LiCl - 5m LiTFSI system

| Phase        | $^1$H | $^{19}$F | $^7$Li |
|--------------|-------|---------|--------|
| LiTFSI.H$_2$O| 667 ms| 631 ms  | 366 ms |
| LiCl.H$_2$O  | 510 ms| 859 ms  | 1.943 s|

It must be noted that a small amount of TFSI was detected in the LiCl phase in the 1D spectrum, and its peak is weaker by a factor of around 760. A similar ratio (1/740) is observed in the 1D concentration profile (detail not shown).

**Fourier-Transform Infrared Spectroscopy**

FTIR spectra are recorded on a Nicolet iS5 FTIR spectrometer, mounted with a diamond Attenuated Total Reflectance accessory (iD1 ATR). One drop of solution was analyzed using 16 scans with a 4 cm$^{-1}$ resolution from 4 000 to 500 cm$^{-1}$. The background correction is performed by measuring the ambient atmosphere under the same conditions as for the solutions measured in this work.

**Phase-diagram construction**

The phase diagram is constructed using the point-cloud titration method. Briefly, a precise mass of a concentrated solution of LiTFSI (20 m) or LiCl (18 m) is introduced in a test tube, which was weighted ($m_I$). The other solution is introduced dropwise, until a cloudy solution is observed. The tube is weighted again ($m_c$) so that the mass of the added solution can be deduced ($m_S=m_I-m_c$) and the composition of the system is reported as a point of coexistence (biphasic system). Then, water is added dropwise until the solution turns limpid. The tube is then weighted ($m_L$) to determine the mass of added water ($m_W=m_L-m_C$) and the point corresponding to the monophasic system is reported on the phase diagram. To ensure a proper determination of the required number of drops, the solution is vortexed after every drop addition. To study the system for a large range of compositions, the titration was carried out starting either from a stock solution of LiTFSI or LiCl. The proper junction between the two series of measurements observed in the phase diagram (Figure 3, main text) validates the accuracy of the method.

**Viscosity measurements**

Viscosity measurements are carried out on a Discovery HR-2 (TA instruments) rheometer using a Peltier concentric cylinders geometry at 25°C (controlled temperature, +/- 0.2°C). Kinematic viscosity is measured for shear rates between 1.0 s$^{-1}$ and 30.0 s$^{-1}$. Retained values for the viscosity resulted from the average of 5 measurements recorded with shear rates comprised between 12.6 s$^{-1}$ and 30 s$^{-1}$. Error bars are calculated from the standard deviation of the 5 measurements with the average value.

**Surface-tension measurement**

Surface tension measurement between liquids is performed using an automatic tensiometer (Tracker- Single drop).
Electrochemical measurements

Dual ion batteries using Mo₆S₈ as lithium insertion electrode and polypyrrole as chlorine insertion electrode are prepared and assembled as follows. Mo₆S₈ is obtained by leaching Cu₂Mo₆S₈ in a 6 M HCl aqueous solution under oxygen. Cu₂Mo₆S₈ is prepared by a solid-state synthesis method (elemental precursors are introduced in a stoichiometric amount in a glass tube, that is sealed under vacuum and heated up at 1100°C for 72h). Self-standing electrodes are prepared by mixing in acetone Mo₆S₈ powder with carbon super-P, PVDF and dibutylphthalate (DBP) in the following weight ratios: 100/12.5/25/40. The as prepared slurry is spread in a petri-dish. Once the acetone is evaporated, half-inch electrodes are punched from the film. DBP is removed from the electrodes by washing them 3 times for 30 minutes in diethylether. Electrodes are dried under vacuum overnight at room temperature. Polypyrrole (PP) electrodes are obtained by electropolymerizing pyrrole (Alfa, 98+%) in 1.2 M HCl on a carbon paper, as described elsewhere. Before use, PP electrodes are dechlorinated by holding them at -0.840 V vs SCE in a 1m LiCl solution. Plastic Swagelok cells with a PTFE-disk spacer are assembled by placing the Mo₆S₈ electrode on the bottom plunger, adding first the 20 m LiTFSI and then the 18 m LiCl solution. The polypyrrole electrode – soaking only in the LiCl electrolyte - is then placed on the top of the PTFE-disk spacer and is directly in contact with the top plunger. A scheme of the assembly is represented below. As made Swagelok cells are cycled on a VMP3 potentiostat from Biologic.

Scheme S1. Custom Swagelok cell used to cycle the ABS dual ion battery.
Results and Discussion

S1. Photography of drop of LiTFSI in LiCl aqueous solutions

Figure S1. Optical microscopy images showing the evolution over time of a ~10 µL drop of 5 m LiTFSI solution in 18 m LiCl solution.

The decrease of the drop diameter reveals a mass transfer from the 5 m LiTFSI phase to the 18 m LiCl solution, which could be attributed to a transfer of water. After 20 minutes, no more evolution was observed. This confirms the formation of a stable ABS even for small volumes.
S2. Concentration profiles calculated from MD simulations with different global compositions

Figure S2. Concentration profiles obtained by Molecular Dynamics simulations for the 1m-1m (A), 4m-4m (B) and 6m-6m (C) systems. Snapshots of the simulations are also shown, with Cl$^-$ anions in green, TFSI$^-$ anions in red, and Li$^+$ cations in orange (water not shown).

While the systems are clearly monophasic for 1m LiCl – 1m LiTFSI and biphasic for 6m- 6m, the 4m-4m system does not show sharp interfaces, even though the density profiles are reasonably converged. The composition of each phase of the ABS (as reported by full symbols in Figure 3 of the manuscript) is computed from these density profiles as averages in the corresponding regions, summarized in Table S4.

Table S2. Regions used to compute the composition of each phase from the density profiles (Figure 2 of the manuscript for the 12m + 5m system, S2B for 4m+4m and S2C for 6m+6m).

| System   | Region for Cl-$^-$ rich phase [nm] | Region for TFSI-$^-$ rich phase [nm] |
|----------|-----------------------------------|--------------------------------------|
| 12m+5m   | 4.3 to 9.3                         | 17.5 to 22.5                         |
| 4m +4m   | 2 to 7                             | 13.5 to 25                           |
| 6m + 6m  | 4.7 to 7.2                         | 18 to 29                             |
S3. Solvation of Li⁺ cations in the LiCl and LiTFSI rich phases

Figure S3. (a) MD snapshot of the 12m LiCl – 5m LiTFSI system, showing the solvation structures of Li⁺ cations (orange) in the LiCl (Cl⁻ in green in top panel and bottom left panel) and LiTFSI (TFSI⁻ in red in top panel, with separate colors for each atom in bottom right panel) rich phases. Li⁺ cations remain partially solvated by water molecules (O in red, H in white) in both phases. (b) Radial distributions around Li⁺ cations in the TFSI⁻ rich phase. (c) Running coordination numbers around Li⁺ cations in the TFSI⁻ rich phase.

The Li⁺ cations are solvated by water molecules in both phases, as illustrated in Figure S3a. In order to investigate quantitatively the environment of the cations in the TFSI⁻ rich phase of the ABS formed in the 12m LiCl – 5m LiTFSI system, we conducted additional molecular dynamics simulations of a bulk system with the same composition. Specifically, the system consists of 1956 Li⁺, 1956 TFSI⁻, 200 Cl⁻ and 10038 water molecules in a cubic box. The molecules are inserted into the simulation box randomly using the PACKMOL package and relaxed with the steepest descent algorithm. After a simulated annealing from 500 K down to 298 K within a time interval of 3 ns in the NVT ensemble, the system is compressed in the NPT ensemble at 50 bar and 298 K for 1.5 ns. After further equilibration for 5 ns at 1 bar (the equilibrated box length is L=8.86 nm), we perform a 96 ns production run at 1 bar, from which we compute the radial distribution functions, g(r), between Li⁺ cations, water O atoms, TFSI N atoms and Cl⁻ anions. They are reported in Figure S3b, which clearly shows that the direct environment of the Li⁺ cations consists essentially of water molecules and Cl⁻ anions. Despite the larger peak for the latter, the first coordination shell of the cations mainly consists of water, which is present in much larger quantities than Cl⁻ in the TFSI⁻ rich phase. This is obvious in Figure S3c, which shows the running coordination numbers \( N(r) = \int_{r_0}^{r} \rho g(r') 4\pi r'^2 dr' \) with \( \rho \) the density of the species of interest. The plateaus around 0.3 nm indicate that there are on average almost no TFSI⁻, 3.6 water molecules and 0.3 Cl⁻ anions in the first coordination shell of Li⁺.
S4. Viscosity measurements and Jones-Dole coefficients for LiTFSI, LiCl and KCl aqueous solutions

As described in the main manuscript, the formation of an ABS using different salts was explained in the literature to result from the presence of water structuring (kosmotropic) ions in one phase and disorder-making ions in the other phase (chaotropic). A common way to assess individual ions effect on water structure is to measure the viscosity of dilute solutions (from 5 mM to 500 mM) and to determine the B-coefficient in the Jones-Dole equation \( \frac{\eta}{\eta_w} - 1 = \frac{A}{c^{1/2}} + Bc \) by comparing with the results obtained for KCl, assuming the additivity of ionic contributions (and using the fact that \( B_{K^+} = -B_{Cl^-} \), see below). The viscosity measured for LiTFSI, LiCl and KCl solutions from 50 mM to 1 M are well described by the Jones-Dole equation for the three salts, which allows us to determine the corresponding A and B parameters.

The positive B-coefficient of +0.18 dm\(^{3/2}\) mol\(^{-1/2}\) found for Li\(^+\) cations indicates its water-structuring role (kosmotropic) and is in excellent agreement with the literature (+0.15 dm\(^{3/2}\) mol\(^{-1/2}\) in reference 12). Finally, a B-coefficient for TFSI\(^-\) anions of +0.59 dm\(^{3/2}\) mol\(^{-1/2}\) can be deduced from the slope obtained for LiTFSI and the above value for Li\(^+\). As discussed in the main text, such positive coefficients may indicates a kosmotropic effect for TFSI\(^-\) anions, which may seem counter-intuitive based on previous reports. From reference 13, it can be concluded that this positive coefficient is rather due to the large size and hydrophobic character of TFSI anions.
This experiment confirms the possibility of using ABS to develop dual ion batteries with different anolyte and catholytes in absence of any membrane. The “water-in-salt” electrolyte (20 m LiTFSI) allows the cycling of MoS$_2$ in aqueous electrolyte$^{12}$, while the 18 m LiCl electrolyte allows the PP electrode to work as a pseudo-capacitor for Cl$^-$ ions.$^{12}$ In particular, the interface between the two phases remains stable even when an electric field is applied. Further improvements, such as stability of the positive current collector in presence of Cl$^-$ and reducing the large hysteresis observed in this preliminary experiment, would be required to assemble a practical dual ion battery based on ABS electrolytes.
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Author Contributions

ND prepared the solutions, conducted the FTIR experiments, performed the electrochemical measurements and realized the phase diagram. AG and ND analyzed those experimental results. SAI and ND measured the viscosity and followed the evolution of the ABS by microscopy, these results were further analyzed by AC. MD conducted and analyzed NMR measurements. BR, JD and MS designed the simulations, which were performed by CP and MK and analyzed by all 5. ND and CP produced the figures; all authors contributed to writing the manuscript under the coordination of the corresponding authors.
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