Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary Information on:

The transition from salt-in-water to water-in-salt nanostructures in water solutions of organic ionic liquids relevant for biological applications

P Kumari,(1,2) V. V. S. Pillai,(1,2) D. Gobbo,(3)† P. Ballone,(1,2) and A. Benedetto(1,2,4)

(1) School of Physics, University College, Dublin, Ireland

(2) Conway Institute for Biomolecular and Biomedical
Research, University College, Dublin, Ireland

(3) Computational and Chemical Biology,
Fondazione Istituto Italiano di Tecnologia, Genova, Italy and

(4) Department of Sciences, University of Roma Tre, Rome, Italy

I. ATOMISTIC STRUCTURE OF THE IONS

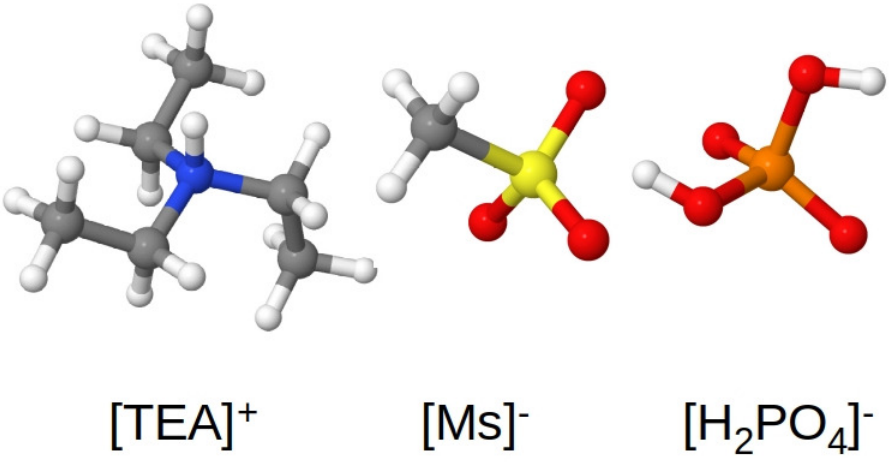

FIG. 1: Structure of the $[\mathrm{Tea}]^+$, $[\mathrm{Ms}]^-$ and $[\mathrm{H_2PO_4}]^-$ ions.

All structures (including that of $[\mathrm{DxC10}]^{2+}$ shown in the main text) have been determined by optimising the total energy of the system at density functional level with the PBE[1] exchange-correlation functional. Computations have been carried out using the CPMD package.[2] RESPA atomic charges and vibrational frequencies have been computed using the same DFT approximation and computer package. The DFT results for: (i) the geometry of single ions, ion pairs and two ion pairs; (ii) atomic charges; (iii) vibrational frequencies; have been compared to those of the empirical force field, achieving an agreement in line with the results of a similar comparison carried out by our group for several other RTIL systems.

II. STRUCTURE FACTORS OF THE [DXC10][CL]$_2$/WATER SAMPLES

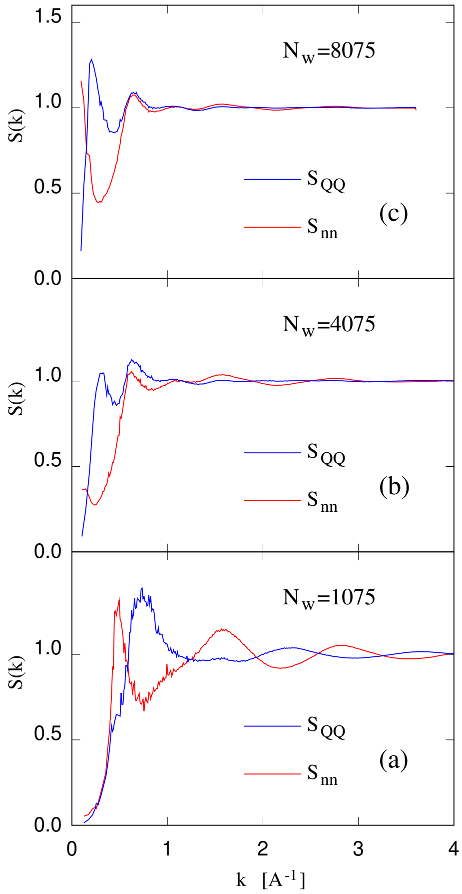

FIG. 2: Density-density and charge-charge structure factors in [DxC10][Cl]$_2$/water samples of different concentration.

The first apparent difference between the S_{nn} and S_{QQ} for [DxC10][Cl]$_2$ and those for [Tea][Ms] and [Tea][H$_2$PO$_4$] is that peaks and dips occur at lower k values in the [DxC10][Cl]$_2$ case than for the other solutions. Moreover, the amplitude of the decaying oscillations is lower in the [DxC10][Cl]$_2$ case. These observations are rationalised by the large size of the [DxC10]$^{2+}$ cation, and by the softer cation-cation and cation-anion interactions. The second apparent difference is that at low salt concentrations (panels (b) and (c)), the first peak of S_{QQ} occurs at a k that is lower than the k of the first S_{nn} peak. This differs from the usual picture of simpler and more symmetric salts, in which the first peak in S_{QQ} occurs at a k that is roughly twice that of the first peak in S_{nn}, reflecting the fact that nearest cation-anion distances are shorter than nearest cation-cation and anion-anion distances. The anomalous result for [DxC10][Cl]$_2$ is due to the fact that, in this case, at low salt concentration the nearest anion-anion distance is significantly shorter than the cation-cation and cation-anion distances. At higher salt concentration (panel (c)) the usual picture is restored by the penetration of $[\mathrm{Cl}]^-$ into the neutral corona of the phosphonium cation, as apparent from the radial distribution functions shown in Fig. 5 of the main text.

III. ION-ION RADIAL DISTRIBUTION FUNCTION OF [TEA][MS] AND [TEA][H_2PO_4] WATER SOLUTIONS

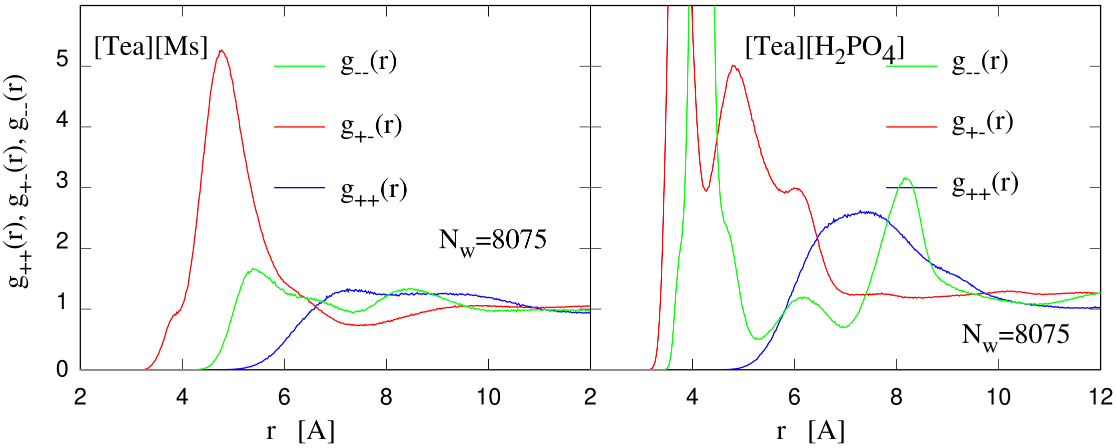

FIG. 3: Radial distribution functions (coarse grained from atomistic trajectories) for the $[\mathrm{Tea}]^+$, the $[\mathrm{Ms}]^-$ and the $[H_2PO_4]^-$ ions in [Tea][Ms]/ and [Tea][H_2PO_4]/water solutions at low salt concentration ($N_w = 8075$).

IV. PENETRATION OF PARTIALLY HYDRATED [CL]$^-$ INTO THE ALKYL CORONA OF PHOSPHONIUM

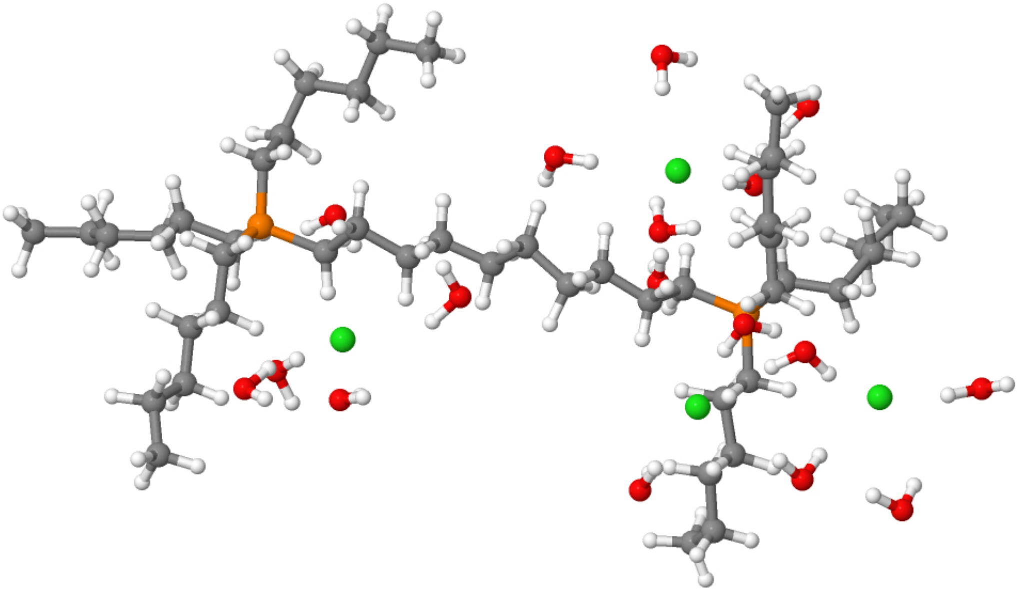

FIG. 4: Representative cation-anion-water configuration in [DxC10][Cl]$_2$ showing the penetration of partially hydrated [Cl]$^-$ into the alkyl corona of phosphonium. [Cl]$^-$ ions are represented by the green circles.

The [Cl]$^-$ reported in the figure are within a nearest-neighbour distance ($r_{nn} = 6$ Å) from the P atoms of [DxC10]$^{2+}$, while the oxygen of the water molecules are within 4.5 Å from the [Cl]$^-$ ions.

V. CATION-ANION RUNNING COORDINATION NUMBER IN [TEA][MS]/WATER SAMPLES

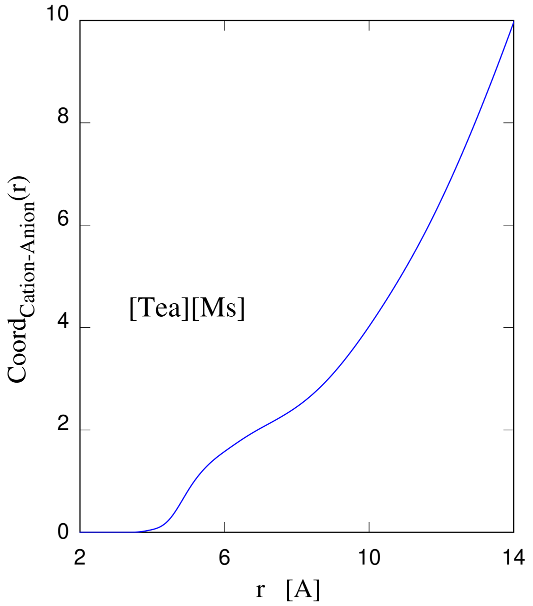

FIG. 5: Cation-anion running coordination number in the [Tea][Ms]/8075 sample.

VI. SIMULATION SNAPSHOTS OF RTIL/WATER SAMPLES

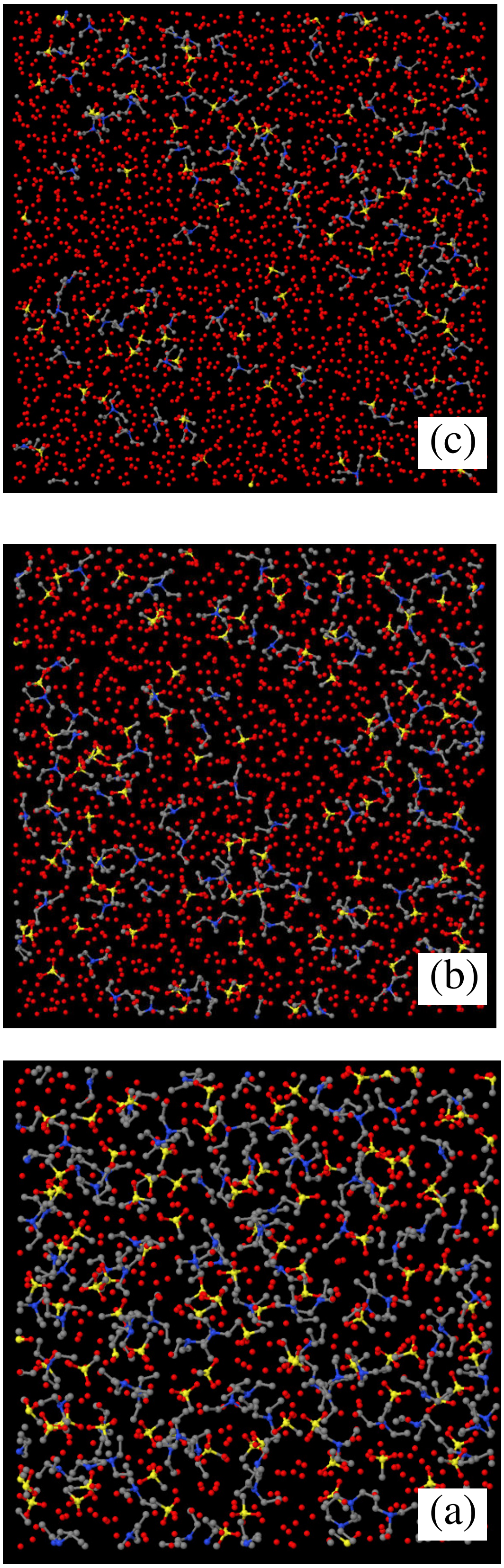

FIG. 6: Simulation snapshots for the [Tea][Ms]/water system. (a) $N_w = 1075$; (b) $N_w = 4075$; (c) $N_w = 8075$. Hydrogen atoms have been removed, hence water is represented by a single red dot.

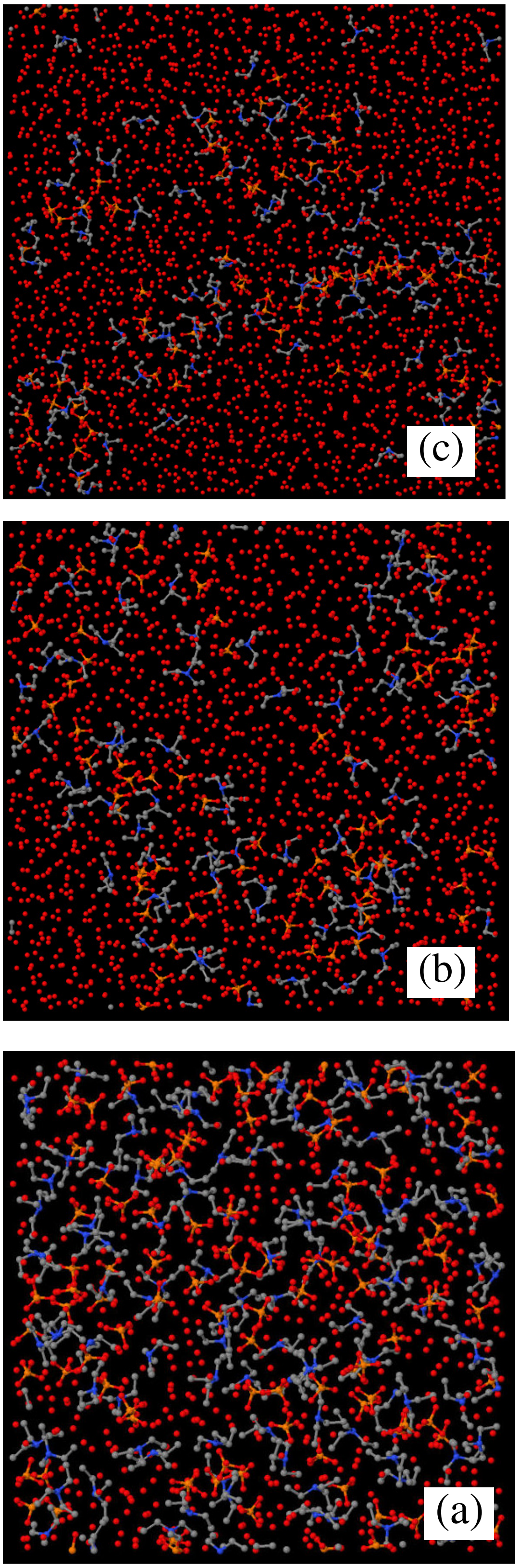

FIG. 7: Simulation snapshots for the [Tea][H_2PO_4]/water system. (a) $N_w = 1075$; (b) $N_w = 4075$; (c) $N_w = 8075$. Hydrogen atoms have been removed, hence water is represented by a single red dot.

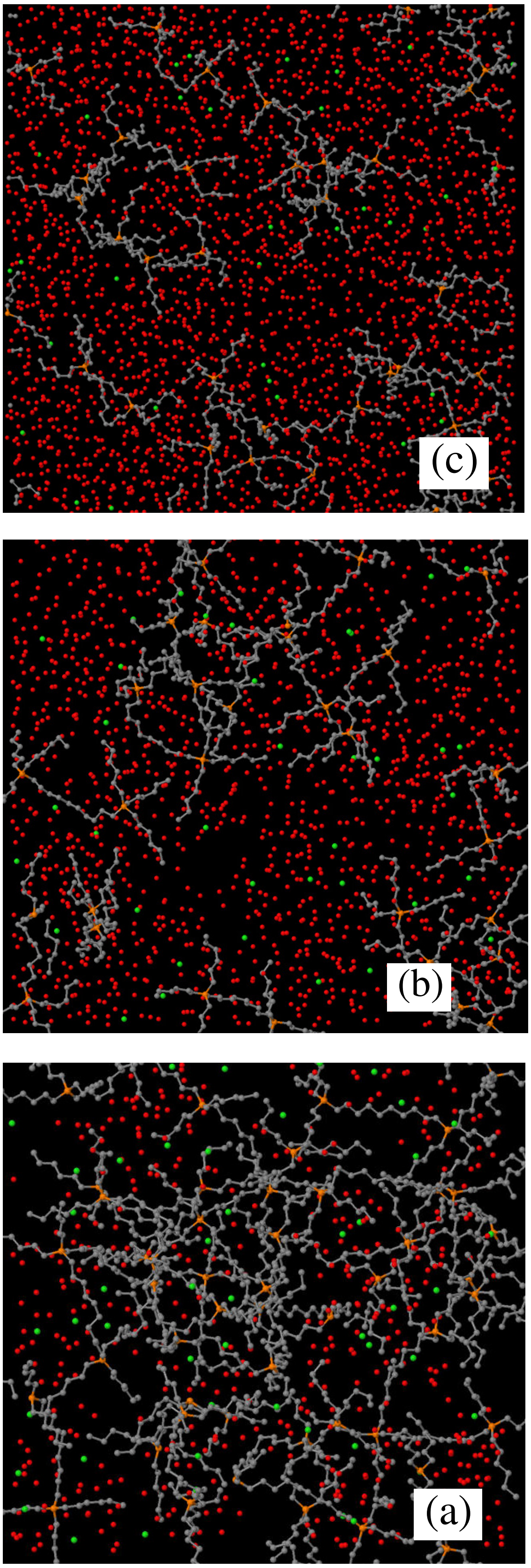

FIG. 8: Simulation snapshots for the [DxC10][Cl]$_2$/water system. (a) $N_w = 1075$; (b) $N_w = 4075$; (c) $N_w = 8075$. Hydrogen atoms have been removed, hence water is represented by a single red dot.

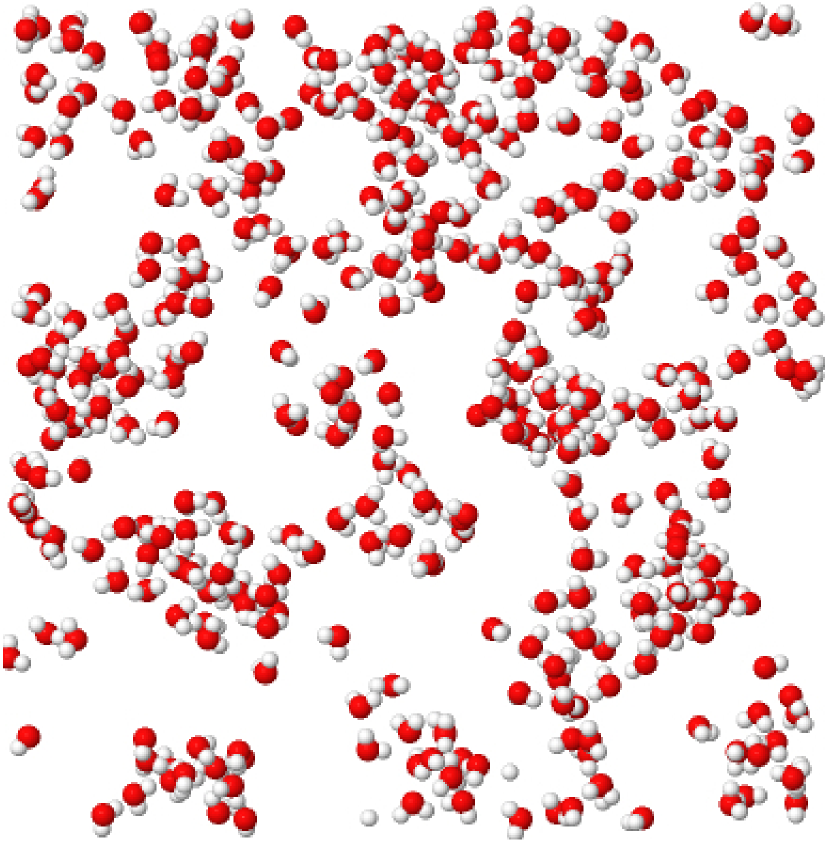

FIG. 9: Water distribution in a slice of the $[DxC10][Cl]_2/1075$ sample of 2 nm width. The holes correspond to the position of $[DxC10]^{2+}$ cations.

VII. CLUSTERING OF ANIONS THROUGH H-BONDING IN [TEA][MS]/ AND [TEA][H_2PO_4]/WATER SAMPLES

To investigate the formation of RTIL hydrates we analysed the abundance and composition of clusters made by anions linked through HBonding by a single bridging water molecule, neutralised by a corresponding number of cations. Clusters have been identified by starting from every anion in turn, identifying all the water molecules HBonded to it, and continuing the process by adding the anions HBonded to the water molecules already in the cluster, etc. The identification of clusters is self-exclusive and exhaustive, meaning that each anion belongs to one and only one cluster. The procedure is very fast, and we could analyse a large number of configurations from the simulation trajectories. In all cases, a significant number ($\sim 50\%$) of anions form a cluster by themselves with a small number of HBonded water molecules. At medium-high salt concentration, clusters with up to 20-25 anions can be found in each snapshot. The size distribution for [Tea][Ms]/water samples extends to somewhat higher size than for [Tea][H_2PO_4]/water samples, and, as expected, the population of sizeable clusters increases with increasing salt concentration. Adding to the anion-water clusters all the anions whose distance (measured atom-wise) is shorter than ∼ 3 Å , almost invariably results in neutral aggregates. Both in [Tea][Ms]/ and [Tea][H_2PO_4]/water samples the cluster composition is close to 1:2 in the salt:water ratio. The instantaneous geometry of the clusters is not so regular to suggest the structure of an hypothetical hydrate crystal underlying the liquid solutions.

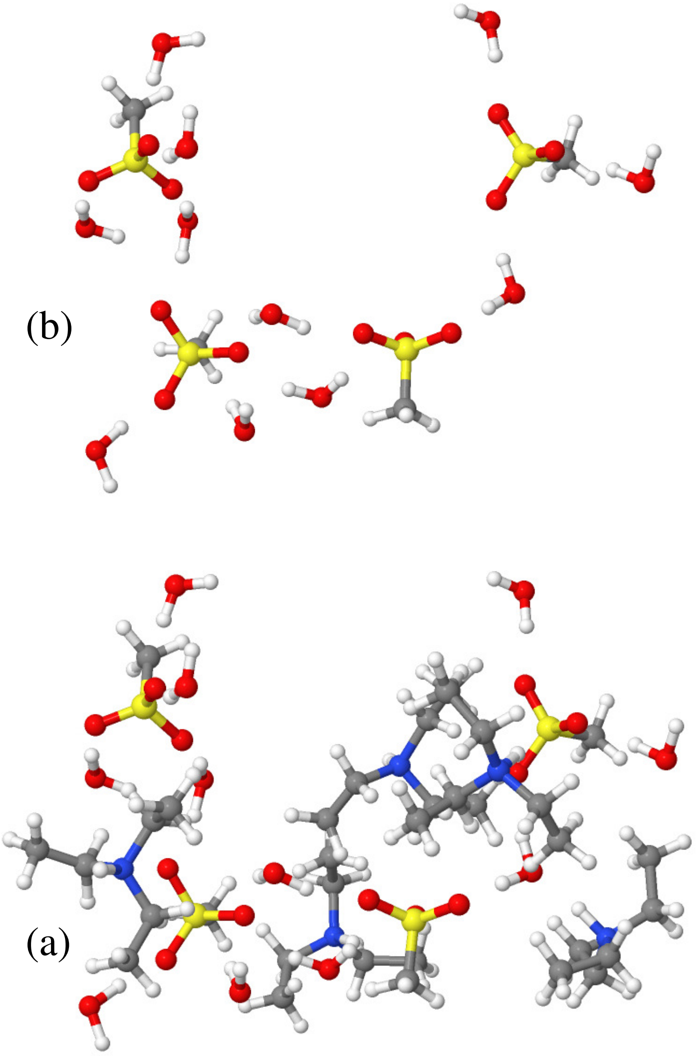

FIG. 10: Example of medium size cluster of HBonded anion and water molecules found in the [Tea][Ms]/2075 sample. (a) Full cluster, including the neutralising cations (see text). (b) Same cluster upon removing the neutralising cations.

However, in [Tea][Ms]/water clusters appear as single chain aggregates, linked by water molecules (by construction) and neutralised by cations. Chains do not tend to be linear (also because their charge is screened) and should not be confused with the -cation-anion- (without water in between) chains seen in low salt concentration samples and discussed in the main text in connection to a dilute dipolar phase of RTILs. In [Tea][H_2PO_4]/water samples, clusters consist of short chain segments, joined laterally to each other by bridging water molecules. An example for each of these two salts is shown in Fig. 10 and Fig. 11. We intentionally display medium size clusters, avoiding the largest ones, hoping that the structure is more clearly visible.

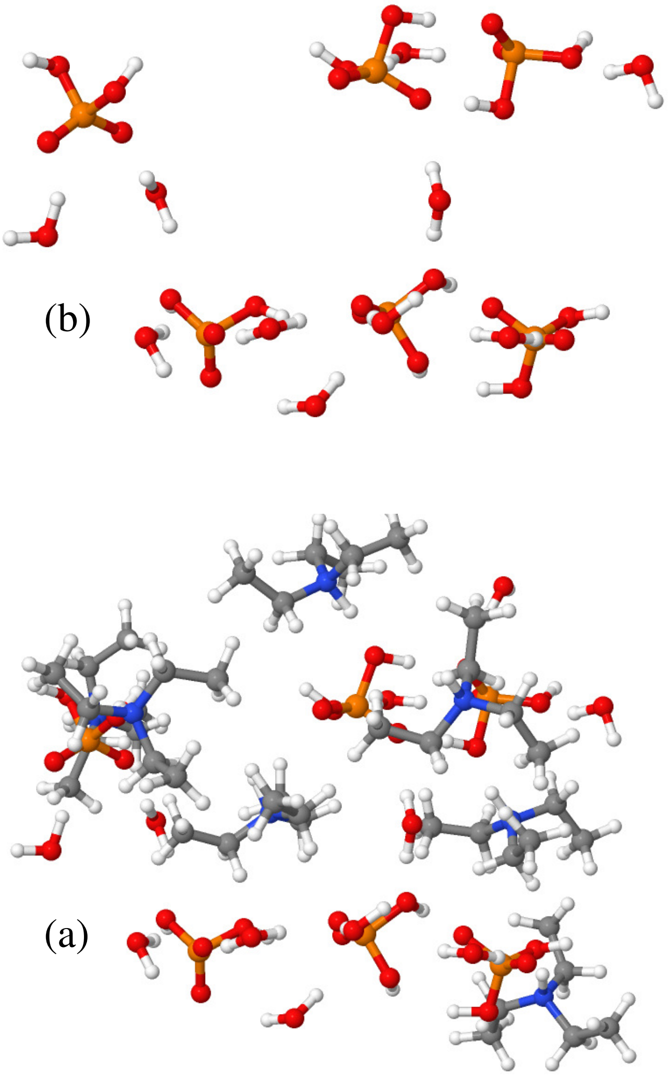

FIG. 11: Example of medium size cluster of HBonded anion and water molecules found in the [Tea][H_2PO_4]/2075 sample. (a) Full cluster, including the neutralising cations (see text). (b) Same cluster upon removing the neutralising cations.

VIII. ELECTRICAL CONDUCTIVITY OF [NA][CL]/WATER SAMPLES

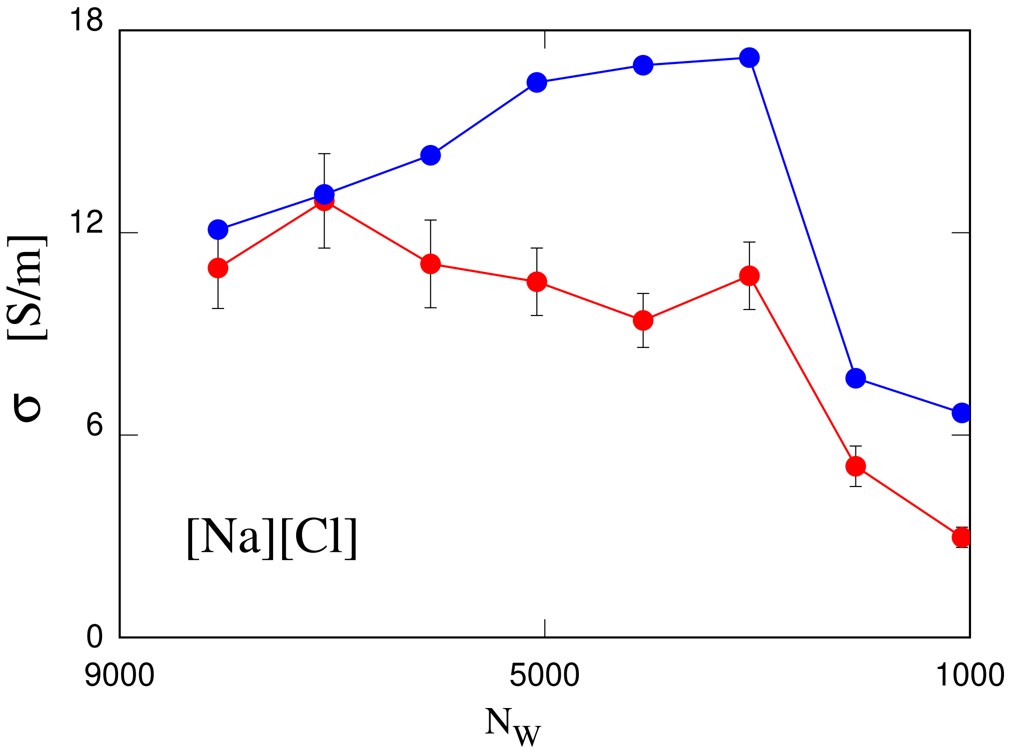

FIG. 12: Electrical conductivity as a function of decreasing number N_w of water molecules in the sample. Red dots: conductivity computed according to the Einstein approach. Blue dots: predictions from the Nernst-Einstein model. The full lines are a guide to the eyes.

IX. MISCELLANEOUS TABLES

	SAMP8	SAMP7	SAMP6	SAMP5	SAMP4	SAMP3	SAMP2	SAMP1
[Tea][Ms]	1.352	1.341	1.328	1.308	1.279	1.234	1.154	0.961
[Tea][H_2PO_4]	1.385	1.378	1.370	1.358	1.341	1.314	1.267	1.139
[DxC10][Cl]$_2$	1.220	1.209	1.194	1.173	1.142	1.093	1.003	0.784
[Na][Cl]	1.268	1.247	1.213	1.173	1.117	1.020	0.832	0.432

TABLE I: Average number of hydrogen bonds per water molecule. The reference value is provided by the average number of HB per molecule in pure water, equal to $\langle n_{HB} \rangle = 1.432$.

	SAMP8	SAMP7	SAMP6	SAMP5	SAMP4	SAMP3	SAMP2	SAMP1
[Tea][Ms]								
[Tea]$^+$ → Water	185.6	184.7	183.5	181.9	180.5	177.7	173.2	163.2
Water → [Ms]$^-$	1088.4	1075.0	1058.7	1036.5	1010.0	969.9	901.3	747.7
[Tea][H_2PO_4]								
[Tea]$^+$ → Water	30.7				20.2			8.31
Water → [H_2PO_4]$^-$	694.8				646.5			493.9
[H_2PO_4]$^-$ → Water	13.2				9.5			6.4

TABLE II: Average number of hydrogen bonds among ions and water. The total number of HBonds per sample is reported.

	SAMP8	SAMP7	SAMP6	SAMP5	SAMP4	SAMP3	SAMP2	SAMP1
Water	$1.93\ 10^{-5}$	$1.84\ 10^{-5}$	$1.76\ 10^{-5}$	$1.63\ 10^{-5}$	$1.39\ 10^{-5}$	$1.10\ 10^{-5}$	$3.58\ 10^{-6}$	$2.12\ 10^{-6}$
Cation	$9.49\ 10^{-6}$	$8.23\ 10^{-6}$	$7.85\ 10^{-6}$	$7.74\ 10^{-6}$	$6.63\ 10^{-6}$	$5.38\ 10^{-6}$	$1.74\ 10^{-6}$	$9.54\ 10^{-7}$
Anion	$1.06\ 10^{-5}$	$1.07\ 10^{-5}$	$1.02\ 10^{-5}$	$9.71\ 10^{-6}$	$7.96\ 10^{-6}$	$6.45\ 10^{-6}$	$1.84\ 10^{-6}$	$8.79\ 10^{-7}$

TABLE III: Diffusion constant of water and ions in the [Na][Cl] / water samples. Data in cm^2 s^{-1}. Error bars implicitly given by the number of digits.

---

[1] Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized gradient approximation made simple. *Phys. Rev. Lett.* **1996**, *77*, 3865-3868.

[2] CPMD, http://www.cpmd.org/, Copyright IBM Corp 1990-2015, Copyright MPI für Festkörperforschung Stuttgart 1997-2001.