

Supplemental Information

Structure and transport of aqueous electrolytes: from simple halides to radionuclide ions

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TABLE S I: Lennard-Jones parameters and charges taken from the literature.

	σ [Å]	ϵ [kcal/mol]	q [e]	Ref.
Ions				
Na ⁺	2.3359	0.1	+1	[1]
K ⁺	3.332	0.1	+1	[2]
Cs ⁺	3.884	0.1	+1	[3]
Ca ²⁺	2.41	0.94	+2	[4]
Sr ²⁺	3.1	0.25	+2	[4]
Cl ⁻	4.3387	0.1	-1	[1]
Water (TIP4P/2005)				
O ²⁻	3.1589	0.1852		[5]
H ⁺			+0.5564	[5]
M			-1.1128	[5]

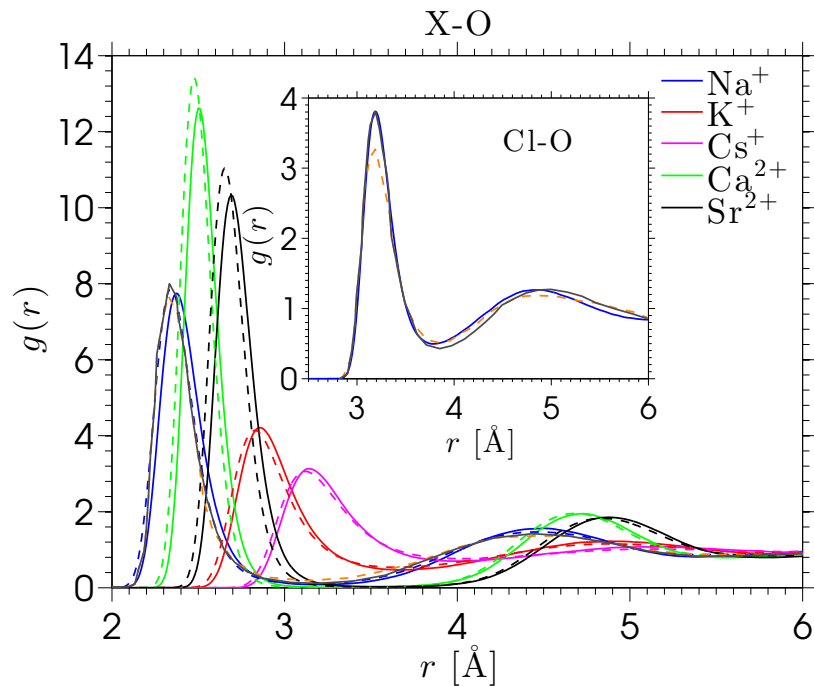


FIG. S1: Comparison between the hydration of ions solvated in TIP4P/2005 water (solid lines, except for the grey line) and the same ions in SPC/E water (dashed lines). The data correspond to chloride solutions with an ion concentration of 0.3M. The temperature of the solution is 300K and the pressure is 1 atm. The different colors of the lines correspond to the cations species in the chloride solutions: Na^+ (blue), K^+ (red), Cs^+ (magenta), Ca^{2+} (green), and Sr^{2+} (black). Furthermore, the solid grey line and the dashed orange line correspond to data from Smith and Dang;⁶ These profiles correspond to Na – O radial distribution functions in an aqueous NaCl-solution where the grey line corresponds to simulations with SPC/E water and the orange line to simulations with (polarizable) RPOL water. The inset shows the Cl – O radial distribution function for TIP4P/2005 (solid blue line) obtained from the 0.3M NaCl solution data. The profile shows good agreement with the profiles from Smith and Dang,⁶ where the grey line again corresponds to a NaCl solution with SPC/E water and the orange line to a solution with RPOL water.

TABLE S II: The volume fractions of the simulation systems calculated as $\Phi = \pi/(6V) \sum_i N_i \sigma_i^3$. The volume fractions of the KCl and the CsCl solutions are slightly lower than those of the other solutions. This is consistent with the fact that these electrolytes do not have a densely packed hydration shell, as discussed in the paper. The volume fractions measured here are very close to those typically seen in dense monodisperse⁷ and polydisperse granular materials.⁸

Pure water			
	0.554		
Solutions			
	0.3M	0.6M	0.9M
Na ⁺	0.562	0.571	0.579
K ⁺	0.556	0.5700	0.573
Cs ⁺	0.560	0.569	0.570
Ca ²⁺	0.561	0.571	0.572
Sr ²⁺	0.562	0.571	0.572

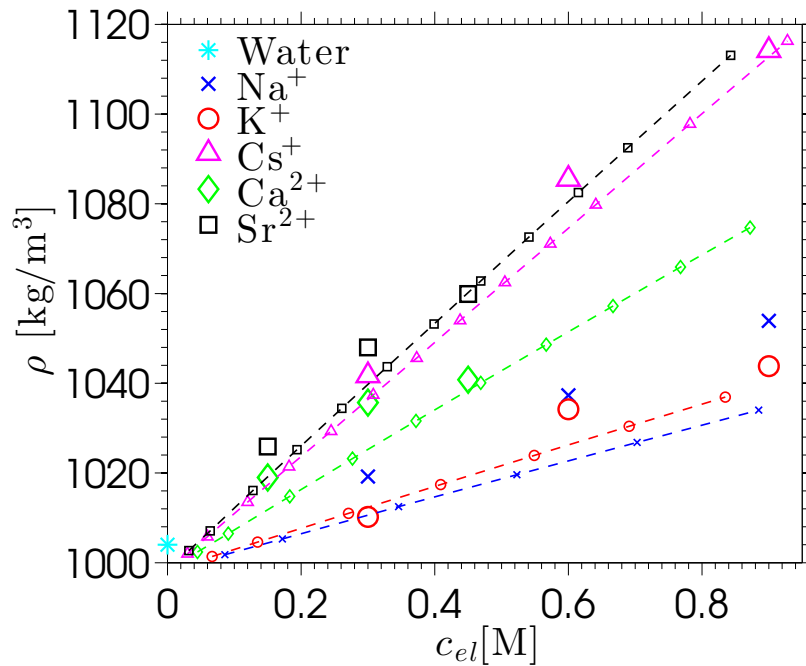


FIG. S2: Density ρ of the bulk solutions as a function of the concentration of electrolytes c_{el} . The large markers correspond to our simulations and the small markers with the dashed lines to experimentally measured densities at a temperature of 293.15 K.⁹ The concentration denotes here the number of electrolytes present in the solution, rather than the concentration of anions (or equivalently charges). The different colors of the lines correspond to the cations species in the chloride solutions: Na⁺ (blue), K⁺ (red), Cs⁺ (magenta), Ca²⁺ (green), and Sr²⁺ (black).

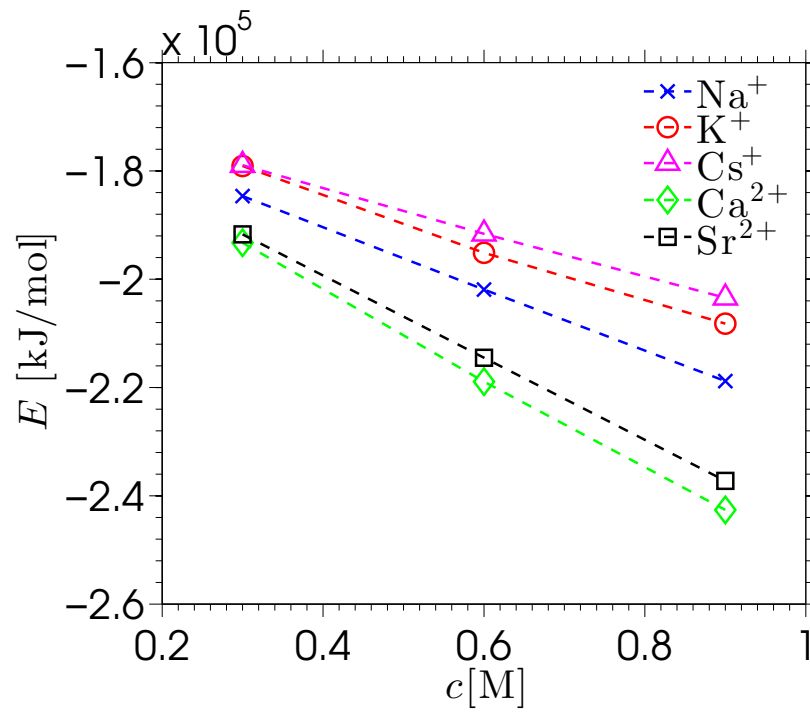


FIG. S3: Total energy E of bulk aqueous chloride solutions as a function of ion concentration c in aqueous chloride solutions. The fluid is at a temperature of 300 K and a pressure of 1 atm. The different colors of the lines correspond to the cations species in the chloride solutions: Na^+ (blue), K^+ (red), Cs^+ (magenta), Ca^{2+} (green), and Sr^{2+} (black).

TABLE S III: Coordination numbers of cations in solution: Comparison to values found in the literature.

$NC(X-O)$	Concentration (M)	Method	Year	Ref.
X=Na⁺				
5.8	0.3-0.9	MD		this study
5.3 ± 0.8	≈ 0.6	neutron diffraction	2007	[10]
6	inf. dilution	MD	2001	[11]
5.8	inf. dilution	MD	1998	[12]
5.9	inf. dilution	MD	1996	[13]
5.6 ± 0.3	0.28	QM/MM MD	1998	[14]
X=K⁺				
6.9-7.1	0.3-0.9	MD		this study
6.0 ± 1.2	≈ 0.6	neutron diffraction	2007	[10]
7	inf. dilution	MD	2001	[11]
7.1	inf. dilution	MD	1998	[12]
7.2	inf. dilution	MD	1996	[13]
8.3 ± 0.3	0.28	QM/MM MD	1998	[14]
X=Cs⁺				
8.2-8.4	0.3-0.9	MD		this study
8	inf. dilution	MD	2001	[11]
8.3	inf. dilution	MD	1998	[12]
9.6	inf. dilution	MD	1996	[13]
X=Ca²⁺				
7.9	0.3-0.9	MD		this study
8	inf. dilution	MD	2001	[11]
7.9	inf. dilution	MD	1998	[12]
8.0	1.0	X-ray diffraction	2004	[15]
8.3	0.28	QM/MM MD	1997	[16]
8.0	inf. dilution	MD	2010	[17]
X=Sr²⁺				
8.4-8.6	0.3-0.9	MD		this study
7.8	0.1	EXAFS spectroscopy	1999	[18]
7.9	1.0	MD	2012	[19]
8.4	inf. dilution	MD	2010	[17]

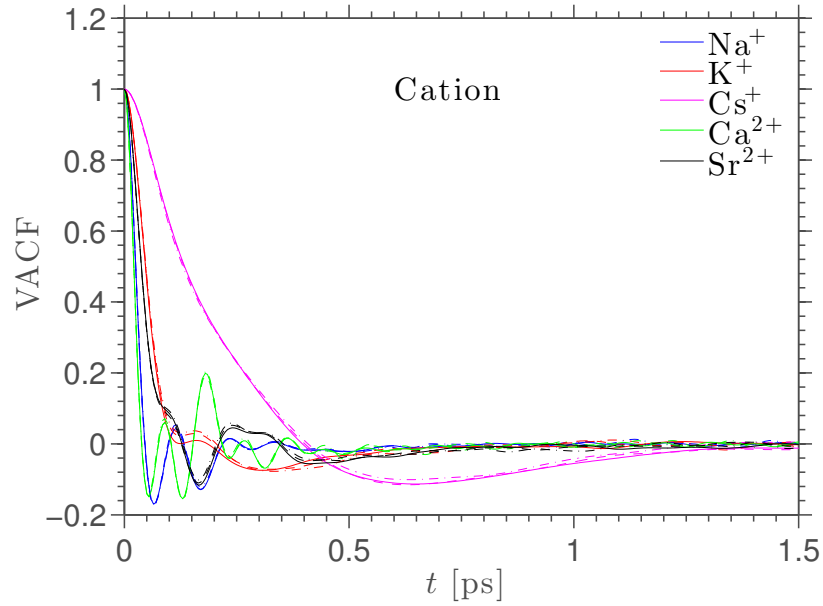


FIG. S4: Normalized velocity-autocorrelation functions in different aqueous chloride solutions and different electrolyte concentrations at a temperature of 300 K and a pressure of 1 atm. The dashed-dotted lines correspond to a molar concentration of 0.3M, the dashed lines to 0.6M and the full lines to 0.9M. These lines are overlapping almost perfectly. The different colors of the lines correspond to the cations species in the chloride solutions: Na^+ (blue), K^+ (red), Cs^+ (magenta), Ca^{2+} (green), and Sr^{2+} (black).

TABLE S IV: Mean life-time (MLT) of ion-ion pairs and ion-water residence for different aqueous chloride solutions and different electrolyte concentrations at a temperature of 300 K and a pressure of 1 atm. The details of the calculations are reported in the paper. The values are reported in ps.

	0.3M	0.6M	0.9M
Cation-anion			
Na^+	44.47	44.65	48.37
K^+	12.46	12.48	13.76
Cs^+	9.03	9.55	9.60
Ca^{2+}	240.16	197.22	143.72
Sr^{2+}	99.67	143.37	256.44
Cation-water			
Na^+	50.56	50.03	52.65
K^+	8.05	8.36	8.38
Cs^+	6.27	6.38	6.57
Ca^{2+}	505.57	445.40	531.40
Sr^{2+}	156.83	176.55	174.08

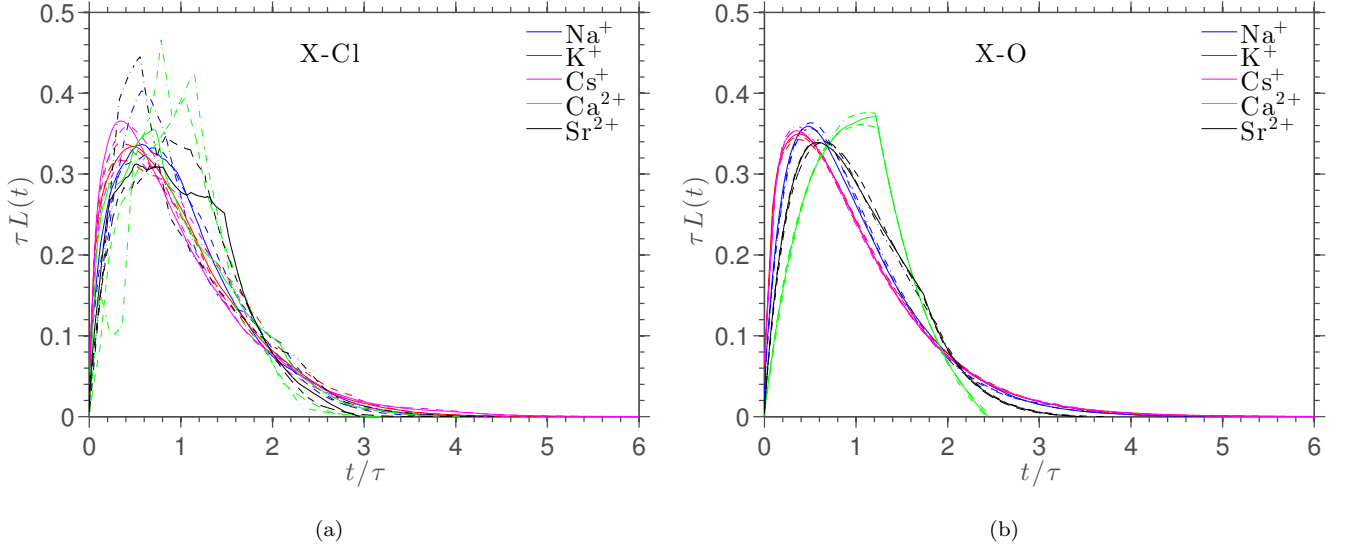


FIG. S5: Rescaled life-time distribution functions in different aqueous chloride solutions and different electrolyte concentrations at a temperature of 300 K and a pressure of 1 atm. The dashed-dotted lines correspond to a molar concentration of 0.3M, the dashed lines to 0.6M and the full lines to 0.9M. The different colors of the lines correspond to the cations species in the chloride solutions: Na^+ (blue), K^+ (red), Cs^+ (magenta), Ca^{2+} (green), and Sr^{2+} (black).

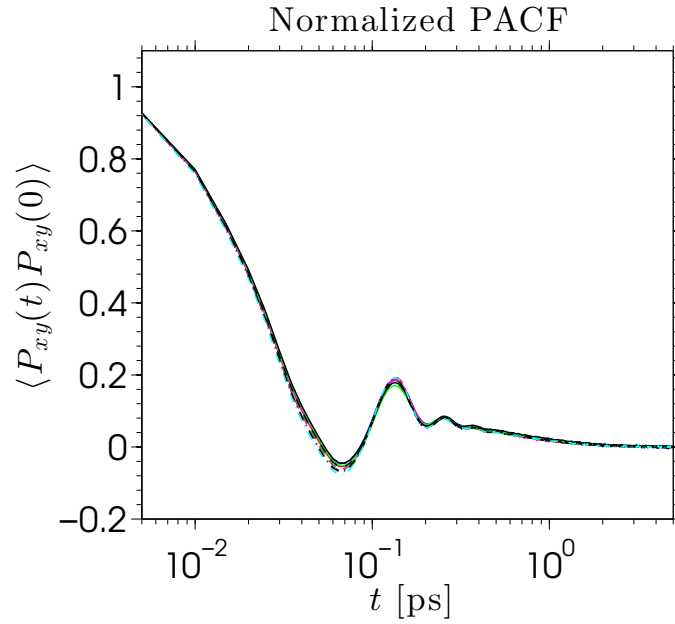


FIG. S6: Normalized pressure-autocorrelation functions in different aqueous chloride solutions and different electrolyte concentrations at a temperature of 300 K and a pressure of 1 atm. Despite the differences in viscosity, the differences between the correlation functions are very small. The dashed-dotted lines correspond to a molar concentration of 0.3M, the dashed lines to 0.6M and the full lines to 0.9M. These lines are overlapping almost perfectly. The different colors of the lines correspond to the cations species in the chloride solutions: Na^+ (blue), K^+ (red), Cs^+ (magenta), Ca^{2+} (green), and Sr^{2+} (black).

TABLE S V: Viscosity values of shear viscosity for different aqueous chloride solutions and different electrolyte concentrations at a temperature of 300 K and a pressure of 1 atm. The values between brackets indicate the standard error of the calculated viscosity values. The details of the viscosity calculation are reported in the paper. The viscosities are expressed in $\text{mPa} \cdot \text{s}$.

Pure water			
	0.96(2)		
Solutions			
	0.3M	0.6M	0.9M
Na ⁺	1.02(2)	1.06(1)	1.16(3)
K ⁺	1.01(2)	1.02(1)	1.05(3)
Cs ⁺	0.95(1)	0.97(3)	1.04(3)
Ca ²⁺	0.99(1)	1.08(4)	1.14(3)
Sr ²⁺	1.02(3)	1.06(1)	1.21(5)

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