

Structural and dynamic properties of some aqueous salt solutions

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SUPPLEMENTARY INFORMATION

Contents

Page number:	
2	Figure S1: dynamic (self-diffusion, shear viscosity) and structural properties of water (radial distribution functions), as predicted by three commonly used water models: TIP3P ¹ , SPC/E ² and TIP4P/2005 ³ .
3	Figure S2: computed ion-ion RDFs in aqueous solution.
4	Table S1: Force field parameters implemented to describe ions, with references.
5	Table S2: Example simulation results for water viscosity, with uncertainties, 12ns duration.
5	Table S3: Example simulation results for water viscosity, with uncertainties, 18ns duration.
5	Table S4: Example simulation results for water viscosity, with uncertainties, 22ns duration.
6	Table S5: Example simulation results for water self-diffusion, with uncertainties.
6-8	FIGURES S3 – S6: ION-WATER RADIAL DISTRIBUTION FUNCTIONS, AT 26°C:
➤ 6	• Fig.S3: Ammonium acetate in aqueous solution: concentration $M=0.1$ to 1.
➤ 7	• Fig.S4: Barium acetate in aqueous solution: concentration $M = 0.1$ to 1.
➤ 7	• Fig.S5. Sodium chloride in aqueous solution: concentration $M = 0.1$ to 1.
➤ 8	• Fig.S6. Barium nitrate in aqueous solution: concentration $M = 0.1$ and 0.3.
8-9	Figure S7: Jones-Dole plots and resulting B-coefficients calculated from experimental viscosity data of the present work.
9	TABLE S6: Approximate proportion of total water 'engaged' in first hydration shells of ions: 1M aqueous solutions.

FIGURE S1.

Dynamic (self-diffusion, shear viscosity) and structural properties of water (radial distribution functions), as predicted by three commonly used water models: TIP3P, SPC/E and TIP4P/2005. Experimental data is shown for comparison^{4,5}, with x-ray diffraction and Empirical Structural Refinement (EPSR) data for RDFs⁶.

<i>DYNAMIC PROPERTIES</i>	EXPERIMENTAL (20°C)	TIP3P	SPC/E	TIP4P/2005
Self-diffusion constant (10^{-9} m ² /s)	2.025 ⁴	3.94	2.22	1.94
Shear viscosity (10^{-3} Pa s)	1.0016 ⁵	0.48	0.77	0.93

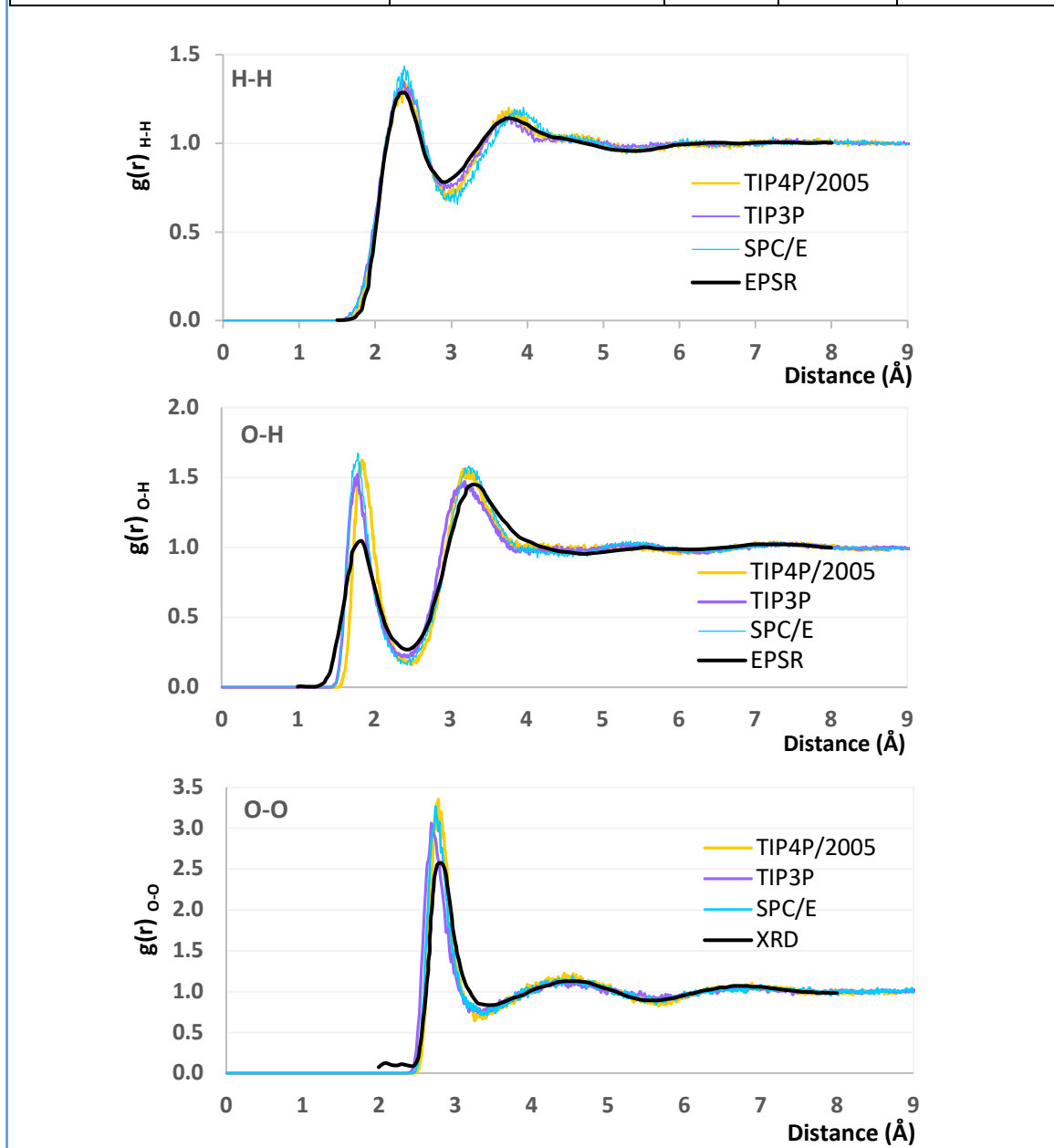


FIGURE S2.

Ion-ion RDFs in aqueous solution at the highest concentrations considered. $T=26^{\circ}\text{C}$.

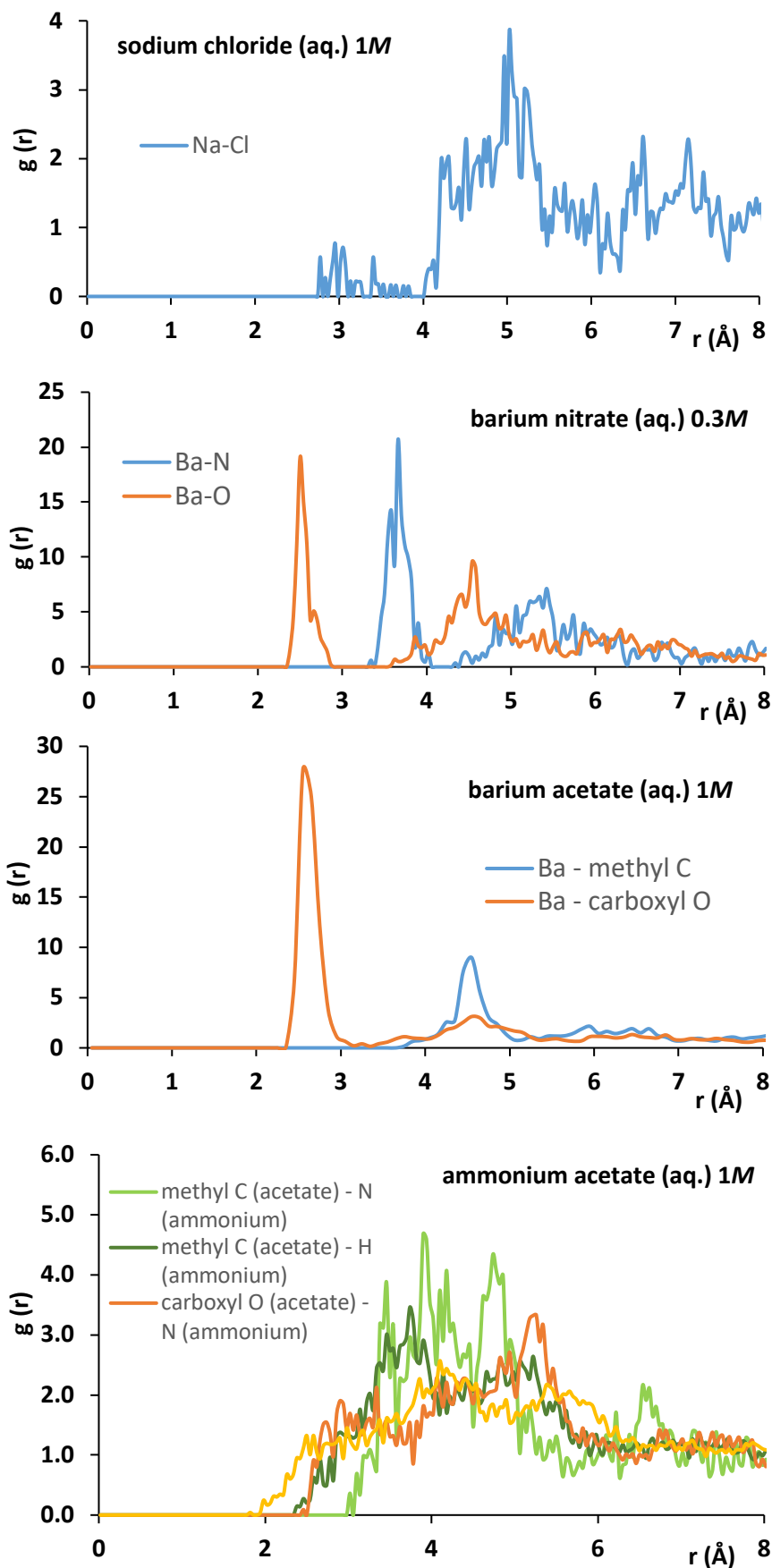


TABLE S1.

Force field parameters implemented to describe ions, with references.

Parameters	ION PAIRS:							
	$\text{NH}_4^+, \text{C}_2\text{H}_3\text{O}_2^-$		$\text{Ba}^{2+}, 2(\text{C}_2\text{H}_3\text{O}_2^-)$		$\text{Ba}^{2+}, 2(\text{NO}_3^-)$		Na^+, Cl^-	
ϵ (kcal/mol), σ (Å)	N-N	0.1700, 3.25	Ba-Ba	0.017686424, 3.82	Ba-Ba	0.017686424, 3.82	Na-Na	0.3526418, 2.159
	H-H	0.0157, 1.06908	CT-CT	0.1094, 3.39967	N-N	0.17000478, 3.15	Cl-Cl	0.0127850, 4.830
	CT-CT	0.1094, 3.39967	HC-HC	0.0157, 2.64953	O-O	0.200, 2.85		
	HC-HC	0.0157, 2.64953	C-C	0.0860, 3.39967				
	C-C	0.0860, 3.39967	O-O	0.2100, 2.95992				
	O-O	0.2100, 2.95992						
q (e)	N	-0.70686	Ba	2.00	Ba	2.00	Na	1.00
	H	0.426715	CT	-0.2126	N	1.118	Cl	-1.00
	CT	-0.2126	HC	0.003577	O	-0.706		
	HC	0.003577	C	0.882473				
	C	0.882473	O	-0.840302				
	O	-0.840302						
Bond coefficients: elastic constant (kcal mol ⁻¹ /Å ²), equilibrium bond length (Å)	N-H	3369.0, 1.033	CT-H	337.3, 1.0920	N-O	5000.0, 1.226		
	CT-H	337.3, 1.0920	CT-C	328.3, 1.5080				
	CT-C	328.3, 1.5080	C-O	648.0, 1.2140				
	C-O	648.0, 1.2140						
Angle Coefficients: K (kcal/mol), angle (θ_0 , in degrees)	H-N-H	40.52, 108.11	H-CT-H	39.43, 108.35	O-N-O	500.0, 120.00		
	H-CT-H	39.43, 108.35	HC-CT-C	47.2, 109.68				
	HC-CT-C	47.2, 109.68	CT-C-O	68.03, 123.11				
	CT-C-O	68.03, 123.11						
Dihedrals: K (kcal/mol), n (integer ≥ 0), d (integer value of degrees), weighting factor (1.0, 0.5, or 0.0)	HC-CT-C-O	1.60, 1, 0.0, 0.0		1.60, 1, 0.0, 0.0				
	CT-O1-C-O2	0.16, 2, 180, 0.0		0.16, 2, 180, 0.0				
References:	10		9, 10		9, 8		7	

Harmonic bond style potential: $E = K (r - r_0)^2$

K : (energy/distance²)

r_0 : equilibrium bond distance

Harmonic angle style potential: $E = K (\theta - \theta_0)^2$

K : prefactor (energy)

θ_0 : equilibrium angle value

Charmm dihedral style potential: $E = K [1 + \cos (n\phi - d)]$

TABLE S2.

Example simulation results for water viscosity, with uncertainties; 12ns duration. Pure water; 3 independent system configurations, SPC/E water model, 11089 water molecules, 20°C.

The first 6ns of the simulations are dropped from analysis, with the remaining 6 ns used for production (the simulation is shown here split into time-blocks of 2ns). Viscosity values, computed every 500 fs, are averaged over the latter 6 ns to yield a mean value for each simulation production run. Prediction uncertainty is calculated as standard deviation from the mean average value of three production runs, and lies within 2%, for all salt types and concentrations considered.

Configuration 1			Configuration 2			Configuration 3			Average of 3 simulations		
Time (ns)	Viscosity [mPa s]	Standard deviation	Time (ns)	Viscosity [mPa s]	Standard deviation	Time (ns)	Viscosity [mPa s]	Standard deviation	Time (ns)	Viscosity [mPa s]	Standard deviation
0-2	0.779	0.021	0-2	0.777	0.016	0-2	0.786	0.011	0-2	0.781	0.005
2-4	0.772	0.003	2-4	0.769	0.001	2-4	0.780	0.002	2-4	0.773	0.006
4-6	0.767	0.001	4-6	0.770	0.002	4-6	0.777	0.001	4-6	0.771	0.005
6-8	0.766	0.001	6-8	0.764	0.001	6-8	0.774	0.001	6-8	0.768	0.005
8-10	0.763	0.001	8-10	0.764	0.000	8-10	0.773	0.001	8-10	0.767	0.006
10-12	0.762	0.000	10-12	0.764	0.000	10-12	0.772	0.000	10-12	0.766	0.005
Mean (6-12ns):	0.764	0.002	Mean (6-12ns):	0.764	0.001	Mean (6-12ns):	0.773	0.001	Mean (6-12ns):	0.767	0.005

TABLE S3.

Example simulation results for water viscosity; 18ns duration. To test the reliability of predictions and adequacy of a 12 ns simulation run-time for obtaining equilibrated viscosity values, simulations for pure water were conducted to 18ns, starting from the same three independent initial system configurations.

Configuration 1			Configuration 2			Configuration 3			Average of 3 simulations		
Time (ns)	Viscosity [mPa s]	Standard deviation	Time (ns)	Viscosity [mPa s]	Standard deviation	Time (ns)	Viscosity [mPa s]	Standard deviation	Time (ns)	Viscosity [mPa s]	Standard deviation
0-2	0.781	0.022	0-2	0.780	0.015	0-2	0.783	0.013	0-2	0.781	0.002
2-4	0.769	0.001	2-4	0.782	0.002	2-4	0.769	0.002	2-4	0.773	0.007
4-6	0.770	0.001	4-6	0.776	0.002	4-6	0.768	0.001	4-6	0.771	0.005
6-8	0.770	0.000	6-8	0.771	0.002	6-8	0.768	0.001	6-8	0.770	0.002
8-10	0.771	0.001	8-10	0.768	0.000	8-10	0.768	0.000	8-10	0.769	0.002
10-12	0.770	0.000	10-12	0.767	0.000	10-12	0.768	0.001	10-12	0.768	0.002
12-14	0.769	0.001	12-14	0.767	0.000	12-14	0.767	0.001	12-14	0.768	0.001
14-16	0.768	0.000	14-16	0.767	0.000	14-16	0.766	0.000	14-16	0.767	0.001
16-18	0.767	0.000	16-18	0.767	0.000	16-18	0.766	0.000	16-18	0.767	0.001

TABLE S4.

Example simulation results for water viscosity; 22ns duration. A final simulation was conducted for 22 ns. Comparing results from Tables S2-S4, we conclude 12ns to be sufficient for obtaining equilibrated viscosity values; within the viscosity range of 0.795 ± 0.0473 mPa s¹¹ reported for SPC/E water at 19.85°C (293K).

Configuration 3		
Time (ns)	Viscosity [mPa s]	Standard deviation
0-2	0.776	0.011
2-4	0.775	0.001
4-6	0.770	0.001
6-8	0.772	0.001
8-10	0.772	0.001
10-12	0.772	0.001
12-14	0.772	0.001
14-16	0.771	0.000
16-18	0.771	0.000
18-20	0.770	0.000
20-22	0.771	0.000

TABLE S5.

Example simulation results for water self-diffusion, with uncertainties.

Self-diffusion coefficients were obtained from three independent simulations of 4.5ns each; 1ns equilibration time and 3.5ns production. Mean-squared displacement (MSD) values were obtained utilising in-built LAMMPS code. Self-diffusion coefficients were subsequently obtained from the slope of MSD over time using the Einstein relation¹². Uncertainty for diffusion coefficient results is calculated as the standard deviation from the mean average of three independent simulations per concentration for each salt type.

Example results for **water self-diffusion in 1M barium acetate aqueous solution**:

	Simulation 1	Simulation 2	Simulation 3	Average of 3 simulations
D ($10^{-9}\text{m}^2/\text{s}$):	1.54	1.57	1.52	1.54
				Standard deviation: 2.41×10^{-11} Expressed as a percentage of the mean: 1.56%

FIGURES S3 – S6: ION-WATER RADIAL DISTRIBUTION FUNCTIONS, AT 26°C.

FIGURE S3. Ammonium acetate in aqueous solution: ion-water RDFs, concentration $M=0.1$ to 1. Simulation results from literature, obtained using MD with SPC/E water for the acetate ion¹³ and Monte-Carlo (MC) methods with SPC/E for both acetate and ammonium ions¹⁴, are shown alongside for comparison. Reference atoms for the acetate ion are carboxylate group oxygens and methyl group carbon.

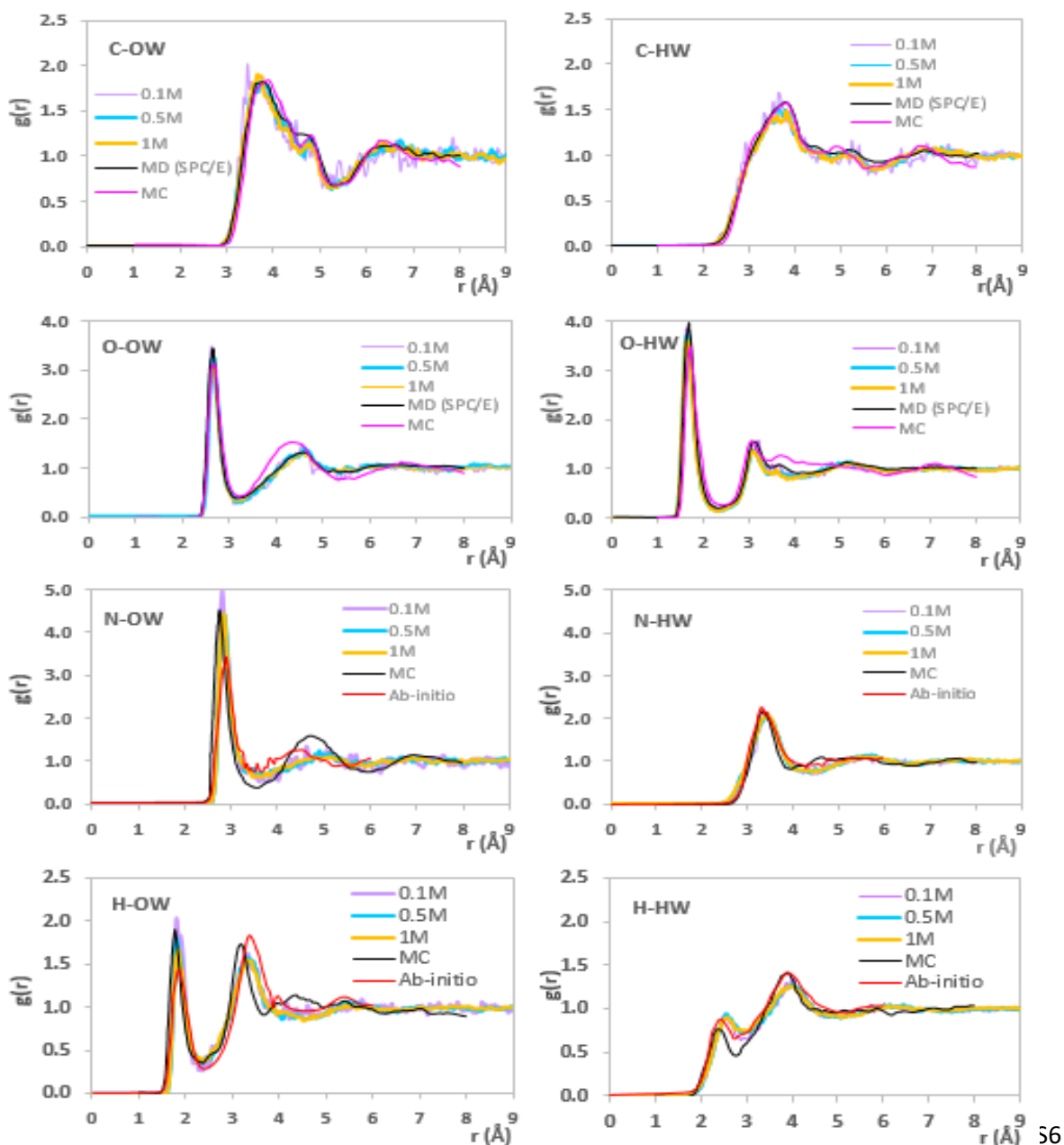


FIGURE S4. Barium acetate in aqueous solution: ion-water RDFs, concentration $M = 0.1$ to 1 :

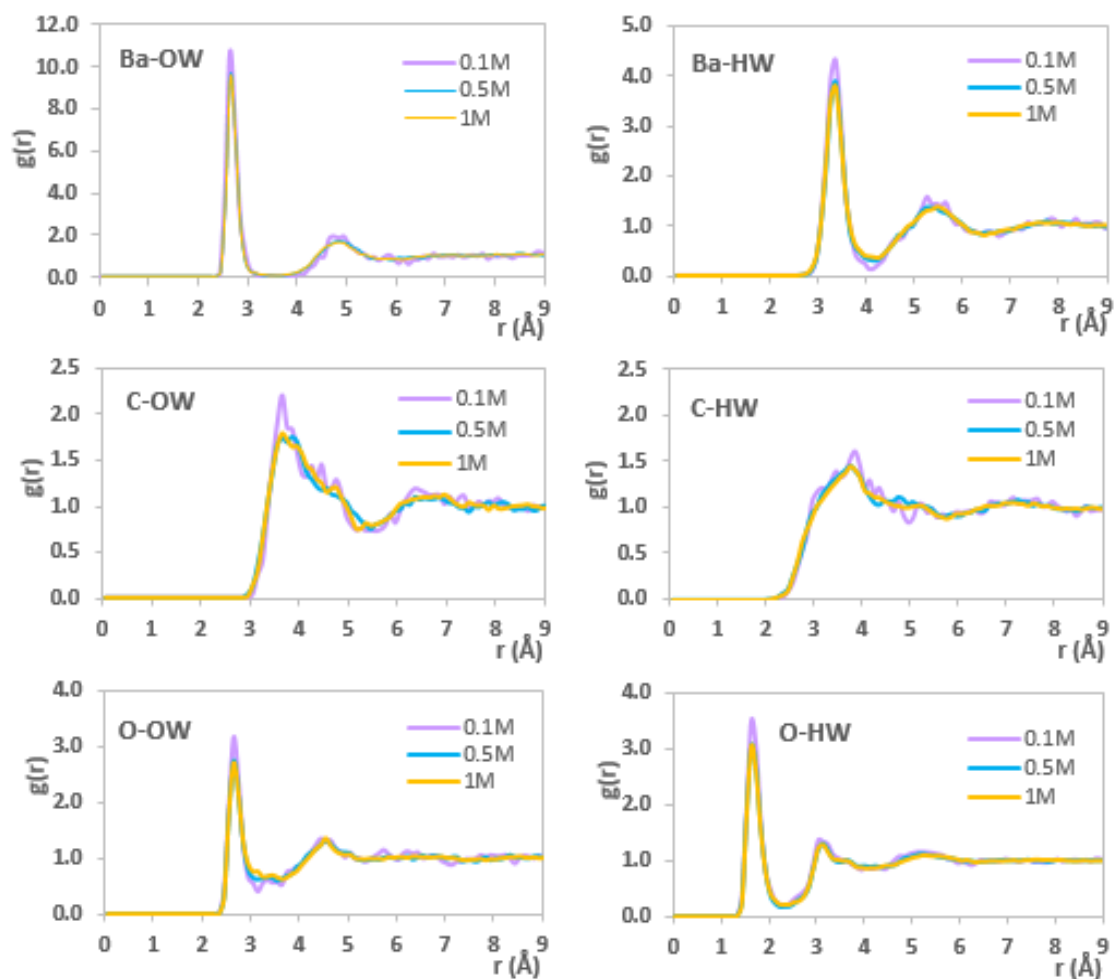


FIGURE S5. Sodium chloride in aqueous solution: ion-water RDFs, concentration $M = 0.1$ to 1 . Literature results, from the Empirical Structural Refinement (EPSR) approach¹⁵ and MD simulations with SPC/E water and Joung-Cheatham ion parameters (24.85°C, $M = 1.3877$)¹⁵, are shown for comparison.

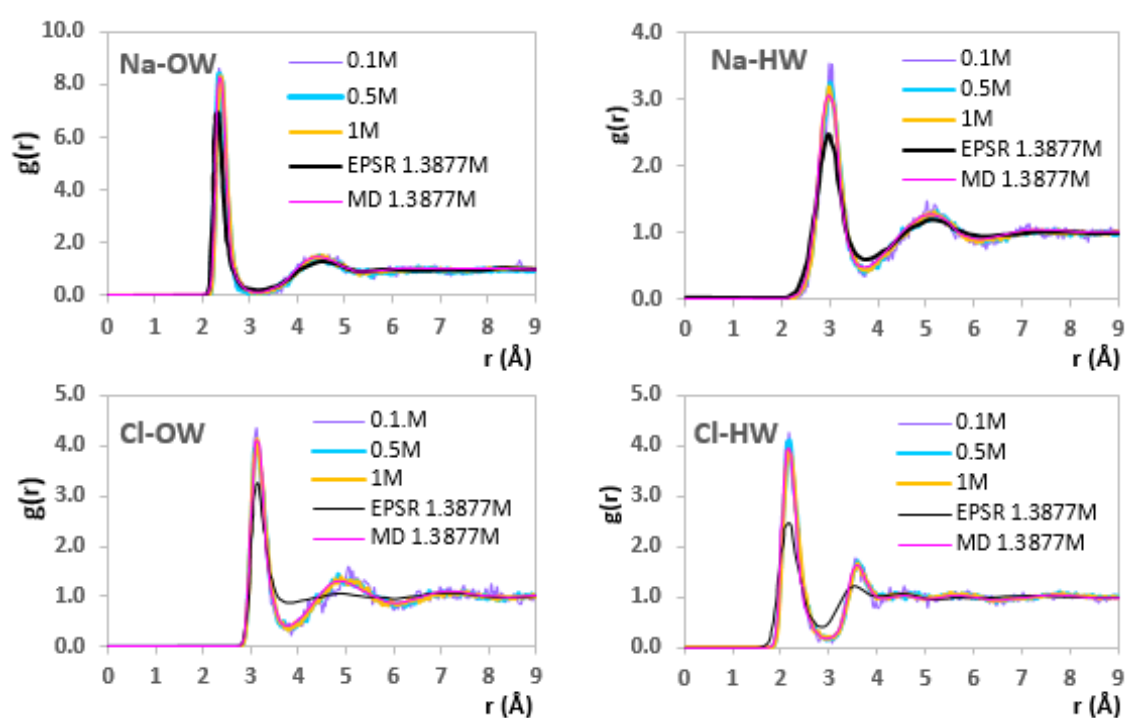


FIGURE S6. Barium nitrate in aqueous solution: ion-water RDFs, at $M = 0.1$ and 0.3 . Literature data for the nitrate ion, shown for comparison: aqueous (SPC/E) potassium nitrate solution at 26.85°C , 0.102 M ¹⁶.

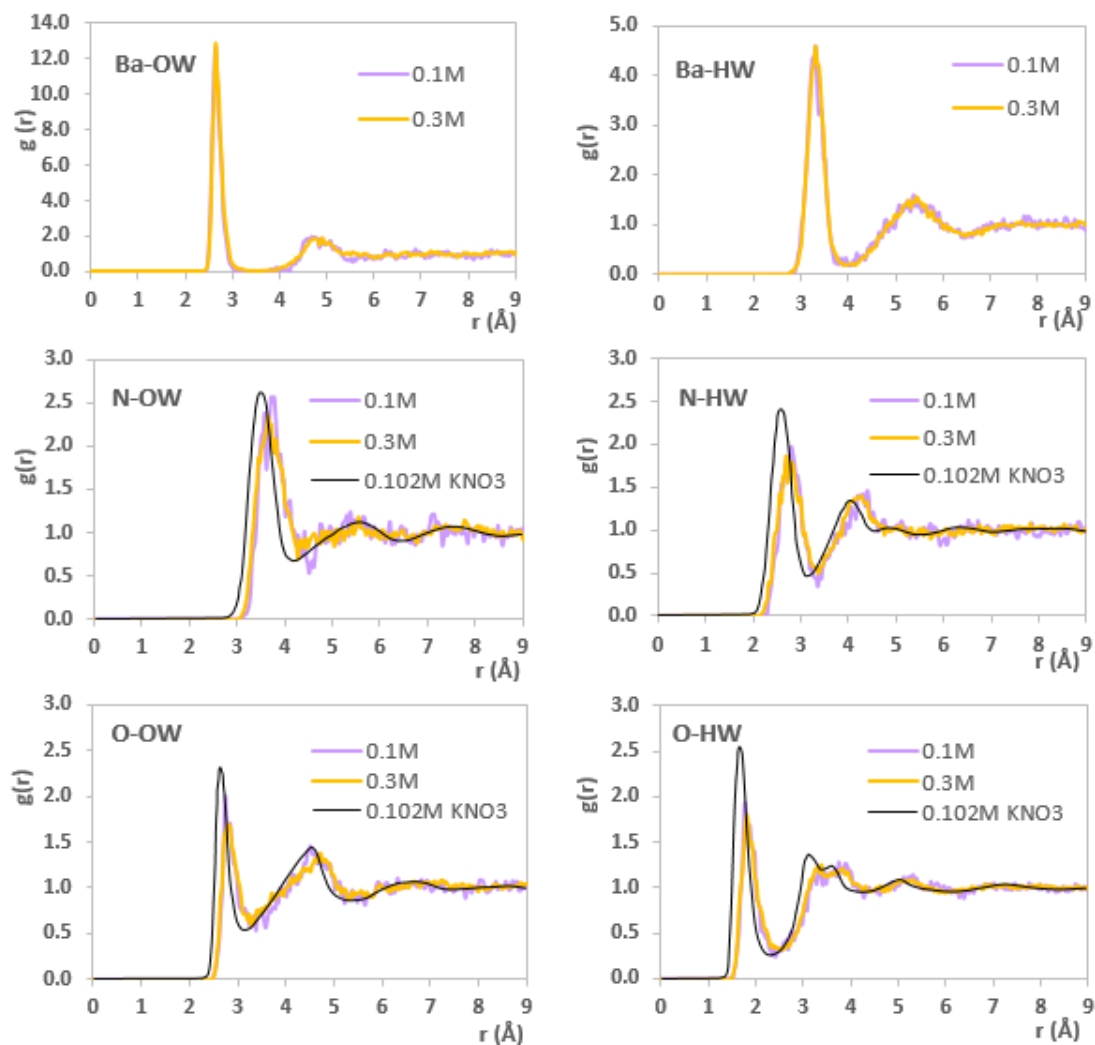


FIGURE S7:

Jones-Dole plots and resulting B-coefficients calculated from experimental viscosity data obtained in the present work (reported in main text). Values are assumed to be additive, and should be viewed tentatively due to the limited number of sample concentrations, but are presented here for readers that may be interested.

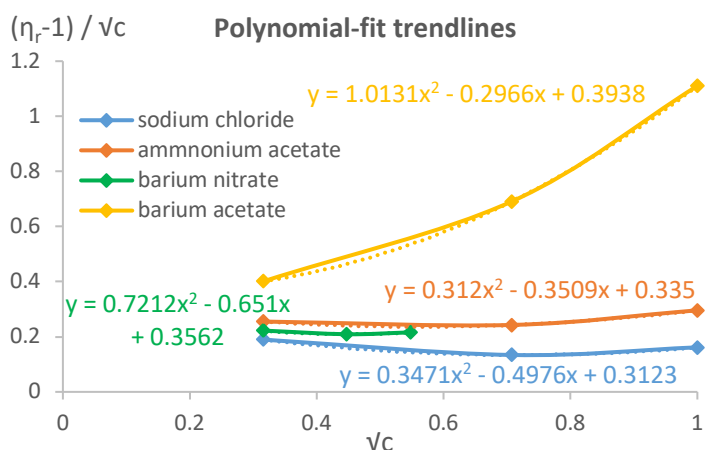
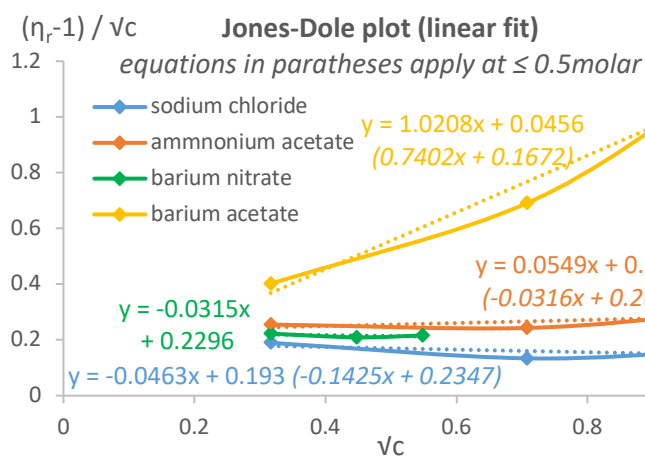
- In very dilute solutions (experimental data concentration range: 0.005 to 1 molal) forces are proportional to the square root of electrolyte concentration, hence the expression for **fluidity** (original Jones-Dole expression)¹⁷) in the form:

$$\varphi = 1 + A\sqrt{c} + Bc$$

implemented by subsequent authors¹⁸) to express **relative viscosity** ($\eta_r = \eta/\eta_0$).

A: accounts for long range electrostatic/Coulombic interactions, dominating at dilute regimes

B: adjustable, additive parameter related to ion size and proportional to partial molar entropies of the ions, accounting for non-electrostatic interactions that emerge at higher salt concentrations (>0.1M).



SALT:	<i>B</i> (concentrations ≤ 1 molar), 26°C	<i>B</i> (concentrations ≤ 0.5 molar), 26 °C	<i>B</i> Compiled from (Table 3 of ref.17): 'selected' values, at 25°C
Barium acetate	1.0208	0.7402	0.708
Barium nitrate	-0.0315	-0.0315	0.13
Ammonium acetate	0.0549	-0.0316	0.238
Sodium chloride	-0.0463	-0.1425	0.08

TABLE S6.

Approximate proportion of total water 'engaged' in first hydration shells of ions: 1M aqueous solutions.

Water molecules: 11089. Number of ions shown at 1 molar concentration, with exception of barium nitrate (0.3 molar). Coordination numbers taken from Table 5 (in main text, with references).

SALT:	Number of ions in the system	(First shell) ion coordination number	Proportion of total water 'engaged'
Sodium chloride	(Na) ⁺ → 200 (Cl) ⁻ → 200	(Na) ⁺ → 5 (Cl) ⁻ → 6	2200/11089 → ~20%
Ammonium acetate	(NH ₄) ⁺ → 200 (CH ₃ CO ₂) ⁻ → 200	(NH ₄) ⁺ → 5 (CH ₃ CO ₂) ⁻ → 16	4200/11089 → ~38%
Barium acetate	Ba ²⁺ → 200 (CH ₃ CO ₂) ⁻ → 400	Ba ²⁺ → 8 (CH ₃ CO ₂) ⁻ → 16	8000/11089 → ~72%
Barium nitrate	Ba ²⁺ → 70 (NO ₃) ⁻ → 140	Ba ²⁺ → 8 (NO ₃) ⁻ → 21	4200/11089 → ~32%

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