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Supporting Information:

Solute Specific Perturbations to Water Structure and Dynamics in Tertiary Aqueous Solution

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List S1. Samples list with isotopic makeup

- H₂O
- D₂O
- HDO
- H₂O, 1.0 M H-TMAO
- D₂O, 1.0 M H-TMAO
- HDO, 1.0 M H-TMAO
- H₂O, 1.0 M D-TMAO
- D₂O, 1.0 M D-TMAO
- HDO, 1.0 M D-TMAO
- HDO, 1.0 M HD-TMAO
- H₂O, 0.2 M Mg(ClO₄)₂
- D₂O, 0.2 M Mg(ClO₄)₂
- HDO, 0.2 M Mg(ClO₄)₂
- H₂O, 1.0 M H-TMAO, 0.2 M Mg(ClO₄)₂
- D₂O, 1.0 M H-TMAO, 0.2 M Mg(ClO₄)₂
- HDO, 1.0 M H-TMAO, 0.2 M Mg(ClO₄)₂
- H₂O, 1.0 M D-TMAO, 0.2 M Mg(ClO₄)₂
- D₂O, 1.0 M D-TMAO, 0.2 M Mg(ClO₄)₂
- HDO, 1.0 M D-TMAO, 0.2 M Mg(ClO₄)₂
- HDO, 1.0 M HD-TMAO, 0.2 M Mg(ClO₄)₂
- H₂O, 2.7 M Mg(ClO₄)₂
- D₂O, 2.7 M Mg(ClO₄)₂
- HDO, 2.7 M Mg(ClO₄)₂
- H₂O, 1.0 M H-TMAO, 2.7 M Mg(ClO₄)₂
- D₂O, 1.0 M H-TMAO, 2.7 M Mg(ClO₄)₂
- HDO, 1.0 M H-TMAO, 2.7 M Mg(ClO₄)₂
- H₂O, 1.0 M D-TMAO, 2.7 M Mg(ClO₄)₂
- D₂O, 1.0 M D-TMAO, 2.7 M Mg(ClO₄)₂
- HDO, 1.0 M D-TMAO, 2.7 M Mg(ClO₄)₂
- HDO, 1.0 M HD-TMAO, 2.7 M Mg(ClO₄)₂

Atomic species	ϵ (kJ/mol)	σ (Å)	Charge (e)
O _w	0.65	3.166	-0.8476
H _w	0.00	0.00	0.4238
C1	0.39	3.70	-0.2600

H1	0.065	1.80	0.1100
N1	0.711	3.25	0.4400
O1	0.585	3.08	-0.6500
Mg	0.4593	0.90	2.0000
Cl _p	0.566	4.19	2.3904
O _p	0.65	3.166	-0.8476

Table S1. Lennard-Jones and Coulomb parameters for atomic species present in simulation. W subscript indicates water atoms, 1 indicates TMAO, p indicates perchlorate ion

Sample	Water Molecules	TMAO Molecules	Mg ²⁺ ions	ClO ₄ ⁻ ions	Box dimension (Å)
H ₂ O	1000	-	-	-	31.0723
1.0 M TMAO	4104	80	-	-	51.0434
0.2 M Mg(ClO ₄) ₂	4104	-	16	32	49.9840
1.0 M TMAO, 0.2 M Mg(ClO ₄) ₂	4104	80	16	32	51.2654
2.7 M Mg(ClO ₄) ₂	4224	-	260	520	54.4902
1.0 M TMAO, 2.7 M Mg(ClO ₄) ₂	4224	80	260	520	55.5774

Table S2. Number of molecules used in each simulation box and length of cubic box

Figure S1. H¹ NMR peak shift for water as a function of increasing concentration of the potassium halide salts: KF, KCl, KBr, KI.

Figure S2. Net magnetization in the z direction following a 180° pulse for four example datasets. The data are all extremely well described using a single exponential decay term, indicating that any dynamic heterogeneities in the sample are minimal.

Solute pair	1.0 M TMAO	0.2 M $\text{Mg}(\text{ClO}_4)_2$	0.2 M $\text{Mg}(\text{ClO}_4)_2$ + 1.0 M TMAO	2.7 M $\text{Mg}(\text{ClO}_4)_2$	2.7 M $\text{Mg}(\text{ClO}_4)_2$ + 1.0 M TMAO
$\text{Cl}_p - \text{Mg}$	-	0.03 (3.50 Å)	0.03 (3.50 Å)	0.58 (3.50 Å)	0.55 (3.50 Å)
$\text{N1} - \text{Cl}_p$	-	-	0.24 (6.28 Å)	-	3.45 (6.61 Å)
$\text{N1} - \text{Mg}$	-	-	0.03 (3.50 Å)	-	0.2 (3.50 Å)
$\text{N1} - \text{N1}$	0.70 (7.04 Å)	-	1.00 (7.82 Å)	-	0.33 (6.24 Å)

Table S3. Coordination numbers for solute – solute interactions present in samples. Distance used to calculate solute – solute coordination number correspond to the location of the first minima in the associated RDF, shown in brackets.

Figure S3. EPSR fits (red lines) to corrected diffraction data (black points) for 1.0 M TMAO (top left), 0.2 M $\text{Mg}(\text{ClO}_4)_2$ (top right), 1.0 M TMAO + 0.2 M $\text{Mg}(\text{ClO}_4)_2$ (bottom left), 1.0 M TMAO + 2.7 M $\text{Mg}(\text{ClO}_4)_2$ (bottom right).

Figure S6. Determining optimal weighting parameter g through numerical differentiation

Figure S8. Replotting inverse T_1 data using effective total concentration described by $[Eff] = [Mg(ClO_4)_2] + g[TMAO]$ where $[x]$ is the concentration of solute x in mol/kg H₂O and g is a weighting factor. Weighting factor is set to the extreme limits used to determine the optimum weighting parameter: 0.9 (a) and 2.4 (b).

Derivation S1. Determination of Excluded Volume

Here we make the very basic assumption that the excluded volume of a solute molecule is equivalent to the volume of a sphere whose radius corresponds to the distance from the solute molecule's central atom to the first peak of the central atom – water RDF. Table below shows the location of the first peak of the radial distribution functions for water around a central atom X (RDFs shown in figure S9) and the volume of the corresponding sphere.

Central atom X	X-O _w RDF first peak location (Å)	Effective volume (Å ³)
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Central TMAO nitrogen	4.52	387
Mg ²⁺	1.61	18
Central ClO ₄ ⁻ chlorine	3.94	256
Table S4. Location of the first peak in the X-O _w radial distribution function where X is the central atom of a solute molecule/ion and the volume of a sphere described by this distance. Data taken using the 0.2 M Mg(ClO ₄) ₂ + 1.0 M TMAO sample to minimise effects of hydration shell overlap.		

A TMAO molecule therefore has an effective volume of 387 Å³, and a completely dissolved Mg(ClO₄)₂ molecule therefore has an effective volume of 530 Å³. If the weighting parameter g were solely due to excluded volume effects it would therefore be equal to the ratio of the TMAO effective volume to the Mg(ClO₄)₂ effective volume, which is 0.73.