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ELECTRONIC SUPPLEMENTARY INFORMATION (ESI): Ion pairing in aqueous tetramethylammonium–acetate solutions by neutron scattering and molecular dynamics simulations

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1 Additional computational details

All performed the simulations are listed in Table S1.

Table S1: List of all simulated TMA–acetate systems

	System	Scaling factor	TMA force field	Acetate force field	Water model
1	CHARMM36-FULL	1.00	FULL	FULL	CHARMM-TIP3P
2	CHARMM36-ECC85	0.85	ECC85	ECC85	
3	CHARMM36-ECC75	0.75	ECC75	ECC75	
4	CHARMM36-Low CH dipole		Low CH	ECC75	
5	CHARMM36-Low CO dipole			Low CO	
6	CHARMM36-High CO dipole			High CO	
7	AMBER99SB-FULL	1.00	FULL	FULL	TIP3P
8	AMBER99SB-ECC85	0.85	ECC85	ECC85	
9	AMBER99SB-ECC75	0.75	ECC75	ECC75	

Table S2 lists all the TMA force fields used in the performed MD simulations.

Table S2: Details of the different TMA force fields used in this study. The employed atoms types are specified in parenthesis.

TMA force field		Atom (atom type) partial charge			Overall charge
		N (NTL)	C (CTL5)	H (HL)	
CHARMM36	FULL	-0.60	-0.35	0.25	+1.00
	ECC85	-0.60	-0.35	0.2375	+0.85
	ECC75	-0.61	-0.35	0.23	+0.75
	Low CH	-0.05	-0.10	0.10	
		N (n4)	C (c3)	H (hx)	
AMBER99SB	FULL	0.255981	-0.454050	0.213352	+1.00
	ECC85	0.255980	-0.454051	0.200852	+0.85
	ECC75	0.255980	-0.454052	0.192519	+0.75

Table S3 lists all the acetate (Ac) force fields used in the performed MD simulations.

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Table S3: Details of all acetate force fields used in this study. The employed atoms types are specified in parenthesis.

Acetate force field		Atom (atom type) partial charge				Overall charge
		C (CC)	O (OC)	C (CT3)	H (HA3)	
CHARMM36	FULL	0.620	-0.760	-0.370	0.090	-1.00
	ECC85	0.527	-0.646	-0.3145	0.0765	-0.85
	ECC75	0.465	-0.570	-0.2775	0.0675	
	Low CO	0.225	-0.450	-0.2775	0.0675	-0.75
	High CO	0.925	-0.800	-0.2775	0.0675	
		C (C)	**O (O2)**	**C (CT)**	**H (HC)**	
AMBER99SB	FULL	0.88641	-0.84114	-0.22228	0.00605	-1.00
	ECC85	0.75345	-0.71497	-0.18893	0.00514	-0.85
	ECC75	0.66481	-0.63086	-0.16671	0.00454	-0.75

2 Additional experimental details

Following a similar strategy as presented in the Methods section of the main text, but taking the difference between the diffraction patterns associated with solutions that differ only by the H/D substitution on acetate (both in D_2O and H_2O solutions), we obtained the first-order differences $\Delta S^{X_{H_2O}}_{H_{non}}(Q)$ and $\Delta S^{X_{D_2O}}_{H_{non}}(Q)$ (Fig. S1), that report on the correlation between non-exchangeable H on Ac and every other atom (X) in the system. They are respectively defined as (in units of mbarns):

$$\begin{aligned}\Delta S^{X_{D_2O}}_{H_{non}}(Q) &= S[d_3\text{Ac}\text{–}h_{12}\text{TMA}]^{D_2O}(Q) - S[h_3\text{Ac}\text{–}h_{12}\text{TMA}]^{D_2O}(Q)\\ &= 20.1\cdot S_{H_{Ac}D_W}(Q) + 9.4\cdot S_{H_{Ac}O}(Q)\\ &+ 2.2\cdot S_{H_{Ac}C}(Q) + 0.5\cdot S_{H_{Ac}N}(Q)\\ &- 2.4\cdot S_{H_{Ac}H_{TMA}}(Q) + 0.2\cdot S_{H_{Ac}H_{Ac}}(Q) - 30.0\end{aligned} \tag{S1}$$

$$\begin{aligned}\Delta S^{X_{H_2O}}_{H_{non}}(Q) &= S[d_3\text{Ac}\text{–}h_{12}\text{TMA}]^{H_2O}(Q) - S[h_3\text{Ac}\text{–}h_{12}\text{TMA}]^{H_2O}(Q)\\ &= -11.3\cdot S_{H_{Ac}H_W}(Q) + 9.4\cdot S_{H_{Ac}O}(Q)\\ &+ 2.2\cdot S_{H_{Ac}C}(Q) + 0.5\cdot S_{H_{Ac}N}(Q)\\ &- 2.4\cdot S_{H_{Ac}H_{TMA}}(Q) + 0.2\cdot S_{H_{Ac}H_{Ac}}(Q) + 1.4\end{aligned} \tag{S2}$$

The difference between Equation S1 and S2 yields the second order difference which now reports on a single correlation between the first nuclei that was substituted (H/D on the acetate), and the second nuclei (H/D on water) (see Equation S3) as shown in Figure S1.

$$\begin{aligned}\Delta\Delta S_{H_{Ac}H_W}(Q) &= S[d_3\text{Ac}\text{–}h_{12}\text{TMA}]^{D_2O}(Q) - S[h_3\text{Ac}\text{–}h_{12}\text{TMA}]^{D_2O}(Q)\\ &- (S[d_3\text{Ac}\text{–}h_{12}\text{TMA}]^{H_2O}(Q) - S[h_3\text{Ac}\text{–}h_{12}\text{TMA}]^{H_2O}(Q))\\ &= 31.4\cdot(S_{H_{Ac}H_W}(Q) - 1)\end{aligned} \tag{S3}$$

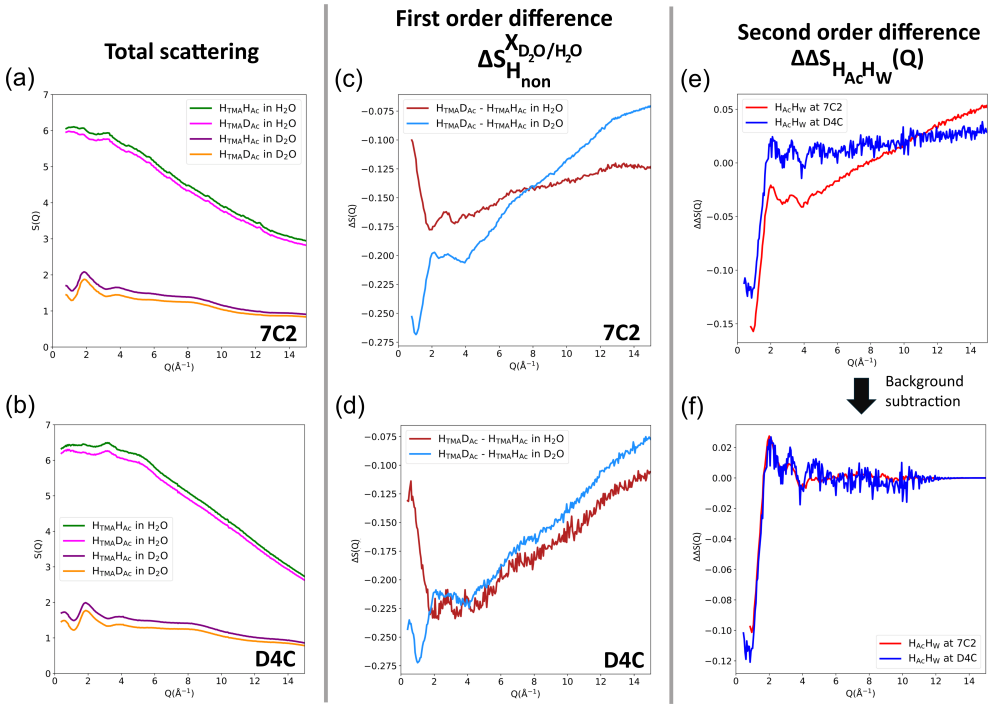

Figure S1: Total diffraction patterns for the solutions of the isotopic compositions of the 4 samples: h_{12}TMA–h_3Ac ($H_{TMA}H_{Ac}$, green) and h_{12}TMA–d_3Ac ($H_{TMA}D_{Ac}$, magenta) in H_2O; h_{12}TMA–h_3Ac ($H_{TMA}H_{Ac}$, violet) and h_{12}TMA–d_3Ac ($H_{TMA}D_{Ac}$, orange) in D_2O for experiments measured at (a) 7C2 and (b) D4C. First order differences of $\Delta S^{X_{H_2O}}_{H_{non}}(Q)$ (red) and $\Delta S^{X_{D_2O}}_{H_{non}}(Q)$ (light blue) for samples measured at (c) 7C2 and (d) D4C. (e) Second order difference $31.4 \cdot (S_{H_{Ac}H_W}(Q) - 1)$, obtained at 7C2 (red) and at D4C (blue). (f) Second order differences after the background subtraction and terminating data up to 13 Å^{-1}.

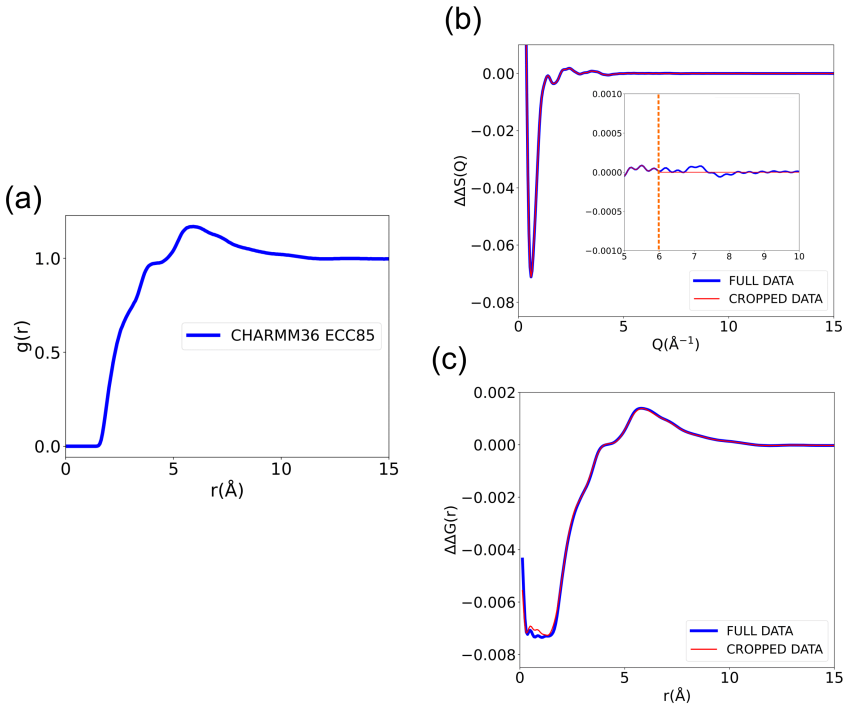

Figure S2: (a) Radial distribution function from TMA hydrogen atoms to acetate hydrogen atoms, $g(r_{H_{TMA}-H_{Ac}})$, from the MD simulation using CHARMM36-ECC85. (b) Comparison of the second order difference of $\Delta\Delta S_{H_{TMA}H_{Ac}}(Q)$ from the full vs. terminated (at 6 Å^{-1}) data in the Q-range. (c) The two sets of MD data transformed back to R-space show no effects of the data terminating.

3 Additional MD analyses

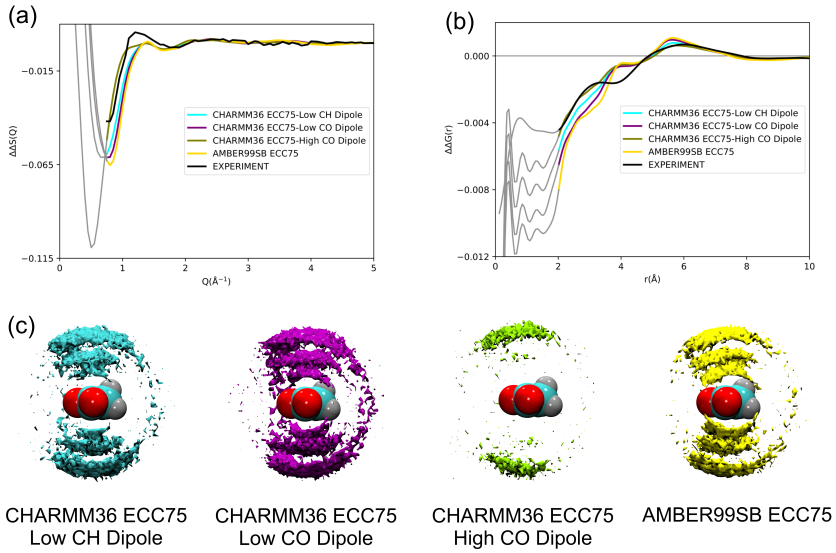

Figure S3: Comparison of the second order difference of $\Delta\Delta S_{\mathrm{H_{TMA}H_{Ac}}}(Q)$ of CHARMM36-Low CH dipole (cyan), CHARMM36-Low CO dipole (purple), CHARMM36-High CO dipole (olive), and AMBER99SB-ECC75 (yellow) versus experiment at 7C2 (black) in (a) reciprocal space (Q-space) and (b) real space (R-space). (c) The density maps show the density of $\mathrm{H_{TMA}}$ around acetate corresponding for the used force fields.

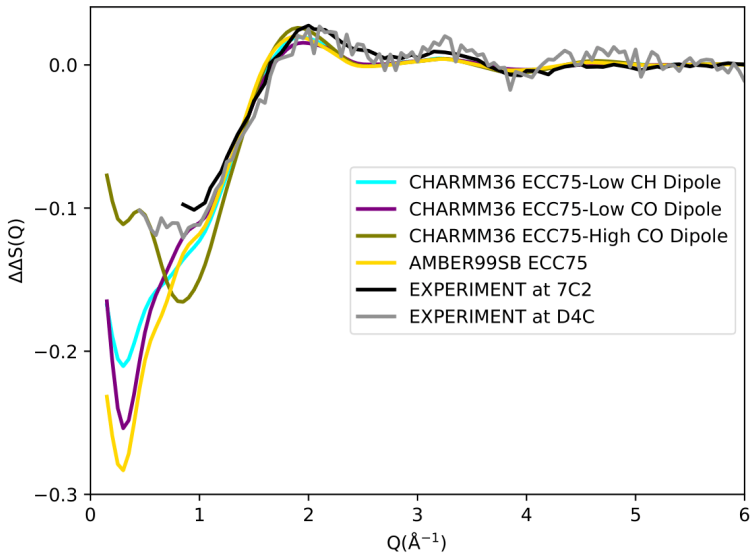

Figure S4: Comparison of second order difference $\Delta\Delta S_{\mathrm{H_{Ac}H_{water}}}(Q)$ of experiments at 7C2 (black) and D4C (gray) vs. FFMD simulations with different force fields: CHARMM36-Low CH dipole (cyan), CHARMM36-Low CO dipole (purple), CHARMM36-High CO dipole (olive), and AMBER99SB-ECC75 (yellow).

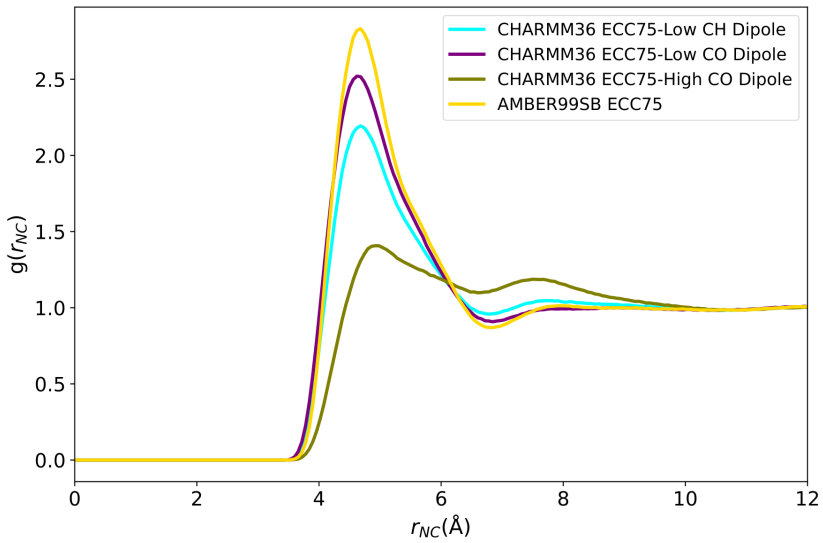

Figure S5: Radial distribution functions from the TMA nitrogen atom to the acetate carboxyl carbon atom, $g(r_{\mathrm{N_{TMA}-C_{Ac}}})$ from CHARMM36-Low CH dipole (cyan), CHARMM36-Low CO dipole (purple), CHARMM36-High CO dipole (olive), and AMBER99SB-ECC75 (yellow) force fields.