

Supporting Information for

Enhanced formation of solvent-shared ion pairs in aqueous calcium perchlorate solution towards saturated concentration or deep supercooling temperature and its effects on water structure

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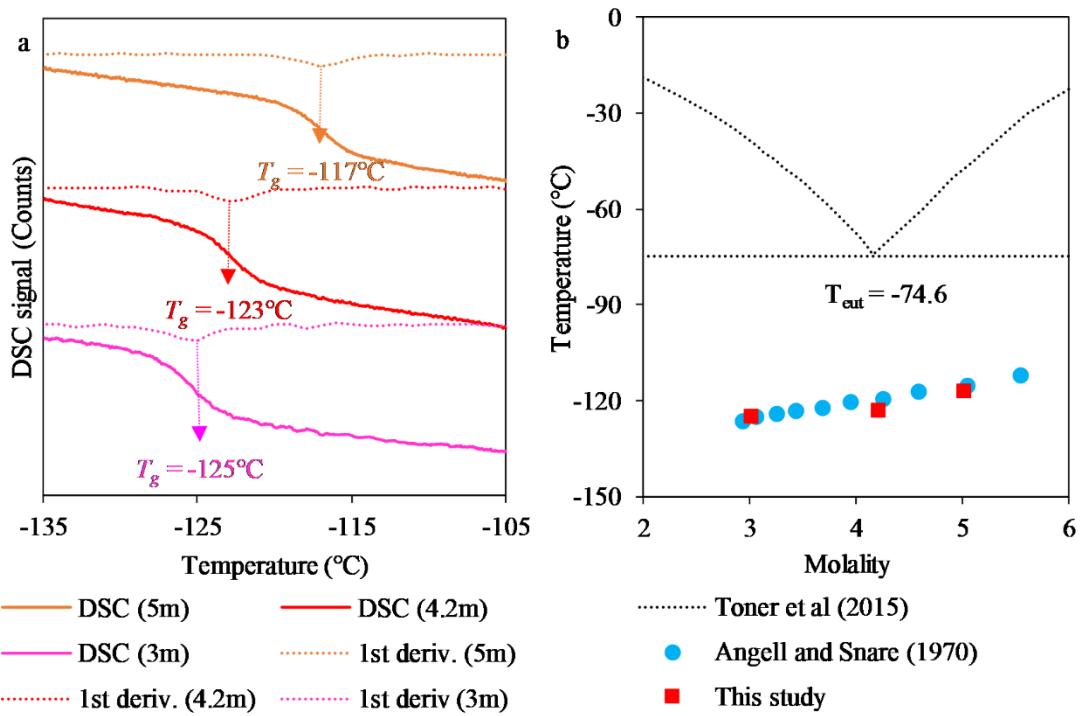


Fig. S1. (a) Glass-liquid transition of 5.0m, 4.2m and 3.0m Ca-perchlorate solutions occurs at the inflection point of the DSC curves (solid lines). T_g was determined by taking the minima of the first derivative (dotted lines) of the DSC curve; (b) T_g plotted on the phase diagram of $\text{Ca}(\text{ClO}_4)_2\text{-H}_2\text{O}$ system measured by Toner et al.¹ (dotted line).

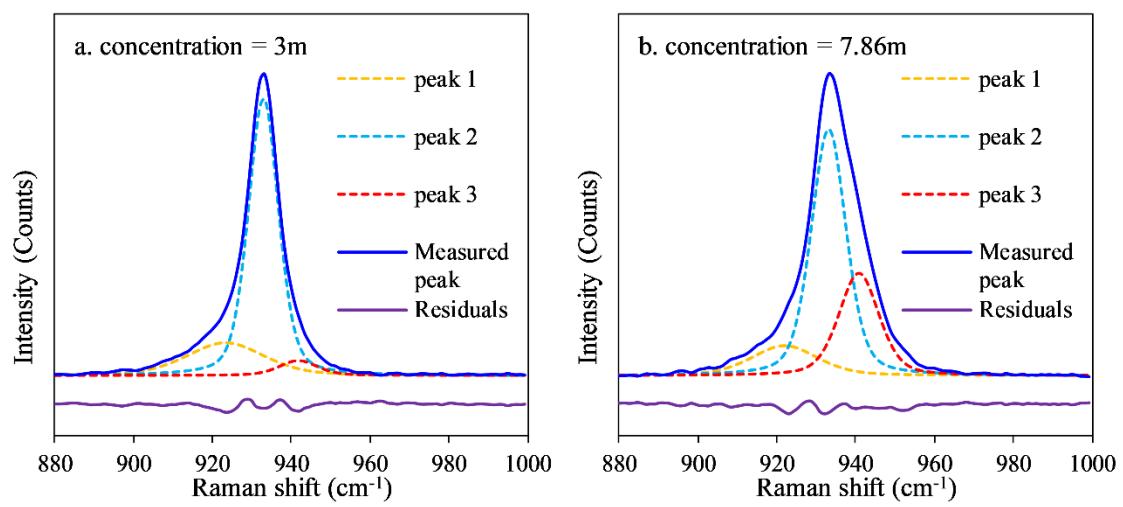


Fig. S2. Deconvolution results of the v_1 band ($\sim 933\text{cm}^{-1}$) of perchlorate ion for (a) 3.0 m Ca-perchlorate solution; (b) 7.86 m Ca-perchlorate solution. Peak analysis was conducted using a Matlab program coded by O'Haver²

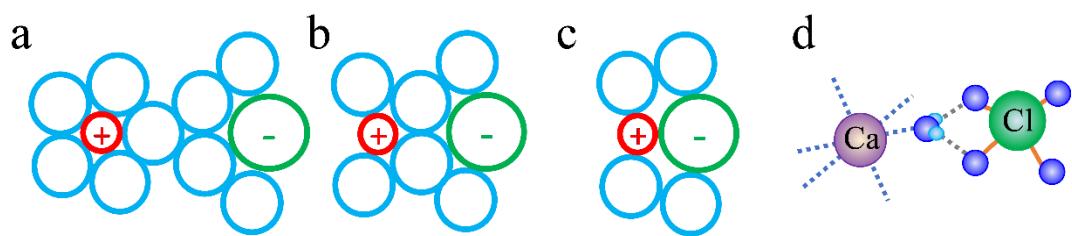


Fig. S3. Simplified scheme of ion-pair types: (a) solvent-separated (2SIP); (b) solvent-shared (SIP); (c) contact (CIP) Marcus and Hefter³; (d) a possible scheme of $[M^{2+}—H_2O\dots ClO_4]^+$. The complete solvation shell of cation and anion is not shown.

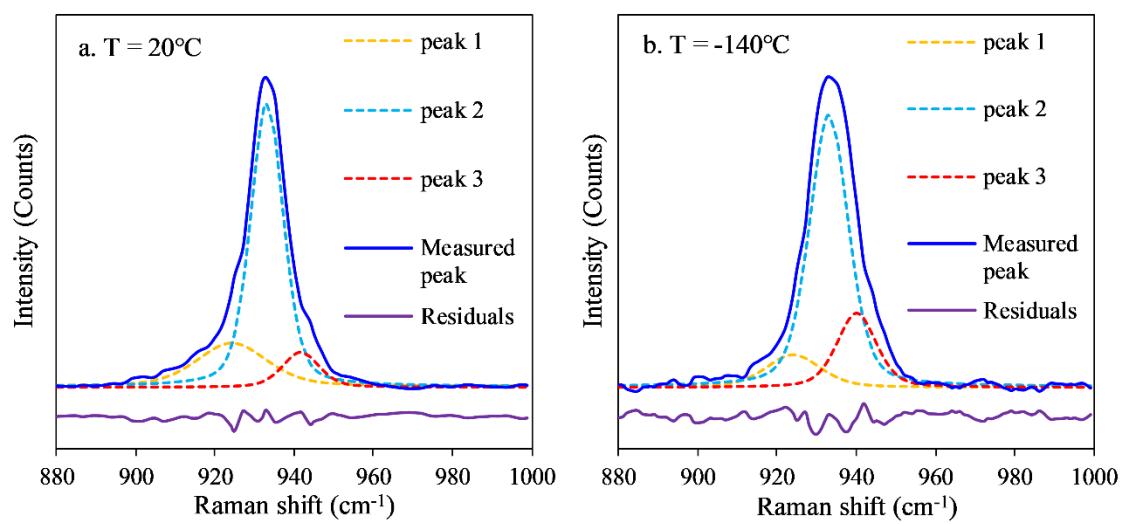


Fig. S4. Deconvolution results of the ν_1 band ($\sim 933 \text{ cm}^{-1}$) of perchlorate ion for (a) 5.0 m Ca-perchlorate spectra obtained at -20°C ; (b) -140°C (glassy state). Peak analysis was conducted using a Matlab program coded by O'Haver ²

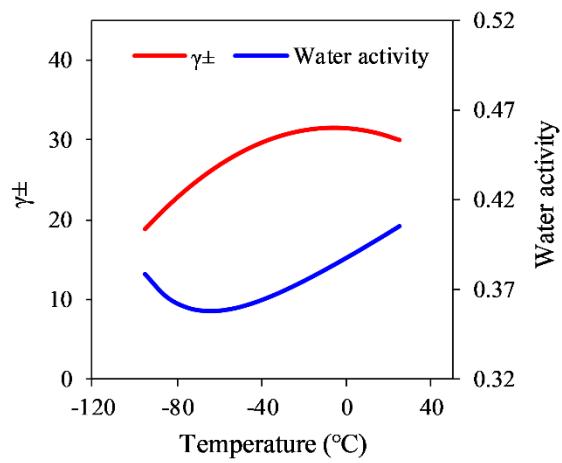


Fig. S5. The mean salt activity coefficient ($\gamma\pm$) calculated by Pitzer equation (red line) and the water activity in the 5.0 m Ca-perchlorate (blue line) from Toner and Catling⁴

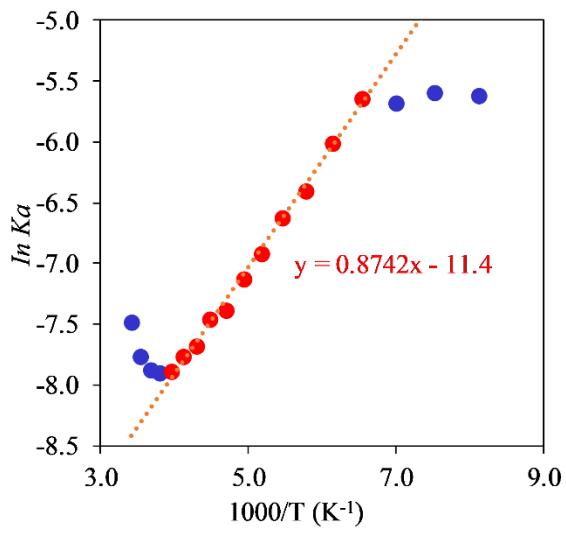


Fig. S6. Plot of $\ln K_a$ 1000/T for the 5.0 m Ca-perchlorate. The linear behavior extends from -20°C to -120°C

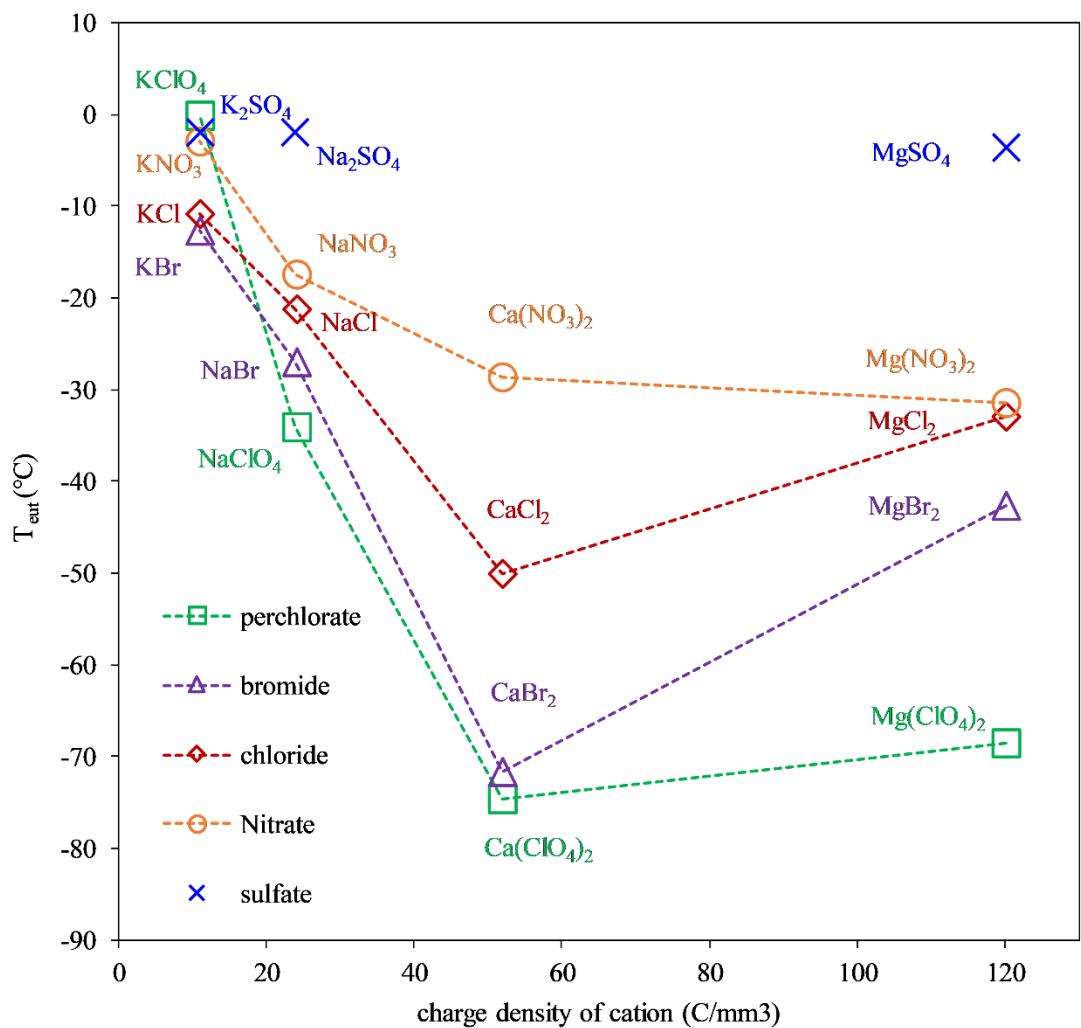


Fig. S7 T_{eut} of each salt versus the charge density of its cations. The value and source of T_{eut} were listed in Table 1 in the main text.

Table S1. Deconvolution analysis parameters of the v_1 band of ClO_4^- for solutions at different concentrations under room temperature.

Peak analysis was conducted using a Matlab program coded by O'Haver²

Conc. (molal)	overtone (Peak 1)				free ClO_4^- (Peak 2)				associated ClO_4^- (Peak 3)				R^2	$I_{\text{asso}}/I_{\text{tot}}$
	Center	Height	Width	Area	Center	Height	Width	Area	Center	Height	Width	Area		
3.0	923.48	109.17	23.20	2780.98	933.12	916.80	9.06	9875.87	941.95	46.20	11.40	614.41	0.9987	0.0586
4.2	923.66	106.28	24.37	2823.55	933.30	903.80	9.46	10145.70	941.56	86.00	10.54	1063.02	0.9987	0.0948
5.0	924.74	128.18	23.20	3278.16	933.56	881.20	9.90	10329.48	942.02	140.17	10.70	1756.13	0.9996	0.1453
6.0	923.25	113.87	19.10	2447.35	933.42	860.80	9.91	10100.42	941.33	285.50	11.09	3703.42	0.9993	0.2682
7.0	921.92	97.17	22.30	2379.11	933.29	820.50	10.53	10199.69	940.98	323.70	12.71	4773.47	0.9992	0.3188
7.86	923.88	129.81	19.50	2845.81	933.40	818.80	9.83	9533.77	941.26	357.57	11.84	4932.66	0.9994	0.3409

Table S2. Deconvolution analysis parameters of the v_1 band of ClO_4^- for 5.0 m solution at different temperatures. Peak analysis was conducted using a Matlab program coded by O'Haver²

T (°C)	overtone (Peak 1)				free ClO_4^- (Peak 2)				associated ClO_4^- (Peak 3)				R^2	$I_{\text{Lasso}}/I_{\text{tot}}$
	Center	Height	Width	Area	Center	Height	Width	Area	Center	Height	Width	Area		
20	924.74	128.18	23.20	3278.16	933.56	881.20	9.90	10329.48	942.02	140.17	10.70	1756.13	0.9996	0.1453
10	923.58	120.17	19.80	2668.70	933.12	910.35	10.00	10774.24	940.67	111.62	11.68	1521.63	0.9985	0.1237
0	925.16	139.75	20.60	3224.83	933.29	903.60	9.64	10326.56	941.73	111.12	11.29	1464.88	0.9986	0.1174
-10	922.79	89.17	22.10	2174.16	933.07	914.30	10.61	11447.75	940.24	92.27	14.37	1526.74	0.9987	0.1176
-20	923.64	87.17	22.15	2135.56	933.05	912.30	10.72	11535.12	940.25	97.98	13.67	1547.94	0.9981	0.1183
-30	923.71	92.17	21.90	2236.52	933.05	908.30	10.77	11535.35	940.31	115.17	12.57	1682.65	0.9977	0.1273
-40	923.83	86.17	21.72	2076.76	933.05	909.40	10.82	11600.16	939.98	126.09	11.71	1724.67	0.9978	0.1294
-50	922.90	81.17	22.42	2004.32	933.13	903.49	10.96	11665.80	939.83	129.80	13.05	1956.24	0.9981	0.1441
-60	923.27	91.37	18.91	1946.43	933.11	904.03	11.28	11995.24	939.73	130.92	12.94	1966.89	0.9984	0.1409
-70	923.62	90.21	19.49	1975.67	932.99	904.99	11.10	11826.95	940.26	157.74	11.79	2170.60	0.9984	0.1551
-80	923.73	76.93	19.15	1659.77	933.01	902.01	11.52	12209.36	939.90	166.73	11.96	2326.41	0.9977	0.1600
-90	924.54	87.72	19.28	1906.08	933.02	886.30	11.60	12075.36	940.04	177.93	12.23	2534.73	0.9978	0.1735
-100	923.08	67.70	16.94	1305.54	932.98	904.17	12.10	12819.20	940.02	190.70	12.26	2722.96	0.9983	0.1751
-110	922.22	63.29	19.52	1383.02	933.03	893.23	11.99	12555.41	939.85	222.50	11.73	3048.89	0.9979	0.1954
-120	922.25	76.80	15.16	1336.13	932.98	887.25	12.12	12598.89	939.85	229.76	12.46	3331.51	0.9955	0.2091

Reference:

- (1) Toner, J. D.; Catling, D. C.; Light, B. A Revised Pitzer Model for Low-Temperature Soluble Salt Assemblages at the Phoenix Site, Mars. *GCA* **2015**, *166*, 327-343.
- (2) O'Haver, T. A Pragmatic Introduction to Signal Processing, *Peakfit.m*, 9.4; University of Maryland at College Park, 1997.
- (3) Marcus, Y.; Hefter, G. Ion Pairing. *Chemical reviews* **2006**, *106*, 4585-4621.
- (4) Toner, J. D.; Catling, D. C. Water Activities of NaClO₄, Ca(ClO₄)₂, and Mg(ClO₄)₂ Brines from Experimental Heat Capacities: Water Activity >0.6 Below 200k. *GCA* **2016**, *181*, 164-174.