

SUPPLEMENTARY MATERIAL

Extending the Madrid-2019 force field to the perchlorate anion: role of charge distribution and validation with experiments on Mars-relevant aqueous solutions

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The Supplementary Material for the publication ‘Extending the Madrid-2019 force field to the perchlorate anion: role of charge distribution and validation with experiments on Mars-relevant aqueous solutions’ contains the compilation of the numerical (raw data) in tabular form of the simulation and experimental results considered in the main body of this work for the following properties:

- Simulation results for the densities as a function of the molality (m).
- Simulation results for the densities as a function of the temperature.
- Experimental results for the densities as a function of the temperature.
- Simulation results for the viscosities as a function of the molality (m).
- Simulation results for the diffusion coefficients of water as a function of the molality (m).

I. Densities as a function of molality

Table S I: Simulation results for the bulk density variation with molality for LiClO_4 aqueous solutions using model A, model B and from experiments [1] at 1 bar and 298.15 K. For Model A the results in parenthesis were obtained using the Flexible version of the force field.

m (mol/kg)	ρ (kg/m ³)		
	Expt.	Model A ($q_{Cl_p} = 0.35e$)	Model B ($q_{Cl_p} = 0e$)
0	997.1	997.3	997.3
2	1110.0	1108.0(1107.7)	1108.9
5	1245.1	1238.3(1238.4)	1241.4

Table S II: Simulation results for the bulk density variation with molality for NaClO_4 aqueous solutions using model A, model B and from experiments [2] at 1 bar and 298.15 K. For Model A the results in parenthesis were obtained using the Flexible version of the force field.

m (mol/kg)	ρ (kg/m ³)		
	Expt.	Model A ($q_{Cl_p} = 0.35e$)	Model B ($q_{Cl_p} = 0e$)
0	997.1	997.3	997.3
1	1071.3	1072.8 (1072.1)	1072.7
2	1137.9	1139.2 (1138.6)	1139.1
4	1252.6	1252.0 (1252.0)	1251.8
8	1427.8	1424.6 (1424.8)	1423.7
15	1629.8	1628.8 (1629.3)	1626.6

Table S III: Simulation results for the bulk density variation with molality for KClO_4 aqueous solutions using model A, model B and from experiments [3] at 1 bar and 298.15 K.

m (mol/kg)	ρ (kg/m ³)		
	Expt.	Model A ($q_{Cl_p} = 0.35e$)	Model B ($q_{Cl_p} = 0e$)
0	997.1	997.3	997.3
0.1	1005.5	1006.0	1006.1

Table S IV: Simulation results for the bulk density variation with molality for $\text{Mg}(\text{ClO}_4)_2$ aqueous solutions using model A, model B and from experiments [4] at 1 bar and 298.15 K. For Model A the results in parenthesis were obtained using the Flexible version of the force field. The experimental density at 4 m is an extrapolation obtained from the experimental results at lower concentrations.

m (mol/kg)	ρ (kg/m ³)		
	Expt.	Model A ($q_{Cl_p} = 0.35e$)	Model B ($q_{Cl_p} = 0e$)
0	997.1	997.3	997.3
1	1138.8	1137.0 (1136.4)	1137.9
2	1256.2	1252.9 (1252.4)	1255.2
4	1440.7 (Extrapolated)	1434.3 (1433.7)	1440.1

Table S V: Simulation results for the bulk density variation with molality for $\text{Ca}(\text{ClO}_4)_2$ aqueous solutions using model A, model B and from experiments [2] at 1 bar and 298.15 K. For Model A the results in parenthesis were obtained using the Flexible version of the force field. The experimental density at 7 m is an extrapolation obtained from the experimental results at lower concentrations.

m (mol/kg)	ρ (kg/m ³)		
	Expt.	Model A ($q_{Cl_p} = 0.35e$)	Model B ($q_{Cl_p} = 0e$)
0	997.1	997.3	997.3
2	1275.9	1274.1(1274.2)	1275.4
4	1472.5	1458.5(1459.5)	1462.1
7	1677.6 (Extrapolated)	1631.9(1632.8)	1637.6

II. Densities as a function of temperature

Table S VI: Simulation results for the bulk density variation with temperature for a 0.4 m $\text{Mg}(\text{ClO}_4)_2$ aqueous solution using model A and model B at 1 bar.

T (K)	ρ (kg/m ³)	
	Model A ($q_{Cl_p} = 0.35e$)	Model B ($q_{Cl_p} = 0e$)
255	1064.13	1062.83
260	1064.44	1063.65
265	1064.47	1063.75
270	1064.05	1063.46
275	1063.39	1062.97
280	1062.33	1062.06
298.15	1056.58	1056.90

Table S VII: Experimental results for the bulk density variation with temperature for a 0.4 m $\text{Mg}(\text{ClO}_4)_2$ aqueous solution at 1 bar measured in this work.

T (K)	ρ (kg/m ³)	
	Expt	
273.80	1062.67	
272.80	1062.79	
271.80	1062.91	
270.79	1063.06	
269.79	1063.16	
269.29	1063.21	
268.79	1063.26	
268.29	1063.30	
267.79	1063.34	
267.29	1063.38	
266.79	1063.41	
266.28	1063.45	
265.78	1063.47	
265.28	1063.50	
264.78	1063.51	
264.28	1063.53	
263.78	1063.55	
263.28	1063.56	
262.78	1063.56	
262.28	1063.56	
261.78	1063.56	

Table S VIII: Simulation results for the bulk density variation with temperature for a 0.4 m $\text{Ca}(\text{ClO}_4)_2$ aqueous solution using model A and model B at 1 bar.

T (K)	ρ (kg/m ³)	
	Model A ($q_{Cl_p} = 0.35$)	Model B ($q_{Cl_p} = 0$)
250	1072.1	1070.8
255	1072.6	1071.3
260	1072.5	1071.5
265	1072.2	1071.5
270	1071.4	1070.9
275	1070.5	1070.0
298.15	1062.8	1062.9

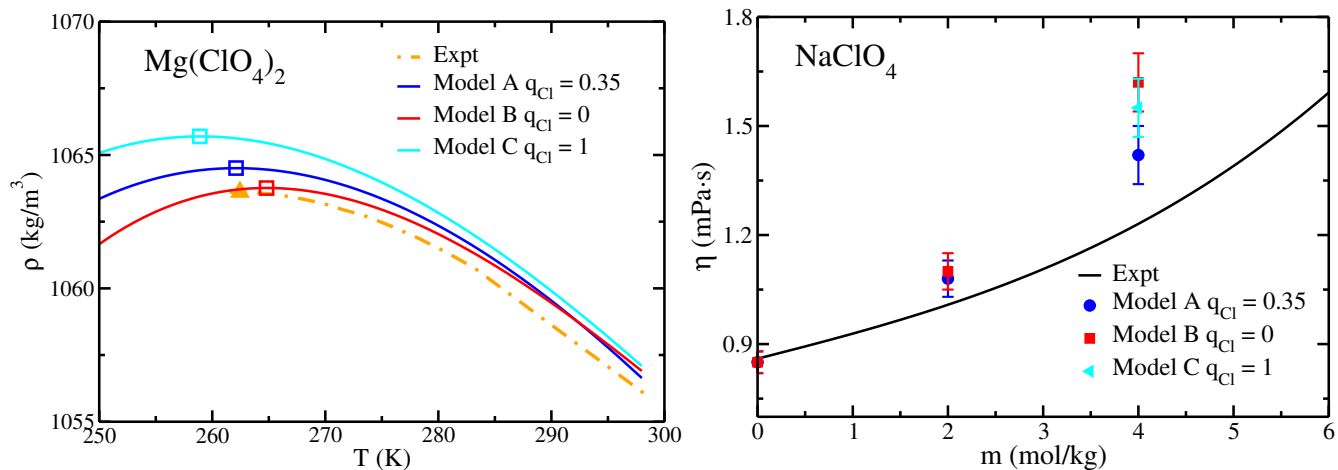


Fig. S 1: (Left) Results at 1 bar for temperatures of maximum density for a 0.4 m $\text{Mg}(\text{ClO}_4)_2$ aqueous solution. The dashed lines are fits of the experimental data measured in this work for $\text{Mg}(\text{ClO}_4)_2$ (orange). Experimental TMD is showed as a filled up triangle. Solid lines are fits of the simulation results by using model A with $q_{\text{Cl}_p} = 0.35$ (blue), model B with $q_{\text{Cl}_p} = 0$ (red) and model C with $q_{\text{Cl}_p} = 1.0$ (cyan). Simulation TMD is showed as an empty square. (Right) Results for viscosities of NaClO_4 aqueous solutions at different concentrations at 1 bar and 298.15 K. The black solid line is a fit of the experimental results [5] and symbols are the simulation results by using model A with $q_{\text{Cl}_p} = 0.35e$ (blue circle), model B with $q_{\text{Cl}_p} = 0e$ (red square) and model C with $q_{\text{Cl}_p} = 1.0e$ (cyan triangle). Notice that models A, B and C, have the same LJ parameters and assign a net charge for the perchlorate anion of $-0.85 e$.

Table S IX: Experimental results for the bulk density variation with temperature for a 0.4 m $\text{Ca}(\text{ClO}_4)_2$ aqueous solution at 1 bar measured in this work.

T (K)	ρ (kg/m ³) Expt
298.15	1060.72
283.15	1065.72
280.65	1066.37
278.15	1066.96
275.65	1067.50
273.65	1067.88
272.50	1068.08
271.50	1068.25
270.51	1068.40
269.51	1068.54
268.51	1068.67
267.51	1068.79
266.52	1068.89
265.52	1068.99
265.46	1068.99
264.96	1069.00
264.46	1069.06
263.97	1069.08
263.47	1069.12
262.97	1069.13
262.47	1069.16
261.97	1069.19
261.48	1069.27
260.98	1069.29
260.48	1069.33
259.98	1069.32
259.48	1069.34
258.99	1069.32
258.49	1069.33
257.99	1069.27
257.49	1069.22
256.99	1069.21
256.50	1069.16
255.00	1069.24
255.50	1069.11
255.00	1068.97
254.50	1069.03
254.00	1068.90
253.51	1068.92
253.01	1068.82

Table S XI: Temperatures of maximum in density (TMD) and densities at the TMD (ρ_{max}) for 0.4 m aqueous solutions of $\text{Mg}(\text{ClO}_4)_2$, at 1 bar for models A and B, for experiments and for model C with the same LJ parameters but with $q_{\text{Cl}_p} = 1.0e$. Notice that total net charge of perchlorate anion is $-0.85e$ for all models. Simulation and experimental results have been obtained in this work.

	Model C	Model A	Model B	Expt
$\text{Mg}(\text{ClO}_4)_2$ 0.4 m				
TMD (K)	258.9	262.1	264.8	262.5
ρ_{max} (kg/m^3)	1065.7	1064.5	1063.8	1063.6

III. Shear viscosity of aqueous solutions

Table S X: Simulation results for the viscosity variation with molality for NaClO_4 aqueous solutions using model A, model B and from experiments [5] at 1 bar and 298.15 K.

m (mol/kg)	η (mPa·s)			
	Expt.	Model A ($q_{\text{Cl}_p} = 0.35$)	Model B ($q_{\text{Cl}_p} = 0$)	Model C ($q_{\text{Cl}_p} = 1$)
0	0.89	0.85	0.85	0.85
2	1.01	1.08	1.10	
4	1.23	1.42	1.62	1.55

IV. Diffusion coefficients of water

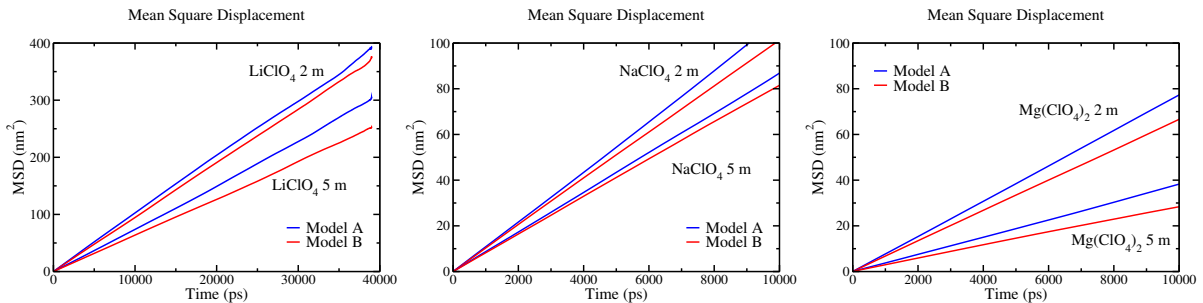


Fig. S 2: Mean Squared Displacement of water as a function of simulation time for models A (blue) and B (red) at 1 bar and 298.15 K. (Left) LiClO_4 . (Center) NaClO_4 . (Right) $\text{Mg}(\text{ClO}_4)_2$.

Table S XII: Simulation results for the diffusion coefficients of water as a function of molality for LiClO_4 aqueous solutions using model A, model B and from experiments [6] at 1 bar and 298.15 K. The results include hydrodynamic corrections of Yeh and Hummer. [7]

m (mol/kg)	$D_{wat} \cdot 10^9$ (m^2s^{-1})		
	Expt.	Model A ($q_{\text{Cl}_p} = 0.35e$)	Model B ($q_{\text{Cl}_p} = 0e$)
0	2.30	2.41	2.41
2	1.98	1.95	1.83
5	1.58	1.34	1.20

Table S XIII: Simulation results for the diffusion coefficients of water as a function of molality for NaClO₄ aqueous solutions using model A, model B and from experiments [6] at 1 bar and 298.15 K. The results include hydrodynamic corrections of Yeh and Hummer. [7]

m (mol/kg)	$D_{wat} \cdot 10^9$ (m ² s ⁻¹)		
	Expt.	Model A ($q_{Cl_p} = 0.35e$)	Model B ($q_{Cl_p} = 0e$)
0	2.30	2.41	2.41
2	2.11	2.03	1.93
4	1.82	1.61	1.53

Table S XIV: Simulation results for the diffusion coefficients of water as a function of molality for Mg(ClO₄)₂ aqueous solutions using model A, model B and from experiments [6] at 1 bar and 298.15 K. The results include hydrodynamic corrections of Yeh and Hummer. [7]

m (mol/kg)	$D_{wat} \cdot 10^9$ (m ² s ⁻¹)		
	Expt.	Model A ($q_{Cl_p} = 0.35e$)	Model B ($q_{Cl_p} = 0e$)
0	2.30	2.41	2.41
2	1.43	1.43	1.27
4	0.75	0.68	0.55

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