SUPPLEMENTARY MATERIAL

Acidifying the Madrid-2019 force field: a rigid model for H_3O^+ with scaled charge.

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The Supplementary Material for the publication 'Acidifying the Madrid-2019 force field: a rigid model for H_3O^+ with scaled charge.' contains the compilation of the numerical (raw data) and complementary graphical and tabular information of the simulation results considered in the main body of this work for the following properties:

- Conversion chart between the uncorrected molality m'=$10^3 \cdot N_{H_3O^+}/(18 \cdot N_{H_2O})$ and the corrected molality. See details below.

- The results for the Lennard-Jones energy parameters, σ_{ij} and ε_{ij} of the HCl force field with $q = \pm 0.75e$.

- Simulation results for the mass density as a function of the molality (m). Results for the HCl model with charge $q = \pm 075e$ are also included.

- Same as previous bullet but for simulated shear viscositiy coefficients. Results for the HCl model with charge $q = \pm 075e$ are also included.

- Simulation results for the TMD of HCl and HNO_3 0.98 m. Results for the HCl model with charge $q = \pm 075e$ are also included.

- Simulation results for the values of $\Delta\gamma$ for HCl and HNO_3 0.98 m.

- Simulation results for the freezing point depression of HCl as a function of m.

- The simulated atom-atom RDFs of interest for the whole set of electrolyte aqueous solutions considered in this work. The comparison between models with charges $q = 0.85e$ and $q = 0.75e$ is included.

Unless otherwise mentioned, the reported data correspond to a thermodynamic state at 298.15 K and 1 bar.

I. Tables

Table S I: Conversion chart between the uncorrected molality m'=10^3·$N_{H_3O^+}$/(18·N_{H_2O}) and the corrected molality, m, with $N_{H_3O^+}$ the number of oxonium cations and N_{H_2O} the corresponding number of water molecules. Molality values in mol·kg^{-1}.

m'	m
1	0.98
2	1.93
3	2.85
4	3.74
5	4.59
6	5.42
7	6.22
8	7.00
9	7.75
10	8.48
11	9.19
12	9.88

Table S II: Lennard–Jones, σ_{ij}, parameters (in Å) of the proposed HCl force field qith $q = \pm 0.75e$. H_2O-H_2O, H_2O-Cl^- and Cl^--Cl^- parameters are reported in Ref. [1].

Atom	O_{ox}
O_w	3.0000
O_{ox}	3.1000
Cl^-	3.6000

Table S III: Lennard–Jones, ε_{ij}, parameters (in kJ·mol^{-1}) of the proposed HCl force field with $q = \pm 0.75e$. H_2O-H_2O, H_2O-Cl^- and Cl^--Cl^- parameters are reported in Ref. [1].

Atom	O_{ox}
O_w	0.78735
O_{ox}	0.80000
Cl^-	0.24800

II. Raw simulation data

A. Bulk densities

Table S IV: Simulation results for the bulk density variation with molality for HCl (including the model with $q = \pm 0.75e$), HBr, HI and HNO_3.

m (mol/kg)	ρ (kg/m^3)				
	HCl ($q = \pm 0.85e$)	**HCl** ($q = \pm 0.75e$)	**HBr**	**HI**	**HNO_3**
0.98	1016.05	1014.80	1051.68	1083.91	1029.73
1.93	1031.73	1030.19	1100.24	1160.66	1058.40
2.85	—	—	—	1230.32	—
3.74	—	1056.18	1057.99	1184.09	1292.45
4.59	—	—	—	1348.94	—
5.42	1078.64	1077.05	1254.15	1399.93	1149.36
6.22	—	—	—	1446.70	—
7.00	1094.41	1093.41	1311.98	1488.83	1184.06
8.48	1106.24	1106.31	1360.19	1562.75	1213.09
9.88	1116.05	1115.75	1409.81	—	1238.55

B. Determination of the temperatures of maximum in density.

Table S V: Simulation results for the bulk density variation with temperature at 0.98 m for HCl ($q = \pm 0.85e$), HCl ($q = \pm 0.75e$), and HNO_3. The temperature of maximum in density (TMD) and the density at the TMD are indicated with boldface type.

HCl ($q = \pm 0.85e$)		**HCl** ($q = \pm 0.75e$)		**HNO_3**	
T (K)	ρ (kg/m^3)	T (K)	ρ (kg/m^3)	T (K)	ρ (kg/m^3)
250	1018.06	255	1017.57	245	1037.11
255	1019.35	260	1018.48	250	1037.95
260	1020.13	265	1019.11	255	1038.40
265	1020.68	270	1019.34	260	1038.58
270	1020.70	275	1019.26	265	1038.36
275	1020.51	280	1018.74	270	1037.66
280	1020.09	285	1018.09	275	1036.92
285	1019.21	290	1017.05	280	1035.69
290	1018.13	**270.9**	**1019.3**	**259.1**	**1038.6**
269.3	**1020.8**	—	—	—	—

C. Shear viscosity coefficients.

Table S VI: Simulation results for shear viscosity variation with molality for HCl (including the model with $q = \pm 0.75e$), HBr, HI and HNO_3.

m (mol/kg)	η (mPa·s)				
	HCl($q = \pm 0.85e$)	**HCl**($q = \pm 0.75e$)	**HBr**	**HI**	**HNO_3**
1.93	1.15(5)	0.99(4)	1.07(6)	1.09(4)	0.92(3)
3.74	1.44(5)	1.15(5)	1.38(8)	1.28(9)	0.94(6)
5.42	2.1(2)	1.33(7)	—	—	1.11(9)

Table S VII: Shear viscosity coefficient for 1.93 m solutions of HCl as obtained for different charge distributions, all with a net scaled charge of $+0.85e$ for the oxonium cation. Lennard-Jones parameters as in Table I of the main text.

m (mol/kg)	η (mPa·s), $q = \pm 0.85e$		
	$q_O = -1.190e$ (q_O and q_H rescaled from Ref.[2]).	$q_O = -1.400e, q_H = 0.750e$ (q_O from Ref.[2], q_H redistributed to $q = +0.85e$)	$q_O = -0.394e$ (from the ADCH method, as illustrated in the main text).
1.93	1.29	1.376	1.13

D. Surface tension.

Table S VIII: Results for $\Delta\gamma = \gamma - \gamma_0$ for HCl and HNO_3 acidic solutions at 298.15 K and 1 bar.

m (mol/kg)	$\Delta\gamma$ (mN/m)	
	HCl	**HNO_3**
1.93	–2.4(6)	–2.1(7)
3.74	–4.2(7)	–4.6(6)

E. Freezing point depression.

Table S IX: Freezing point depression (ΔT = T-T_m) versus equilibrium molality (m_{eq}) of HCl solutions.

ΔT (K)	m_{eq} (mol/kg)
–7	2.2(1)
–12	3.4(3)

III. Figures

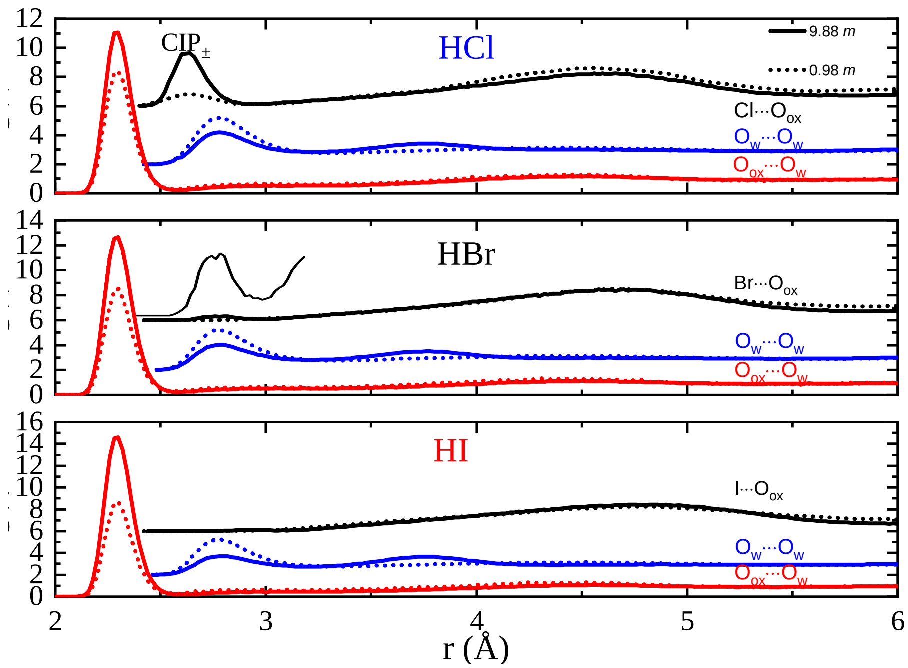

Fig. S 1: Anion–O$_w$ (black line), O$_w$–O$_w$ (blue line) and O$_{ox}$-O$_w$ (red line) radial distribution functions for hydrogen halides (HX) models.

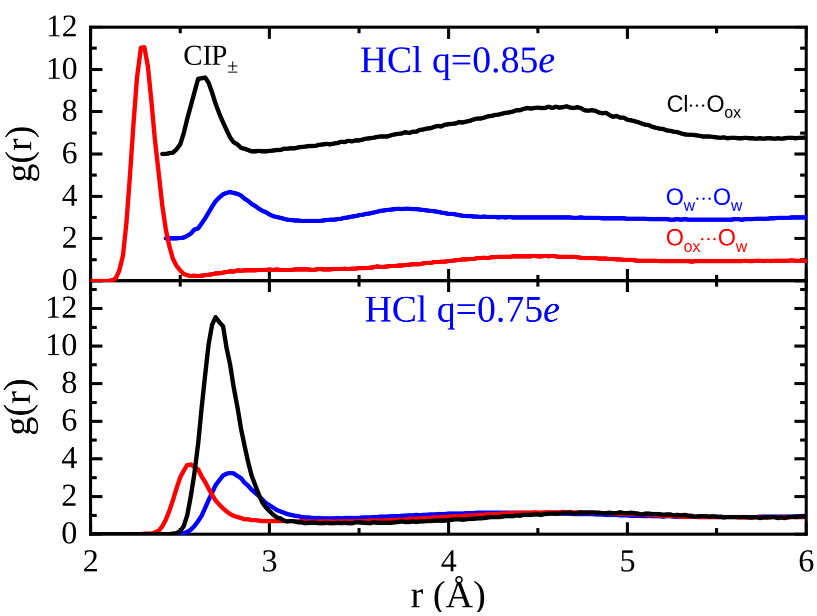

Fig. S 2: Cl–O$_w$ (black line), O$_w$–O$_w$ (blue line) and O$_{ox}$-O$_w$ (red line) radial distribution functions for HCl models with $q = \pm 0.85e$ (top) and $q = \pm 0.75e$ (bottom).

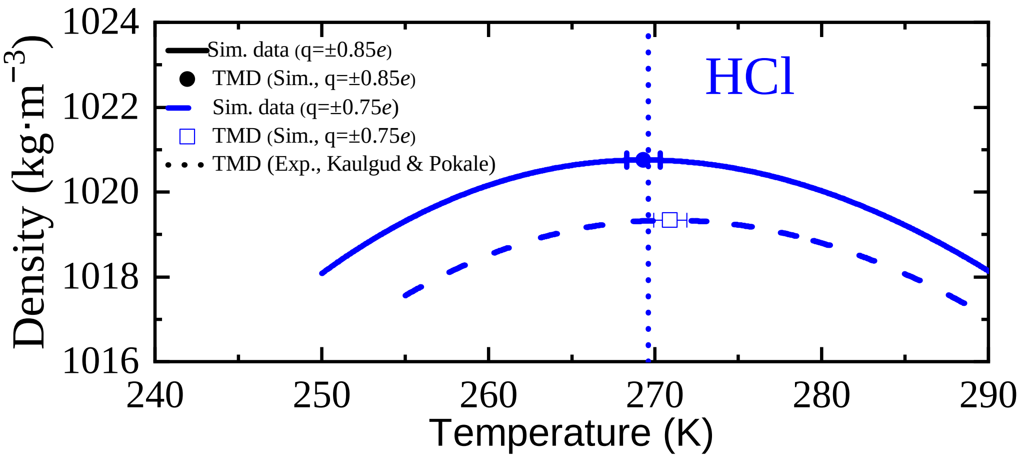

Fig. S 3: Densities as a function of temperature for the HCl models at 0.98 m. Continuous lines stand for the third order polynomial fit to simulation data and full circles denote the TMD obtained for the model with $q = \pm 0.85e$. The results for the HCl with q= $\pm 0.75e$ model are plotted as dashed line (densities) and empty square (TMD). Dotted vertical lines are the estimated experimental values from Refs.[3, 4].

[1] S. Blazquez, M. Conde, and C. Vega, "Scaled charges for ions: An improvement but not the final word for modeling electrolytes in water," *J. Chem. Phys.*, vol. 158, p. 054505, 2023.

[2] D. J. Bonthuis, S. I. Mamatkulov and R. R. Netz, "Optimization of classical nonpolarizable force fields for OH^- and H_3O^+," *J. Chem. Phys.*, vol. 144, p. 104503, 2016.

[3] T. Wakabayashi and K. Takaizumi, "Despretz constants for individual ions," *Bull. Chem. Soc. Jpn.*, vol. 55, pp. 3073–3078, 1982.

[4] M. V. Kaulgud and W. K. Pokale, "Measurement of the temperature of maximum density of aqueous solutions of some salts and acids," *J. Chem. Soc., Faraday Trans.*, vol. 91, no. 6, pp. 999–1004, 1995.