

I. CHARMM functional form

$$U = \sum_{\text{bonds}} K_b (b - b_0)^2 + \sum_{\text{anglrs}} K_\theta (\theta - \theta_0)^2 + \sum_{\text{dihedrals}} K_\phi (1 + \cos(n\phi - \delta)) \\ + \sum_{\substack{\text{improper} \\ \text{dihedrals}}} K_\psi (\psi - \psi_0)^2 + \sum_{\substack{\text{ureg-} \\ \text{Bradley}}} K_{UB} (r_{1,3} - r_{r3;0})^2 \\ + \sum_{\substack{\text{non-} \\ \text{bonded}}} \frac{q_i q_j}{4\pi D r_{ij}} + \varepsilon_{ij} \left[\left(\frac{R_{min,ij}}{r_{ij}} \right)^{12} - 2 \left(\frac{R_{min,ij}}{r_{ij}} \right)^6 \right]$$

Bonded parameters

Non-bonded parameters

2. Parameters defined for NaCl and NH₄Cl (forcefield.itp, genff prm)

①	NaCl : / NH ₄ Cl : N - H	\rightarrow <table border="1" style="margin-left: auto; margin-right: auto;"> <tr> <td>IN</td><td>CP3</td><td>1</td><td>1.040000e-01</td><td>3.372304e+05</td></tr> <tr> <td>NG3P3</td><td>HGP2</td><td>1</td><td>1.040000e-01</td><td>3.372304e+05</td></tr> <tr> <td>MM1</td><td></td><td></td><td></td><td></td></tr> </table> $b_0 \quad K_b$	IN	CP3	1	1.040000e-01	3.372304e+05	NG3P3	HGP2	1	1.040000e-01	3.372304e+05	MM1										
IN	CP3	1	1.040000e-01	3.372304e+05																			
NG3P3	HGP2	1	1.040000e-01	3.372304e+05																			
MM1																							
②	NaCl : / NH ₄ Cl : H - N - H	\rightarrow <table border="1" style="margin-left: auto; margin-right: auto;"> <tr> <td>HGP2</td><td>NG3P3</td><td>HGP2</td><td>5</td><td>1.095000e+02</td><td>3.6819200e+02</td><td>0.000000e+00</td><td>0.000000e+00</td></tr> <tr> <td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td></tr> </table> $\theta_0 \quad K_\theta \quad K_B$	HGP2	NG3P3	HGP2	5	1.095000e+02	3.6819200e+02	0.000000e+00	0.000000e+00													
HGP2	NG3P3	HGP2	5	1.095000e+02	3.6819200e+02	0.000000e+00	0.000000e+00																
⑥	NaCl : Na Cl	\rightarrow <table border="1" style="margin-left: auto; margin-right: auto;"> <tr> <td>SOD</td><td>11</td><td>22.9898</td><td>1.000</td><td>A</td><td>2.51367073323e-01</td><td>1.962296e-01</td></tr> <tr> <td>CLA</td><td>17</td><td>35.4500</td><td>-1.000</td><td>A</td><td>4.04468018036e-01</td><td>6.276000e-01</td></tr> <tr> <td></td><td></td><td></td><td></td><td></td><td></td><td></td></tr> </table> $q \quad \sigma_i \quad \epsilon_i$	SOD	11	22.9898	1.000	A	2.51367073323e-01	1.962296e-01	CLA	17	35.4500	-1.000	A	4.04468018036e-01	6.276000e-01							
SOD	11	22.9898	1.000	A	2.51367073323e-01	1.962296e-01																	
CLA	17	35.4500	-1.000	A	4.04468018036e-01	6.276000e-01																	
⑦	NH ₄ Cl : N H	\rightarrow <table border="1" style="margin-left: auto; margin-right: auto;"> <tr> <td>NG3P3</td><td>7</td><td>14.007000</td><td>0.000</td><td>A</td><td>0.329632525712</td><td>0.8368000</td></tr> <tr> <td>HGP2</td><td>1</td><td>1.008000</td><td>0.000</td><td>A</td><td>0.040001352445</td><td>0.1924640</td></tr> <tr> <td></td><td></td><td></td><td></td><td></td><td></td><td></td></tr> </table> $\sigma_i \quad \epsilon_i$	NG3P3	7	14.007000	0.000	A	0.329632525712	0.8368000	HGP2	1	1.008000	0.000	A	0.040001352445	0.1924640							
NG3P3	7	14.007000	0.000	A	0.329632525712	0.8368000																	
HGP2	1	1.008000	0.000	A	0.040001352445	0.1924640																	
ϵ_{ij} (Default) = $\sqrt{\epsilon_i \times \epsilon_j}$ $R_{min,ij}$ (Default) = $\frac{R_{min,ii} + R_{min,jj}}{2}$ $= (2^\nu \sigma_i) + (2^\nu \sigma_j)$																							
<ul style="list-style-type: none"> NBFIX overwrites default ϵ_{ij} and $R_{min,ij}$ 																							
NaCl : CLA SOD 1 3.32394311738e-01 3.51037600000e-01 $\sigma_{ij} \quad \epsilon_{ij}$																							
NH ₄ Cl : /																							

3. Bonded parameters (① - ⑤)

Step 1: Geometric data

- Fitting to gas-phase structures (Microwave, electron diffraction) & crystal structures (X-ray)
- Adjust geometries manually

Step 2: Force constant

- Fitting to vibrational data (gas-phase infrared, Raman data / solution, crystal data) for model systems
- Supplement with ab initio calculations (assignment of experimental vibrational frequencies to internal coordinates, obtain values for low-frequency torsional modes, determination of intermolecular interaction contributions to vibrational spectra)

CCrenff:

heterocycles & simple functional groups

Step 3: Optimisation

- Introduce Urey-Bradley terms for in-plane deformations and separating symmetric and asymmetric bond stretching modes
- Introduce improper dihedral terms to reproduce out-of-plane modes
- Optimised at MP2/6-31G(d) level (frequencies and PED of vibrational spectrum, potential energy surface)

Step 4: Potential energy scans

- Important for backbone and side chain conformers to describe energy barriers and minimum-energy structures
- Use experimental gas-phase data and ab initio calculations to obtain energy surface
- Test the accuracy of potential function to reproduce structural distortions

4. Non-bonded Parameters (⑥ - ⑦)

Step 1: Solute-Water interaction

- Calculate minimum interaction energies and solvation structure for experimental thermodynamic parameters and molecular volumes with TIP3P water model
- Optimise partial atomic charges and interaction distance or angle at HF/6-31G(d) level (compound-water interaction and dipole moment)
and MP2/

Step 2: Test

- Perform condensed-phase simulations to compare heats of vaporization and molecular volume with experimental data
- Perform crystal simulations to compare heats of sublimation and unit cell parameters

5. Optimisation of non-bonded parameters (R_{min}^{ij} , E_{min}^{ij}) using osmotic pressure (NBFIX Parameters)

R_{min}^{ij}

E_{min}^{ij}

(Default) Lorentz-Berthelot combination rule

NBFIX

CLA	SOD	σ_{ij}	ϵ_{ij}
1	3.32394311738e-01	3.51037600000e-01	$R_{ij} = \sigma_{ij} \cdot 2^{\sqrt{6}} = 0.3726574 \text{ \AA}$

Step 1 : System setup

- Introduce flat-bottom half-harmonic planar restraint on ions

Step 2 : Measurement

- Measure mean force on ions by 'membrane'

$$\langle F_{\text{wall}} \rangle = k \frac{1}{N} \sum_N \sum_i (1z_i - z_{\text{wall}})$$

- Calculate osmotic pressure Π

$$\Pi = \frac{\langle F_{\text{wall}} \rangle}{A}$$

Step 3 : Calibration of R_{min}

- Sample Π at different R_{min} and obtain best-fit line by linear regression

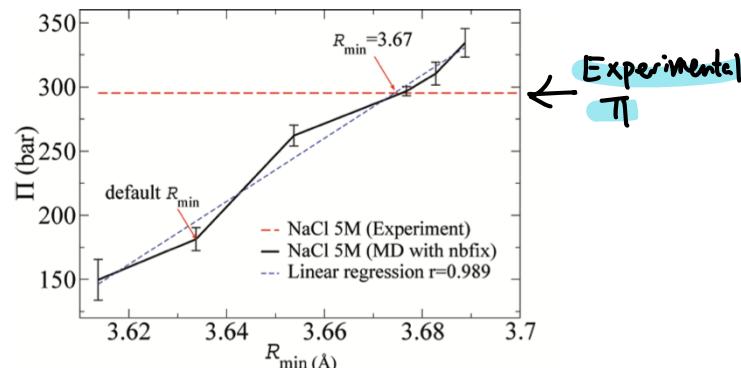
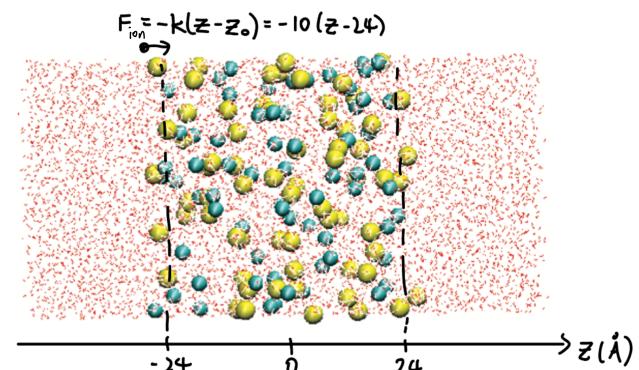


Table 2. Modified Ion–Ion LJ Parameters

ion pair	$R_{min}^{ij} \text{ \AA}$	
	combination rule	NBFIX
$\text{Na}^{+a} - \text{Cl}^{-}$	3.633	3.676
$\text{Na}^{+b} - \text{Cl}^{-}$	3.680	3.731
$\text{K}^{+} - \text{Cl}^{-}$	4.033	4.081

^a Parameterization of Na^{+} in 1994 from ref 2. ^b Reparameterization of Na^{+} in 2008 from ref 39.



6. Optimisation using hydration free energy

A. Ion hydration free energies

- Real hydration free energy $\Delta G_{\text{hyd}}^{\text{real}}$: reversible work to move an ion from vacuum to interior of pure water phase at 298.15 K and 1 atm

$$\Delta G_{\text{hyd}} = \Delta G_{\text{hyd}}^{\text{intr}} + zF\phi + C$$

↑
Intrinsic bulk-phase value = $\Delta G_{\text{elec}} + \Delta G_{\text{disp}} + \Delta G_{\text{rep}}$
(electrostatic) (attractive) (repulsive)

Two-stage

- charge neutralisation
- v.d.W removal / disappear

- $\Delta G_{\text{hyd}}^{\text{intr}}$ found by Free-Energy Perturbation
- Difference in hydration free energy relative to immediate neighbour in series $\Delta \Delta G_{\text{hyd}}$: based on Thermodynamic Integration
- Change in free energy for alchemical $A \rightarrow B$ mutation $\Delta G_{\text{mut}} = \Delta G_{\text{hyd}}(B) - \Delta G_{\text{hyd}}(A) = \Delta \Delta G_{\text{hyd}}(A \rightarrow B)$

ion	ΔG_{elec} (kcal/mol)	ΔG_{disp} (kcal/mol)	ΔG_{rep} (kcal/mol)	$\Delta G_{\text{hyd}}^{\text{intr}\text{a}}$ (kcal/mol)	$\Delta G_{\text{hyd}}^{\text{real}\text{b}}$ (kcal/mol)	$\Delta G_{\text{hyd}}^{\text{exptc}}$ (kcal/mol)	$\Delta \Delta G_{\text{hyd}}^{\text{real}\text{d}}$ (kcal/mol)	$\Delta \Delta G_{\text{hyd}}^{\text{exptc}}$ (kcal/mol)
F ⁻	-124.1	-1.5	5.0	-120.6	-107.2	-99.1 to -121.6	29.1	28.0 to 30.6
Cl ⁻	-95.8	-3.7	7.3	-92.2	-78.8	-70.7 to -91.0	6.3	3.3 to 6.5
Br ⁻	-89.1	-4.9	8.0	-86.0	-72.6	-64.9 to -84.6	8.7	7.7 to 11.1
I ⁻	-79.7	-7.2	9.7	-77.2	-63.8	-57.2 to -76.2		
Li ⁺	-114.6	-0.2	2.0	-112.8	-122.4	-113.8 to -128.4	23.3	23.9 to 27.5
Na ⁺	-91.6	-1.0	3.1	-89.5	-99.1	-88.7 to -103.2	18.4	17.0 to 17.6
K ⁺	-73.7	-1.9	4.5	-71.1	-80.7	-71.2 to -86.0	6.6	5.1 to 5.6
Rb ⁺	-67.2	-2.7	5.4	-64.5	-74.1	-66.0 to -80.6	6.5	5.5 to 7.7
Cs ⁺	-60.8	-3.6	6.5	-58.0	-67.6	-60.5 to -75.1		

Experiment

B. Hydration Free energy of alkali halides

- Total hydration free energy of neutral alkali halide, $\Delta G_{\text{hyd}}(\text{MX}) = \Delta G_{\text{hyd}}(\text{M}^+) + \Delta G_{\text{hyd}}(\text{X}^-)$

Table 4. Calculated (and Experimental) Hydration Free Energy of the Alkali Halides^a

	Hydration Free Energy (kcal/mol)				
	Li ⁺	Na ⁺	K ⁺	Rb ⁺	Cs ⁺
F ⁻	-229.6 (-229.0)	-206.3 (-203.8)	-187.9 (-186.6)	-181.3 (-181.2)	-174.8 (-173.8)
Cl ⁻	-201.2 (-199.3)	-177.9 (-174.0)	-159.5 (-156.8)	-152.9 (-151.4)	-146.4 (-144.0)
Br ⁻	-195.0 (-192.9)	-171.7 (-167.6)	-153.3 (-150.4)	-146.7 (-145.0)	-140.2 (-137.6)
I ⁻	-186.2 (-183.9)	-162.9 (-158.7)	-144.5 (-141.5)	-137.9 (-136.1)	-131.4 (-128.7)

^aExperimental hydration free energies (in kcal/mol) for LiX, NaX, KX, and RbX are from ref 65 and for CsX are from ref 63.

$\rightarrow \Delta G_{\text{hyd}} = f(R_{\min}, \varepsilon)$ hypersurface can be mapped from TI calculations

ε is dependent on R_{\min} for given hydration free energy

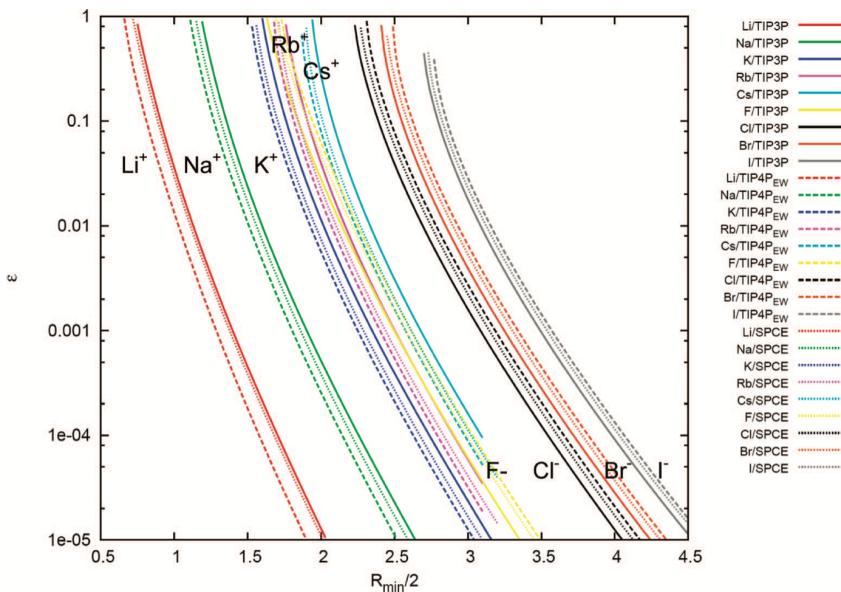
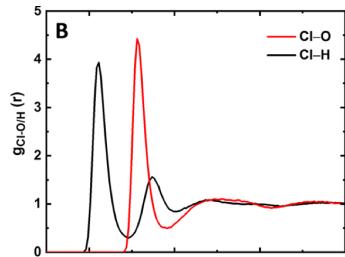


Figure 3. Correlations between R_{\min} and ε for a given free energy of hydration by using the Schmid values. Shown are the correlations in R_{\min} and ε from the $\Delta G_{\text{hydration}} = f(R_{\min}, \varepsilon)$ hypersurface at a given value of the hydration free energies. The chosen values are those from Schmid and co-workers (see Table 10).¹¹⁷ Points on the same line have equivalent hydration free energies. The solid lines are for TIP3P water, the dashed lines are for TIP4P_{EW} water, and the dotted lines are for SPC/E water; each ion is represented by a different color. The units for the x and y axes are Angstroms and kcal/mol, respectively.

7. Optimisation using RDF

- Radial distribution function $g(r) = \frac{\rho(r)}{\rho}$ ρ = density until r_{\max}
- Integration up to first minimum = coordination number (CNs)

$$CNs = \int_0^{r_{\min}} g(r) dr$$



	Hydration Number			
	F ⁻	Cl ⁻	Br ⁻	I ⁻
this work	6.7	7.7	8.0	8.7
experiment	6.9 ^a	5.3–7.3 ^b	6.3–8.9 ^c	6.7–9.1 ^d
polarizable MM	5.1–6.7 ^e	6.0–8.4 ^f	6.6–9.0 ^g	6.7–9.2 ^h
QM	4.9–5.0 ⁱ	5.5–6.5 ^j	5.6–6.5 ^k	6.6–8.5 ^l
QM/MM	5.7 ^m	5.9–6.6 ⁿ	—	—
nonpolarizable MM	6.0–6.9 ^o	7.0–7.6 ^p	7.2–7.7 ^q	7.3–9.7 ^r

ion	atom-type pair (MX) ^a	NBFI ^b	
		ϵ_{MX} (kcal/mol)	$R_{\min,MX}$ (Å)
F ⁻	FLA-LIT	-0.032	3.2125
	FLA-SOD	-0.069	3.32575
	FLA-POT	-0.090	3.67875
	FLA-RUB	-0.100	3.8150
	FLA-CES	-0.120	4.015
Cl ⁻	CLA-LIT	-0.046	3.5675
	CLA-SOD	-0.083875	3.7310
	CLA-POT	-0.114236	4.0810
	CLA-RUB	—	—
	CLA-CES	-0.140	4.370

- Potential of mean Force $W(r) = -k_B T \ln(g(r))$
- Radius of first hydration shell = First minimum

TABLE 13: Radii of the First Hydration Shell^a

	this research	Jensen and Smith–Dang–Garrett		Beglov and Roux	Åqvist	Marcus ¹⁸⁵
		Jorgensen				
TIP3P						
Li ⁺	1.96	2.04	1.97	2.03	2.08	
Na ⁺	2.38	2.49	2.37	2.31	2.41	2.356
K ⁺	2.75	2.86	2.83	2.71	2.72	2.798
Rb ⁺	2.92	3.00	2.93		2.85	2.89
Cs ⁺	3.11	3.19	3.11		3.05	3.139
F ⁻	2.63	2.80	2.70		2.63	
Cl ⁻	3.13	3.29	3.24	3.12	3.187	
Br ⁻	3.29	3.41			3.373	
I ⁻	3.51	3.65	3.64		3.647	
rms	0.07	0.09	0.05	0.07	0.06	

8. Optimisation using crystal properties (LE, LC)

- LE: loss in the total lattice potential energy when crystal structure transform into gas phase, listed in CRC handbook
- LC: length of the edge of the unit crystals / cation-anion distances
- R_{\min} is chosen to minimize the overall deviation with literature cation-anion distance and LE at given ΔG_{hyd}

$$\sqrt{\sum_{\text{ion pair}} ((\delta_{\text{dis}} W_{\text{dis}})^2 + (\delta_{\text{LE}} W_{\text{LE}})^2)}$$

deviation weight

- Choose solutions that lead to stable crystals

TABLE 4: Range of Acceptable Solutions at Different Ratios of Weights on Interionic Distance and LE on the Ion Radii Optimization ($W_{\text{LE}} = 1$)^a

	$W_{\text{dis}} = 107$	$W_{\text{dis}} = 150$	$W_{\text{dis}} = 200$	$W_{\text{dis}} = 250$	$W_{\text{dis}} = 300$
$R_{\min}/2$					
Li ⁺	0.886	0.986	1.079	1.078	1.078
Na ⁺	1.325	1.361	1.379	1.384	1.387
K ⁺	1.687	1.702	1.709	1.712	1.713
Rb ⁺	1.803	1.811	1.815	1.817	1.818
Cs ⁺	1.968	1.974	1.978	1.979	1.980
F ⁻	2.377	2.346	2.259	2.180	2.144
Cl ⁻	2.614	2.526	2.500	2.498	2.497
Br ⁻	2.657	2.616	2.602	2.602	2.601
I ⁻	2.876	2.862	2.856	2.855	2.855
rms (Distance)					
	0.028	0.022	0.018	0.018	0.017
rms (LE)					
	3.28	3.97	4.49	4.62	4.68

^a By using eq 3, the radii of the ions (R_{\min}) were optimized at various ratios of the respective weights on the inter-ionic distance (W_{dis}) and LE (W_{LE}). Displayed are the different $R_{\min}/2$ values optimized for the Schmid hydration free energy target values with TIP3P water. Acceptable solutions were those that led to stable crystals (as per Figure 5), maintained size consistency across the monovalent ion series, and had $\text{Cs}^+ < 2.5 \text{ \AA}$ and $\text{I}^- < 3.5 \text{ \AA}$. The units of the weights are $\text{kcal}^{-1}\text{mol}$ (W_{dis}) and \AA^{-1} (W_{LE}). The same data for the TIP4P_{EW} and SPC/E models are shown in the Supporting Information, Tables S4 and S5.

	Li	Na	K	Rb	Cs
Theory					
F	246.2	217.5	193.1	185.0	177.8
Cl	199.3	183.8	167.5	162.5	157.0
Br	188.3	175.0	160.4	155.6	151.1
I	174.5	163.0	151.1	147.5	143.4
Experiment					
F	250.7	222.3	198.1	190.0	181.4
Cl	206.5	188.8	172.1	166.1	160.1
Br	196.0	180.2	165.2	159.7	154.6
I	182.6	168.5	155.4	151.1	146.5

TABLE 3: LC (Angstroms) of Crystals of Alkaline Halide Salts (Top Half) and Interionic Distance (Angstroms) Calculated from the LC at Room Temperature (Bottom Half)^a

	Li	Na	K	Rb	Cs
LC					
F	4.027	4.634	5.347	5.652	6.014
Cl	5.140	5.640	6.293	6.581	4.123
Br	5.501	5.977	6.600	6.889	4.295
I	6.023	6.473	7.066	7.342	4.568
Distance					
F	2.014	2.317	2.674	2.826	3.007
Cl	2.570	2.820	3.147	3.291	3.571
Br	2.751	2.989	3.500	3.445	3.720
I	3.011	3.236	3.533	3.671	3.956

^a The data were obtained from the first column of Table 1.2 from Sirdeshmukh et al.^{10a}

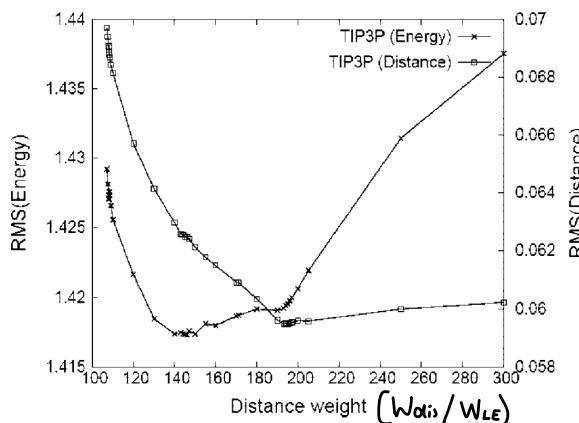


Figure 7. rms deviations of single water-ion binding energies and distances. The rms deviations are plotted as a function of the weight on interionic distance (\AA^{-1}) with a fixed weight on the LE (1 $\text{kcal}^{-1}\text{mol}$) over the range of acceptable weight ratios (as per Table 4). The units are kcal/mol for the energy and Angstrom for the distance. TIP3P ions have the minimal rms in energy at a weight ratio of 146:1, whereas the minimal rms in distance occurs at 195:1. TIP4P_{EW} ions have the minimal rms deviation for both the energy and the distance at a weight ratio of 50.36:1. SPC/E is somewhat anomalous because the rms of the energy keeps increasing as the rms of the distance decreases. With the SPC/E model, because the minima are not colocalized, the weight ratio was taken at the middle point of both curves or at 27:1. Plots of the rms deviations for TIP4P_{EW} and SPC/E are shown in the Supporting Information.

9. Madrid-2019 force field: Parametrization of NO_3^- and NH_4^+ ions [6]

Overview

- Parametrize using scaled charges, obtain ρ , $g(r)$ from NPT and NVT simulation,
- Test electrolytes' densities, ion-ion, ion-solvent structures and transport properties
- Solvent: TIP4P/2005 water.
- $U(r_{ij}) = 4 \varepsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right] + \frac{1}{4\pi\varepsilon_0} \cdot \frac{q_i q_j}{r_{ij}}$
- Parameters for counterions are obtained from Madrid-2019 ff

Force field

- Charges: (NH_4^+) OPLS-based model ("MC simulations of hydration of ammonium and carboxylate ions", 1986) (NO_3^-) Fitting gas-phase potential energy surfaces derived from high-level QM calculation,
 - Scaled by 0.85 in this paper
- LJ param: (ε_{ii}) Same as charges
(σ_{ii}) Fixed to 3.15 Å [Table 1]
- Geometry: (ε_{ij} , σ_{ij}) Fitting by matching experimental data w/o combination rule ("Interfacial and bulk properties of concentrated solutions of ammonium nitrate", 2020)
 - [Table S1, S2]

Test 1 : Bulk density

- Experimental data from Ref 92-94, up to solubility limit \rightarrow experimental values : [Table III]
- $\rho_{\text{NH}_4\text{F}} > \rho_{\text{NH}_4\text{Cl}}$ due to mass effect, not shrinking of solution, proved with Fig 1b.

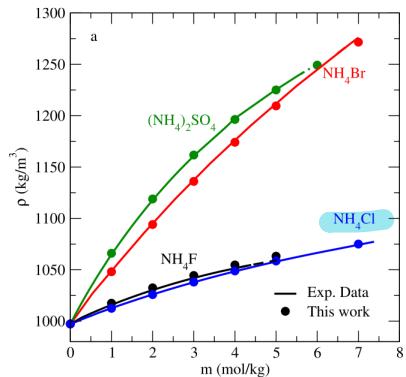


Fig 1a. Bulk densities

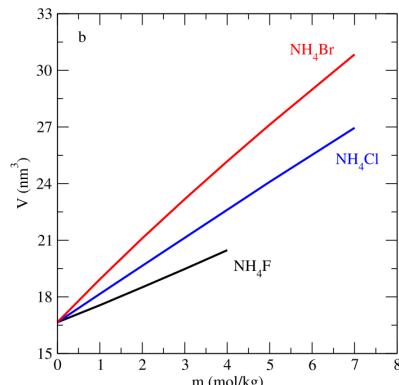


Fig 1b. Volume by 555 water molecules (Experiment)

Test 2: $g(r)$

- RDF taken by considering central N atom

$$\text{CIP} = 4\pi P_{\pm} \int_0^{r_{\text{max}}} g_{\pm}(r) r^2 dr$$

- NH_4^+
- Seminal classical MD simulations : coordination number = 8 ; $\text{N} \cdots \text{O}_{\text{w}}$ distance = 3.05 \AA
 - Ab initio and classical MD simulations : coordination number = 5 (H_2O)
 - First principles ab initio MD employing accurate functionals, classical MD, quantum MD calculations :
coordination number = 6 (H_2O)
 - X-ray scattering of NH_4Cl : $\text{N} \cdots \text{O}_{\text{w}}$ distance = 3.06 \AA
 - Neutron diffraction of ND_4Cl : coordination number = 4 (H_2O)
soft-X-ray spectroscopy,
MD, MC simulations
Total in first & second shell = 8 (H_2O)
 $\text{N} \cdots \text{O}_{\text{w}}$ distance = 2.8 \AA

L

Results : N_a...O_w distance = 2.7 Å

[Table IV]

Coordination number = 5.25 (H₂O)

N_a...Cl distance > N_a...O_w and Cl...O_w distance \Rightarrow SSIP

Salt	<i>m</i>	Cation-Anion structure	CIP _±	CIP _N	HN _N	HN _{Cl}	<i>d</i> _{N...O_w}	<i>d</i> _{N...H_w}	<i>d</i> _{Cl...O_w}	δ
NH ₄ F	1	CIP	0.2	0	5.4	5.4	2.65	3.18	2.76	0.10
	5	CIP	0.7	0	4.7	4.8	2.66	3.18	2.77	0.09
NH ₄ Cl	1	SSIP	0	0	5.5	5.8	2.66	3.22	3.05	-0.06
	7	CIP	0.1	0	5.3	5.6	2.65	3.20	3.04	-0.05
NH ₄ Br	1	SSIP	0	0	5.6	6.2	2.66	3.22	3.14	-0.10
	7	CIP	0.1	0	5.2	5.6	2.66	3.20	3.15	-0.11
(NH ₄) ₂ SO ₄	1	CIP	0.4	0	5.2	7.7	2.64	3.18	3.76	-0.40
	6	CIP	1.0	0	4.1	5.3	2.68	3.16	3.75	-0.42
NH ₄ ⁺ (expt.)	[4-5]	...	[2.91-3.06]

Table IV : Contact ion pair, hydration number, peak location

Test 3: Viscosities

- Shear viscosity η based on pressure tensor P_{αβ}(t) saved from NVT simulation

$$\eta = \frac{V}{kT} \int_0^\infty \langle P_{\alpha\beta}(t) P_{\alpha\beta}(0) \rangle dt$$

- Controlled by ion-water interaction at low concentration, electrostatic ion-ion interactions at high concentration

- Experiments: results match net ion charge of $q = \pm 0.75e$

- Results: Do not predict NH₄Cl experimental viscosity

reduce viscosity increase viscosity
 \therefore Domination of Cl⁻ ion

Accurate for other anions

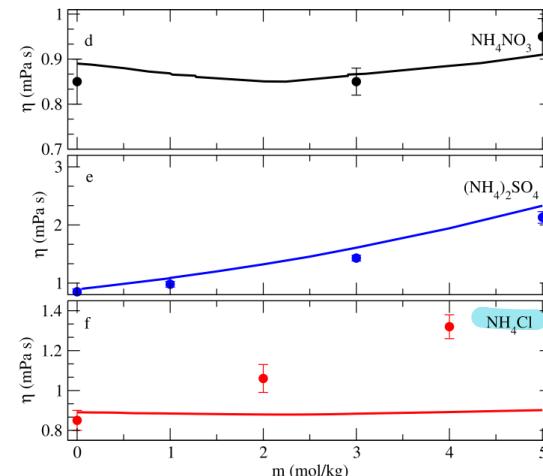


Fig. 4 Shear viscosity coefficient

Test 4: Diffusion coefficients

- Diffusion coefficient D based on mean square displacement from NVT simulation

$$D = \lim_{t \rightarrow \infty} \frac{1}{6t} \langle [\vec{r}_i(t) - \vec{r}_i(0)]^2 \rangle$$

- D modified with hydrodynamic correction

$$D_{\text{corr}} = D + \xi \frac{kT}{6\pi\eta L}$$

- Experimental data for NH_4Cl only exists at $m \leq 1$

Experimental data normalized by a factor of $2.2 \times 10^{-5} \text{ cm}^2/\text{s} \rightarrow D$ from Tanaka

Simulation data normalized by a factor of $2.3 \times 10^{-5} \text{ cm}^2/\text{s} \rightarrow D$ for TIP4P/2005

- Result: Underestimates $D_{\text{NH}_4\text{Cl}}$, consistent with overestimation of η
 \because Domination of Cl^- ion

Overestimates $D_{(\text{NH}_4)_2\text{SO}_4}$

\because Dissimilar selection of distribution of charge / Rotational degrees of freedom

- Self-diffusion coefficient at infinite dilution D^∞ : well documented in literature, unaffected by counterion
- Estimated by linear extrapolation of D for NH_4NO_3 to $m \rightarrow 0$
- Result: Accurate

$$D_{\text{NO}_3^-}^{\infty, \text{MD}} = 1.91 \times 10^{-5} \text{ cm}^2/\text{s} \quad (\text{deviation of } 0.5\%)$$

$$D_{\text{NH}_4^+}^{\infty, \text{MD}} = 1.91 \times 10^{-5} \text{ cm}^2/\text{s} \quad (\text{deviation of } 3.5\%)$$

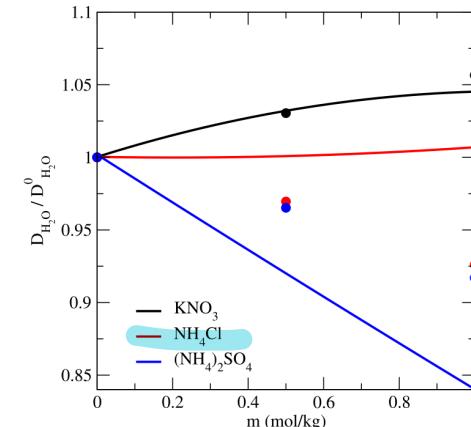


FIG. 5. Normalized self-diffusion coefficients of water in electrolyte solutions in the experimentally available concentration region. Simulation results are shown with filled circles. These data were corrected using the methodology proposed by Yeh and Hummer.⁹¹ Solid lines are fits of the experimental data from Ref. 146.

10. Free energy calculations involving NH_4^+ in water [7]

Overview

- Estimate relative and absolute free energies of hydration by MC simulations
- Uses 2 NH_4^+ model (Jorgenson, ref 6; Kollman, ref 7) in TIP3P and TIP4P [Table 1]
- Uses standard combination rules $\sigma_{ij} = \sqrt{\sigma_i \sigma_j}$; $\epsilon_{ij} = \sqrt{\epsilon_i \epsilon_j}$; $\Delta E = 4 \epsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^2 - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right]$

Step 1:

- Calculate relative hydration energies between 2 models; $\Delta\lambda = 0.1 \Rightarrow \Delta\Delta G_{\text{Hyd}}$
- Calculate relative hydration energies between NH_4^+ and Na^+ ; $\Delta\lambda = 0.1 \Rightarrow \Delta\Delta G_{\text{Hyd}}$
- Calculate absolute free energy of solvation with simultaneous perturbation of all parameters; $\Delta\lambda = 0.1$
- Calculate absolute free energy of solvation by v.d.W & electrostatic decoupling ΔG_{vdW} , ΔG_{elec} , $\Delta\lambda = 0.2/0.1$

Step 1

- $\Delta\Delta G$ (Model 1 \rightarrow Model 2) = 1.63 kcal/mol (TIP3P)
- \therefore Model 1 is better solvated

Step 2

- $\Delta\Delta G_{\text{Hyd}}(\text{NH}_4^+ \rightarrow \text{Na}^+) = -28.9 \text{ kcal/mol}$ [Table V]
- Experimental = -21.7 kcal/mol

Step 3

- First annihilation of NH_4^+ in TIP4P = -79.5 kcal/mol
 - with Born procedure (beyond cutoff) = -98.8 kcal/mol
- Experimental hydration free energy of NH_4^+ = -78.6 kcal/mol

Table I. Parameters of solute and solvent models.^a

Parameters	Atom	q	σ	ϵ
Model 1 NH_4^+	N	-0.400	3.250	0.170
	H	+0.350	0.000	0.000
Model 2 NH_4^+	N	-0.896	3.385	0.200
	H	+0.474	0.000	0.000
Sodium	Na^+	+1.000	1.897	1.607
TIP4P	O	0.000	3.157	0.155
	M	-1.040	0.000	0.000
	H	+0.520	0.000	0.000
TIP3P	O	-0.834	3.151	0.152
	H	+0.417	0.000	0.000

^aIn all NH_4^+ models $r_{\text{OH}} = 1.010 \text{ \AA}$. The point M is between the H's along the bisector of the HOH angle at 0.15 \AA from O. For TIP3P and TIP4P $r_{\text{OH}} = 0.9572 \text{ \AA}$ and $\alpha_{\text{HOH}} = 104.52^\circ$.

Full Perturbation of all Parameters		Electrostatic Decoupling	
$\Delta\lambda$ step	ΔG per step	$\Delta\lambda$ step	ΔG per step
0.10 \rightarrow 0.00	-9.21 \pm 0.23	0.20 \rightarrow 0.00	-27.10 \pm 0.19
0.10 \rightarrow 0.20	+8.64 \pm 0.22	0.20 \rightarrow 0.40	+22.41 \pm 0.22
0.30 \rightarrow 0.20	-8.24 \pm 0.17	0.60 \rightarrow 0.40	-15.14 \pm 0.21
0.30 \rightarrow 0.40	+8.68 \pm 0.17	0.60 \rightarrow 0.80	+10.40 \pm 0.22
0.50 \rightarrow 0.40	-7.73 \pm 0.21	0.80 \rightarrow 1.00	+5.26 \pm 0.20
0.50 \rightarrow 0.60	+8.07 \pm 0.22		
0.70 \rightarrow 0.60	-7.30 \pm 0.40		
0.70 \rightarrow 0.80	+7.42 \pm 0.18		
0.90 \rightarrow 0.80	-5.92 \pm 0.77		
0.90 \rightarrow 1.00	+8.34 \pm 0.22		

$\Delta\lambda$ step v.d.W Annihilation	
0.20 \rightarrow 0.00	+0.40 \pm 0.09
0.20 \rightarrow 0.40	-0.11 \pm 0.04
0.60 \rightarrow 0.40	+0.51 \pm 0.07
0.60 \rightarrow 0.80	-0.16 \pm 0.05
0.80 \rightarrow 1.00	+0.10 \pm 0.04

ΔG Calc.	-79.55	-78.99
ΔG Calc. + Born	-98.85	-98.29
ΔG Experimental	-78.40	-78.40

All energies are in kcal/mol.

Annihilation calculation of NH_4^+ in TIP4P

References

1. All-Atom Empirical Potential for Molecular Modeling and Dynamic Studies of Proteins
2. CHARMM General Force Field: A Force Field for Drug-Like Molecules Compatible with the CHARMM All-Atom Additive Biological Force Fields
3. Simulations of Osmotic Pressure in Concentrated Aqueous Salt Solutions
4. Corrections in the CHARMM36 Parametrization of Chloride Interactions with Proteins, Lipids, and Alkali Cations, and Extension to Other Halide Anions
5. Determination of Alkali and Halide Monovalent Ion Parameters for Use in Explicitly Solvated Biomolecular Simulation
6. Further extension of the Madrid-2019 force field: Parametrization of nitrate (NO_3^-) and ammonium (NH_4^+) ions
7. Free energy calculations involving NH_4^+ in water