

Supporting Information:

**Electrical Conductivity Differences Between
Experiments and Classical Simulations Reveal
Self-diffusion Coefficients and Ion Lifetimes of
Hydroxide and Hydronium in Aqueous Solutions**

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Abstract

In this Supporting Information, we list all simulations performed for this publication, the settings of these simulations, and the force field that were implemented. Tabulated simulation results are listed in the file `SimulationResultsPerStatepoint.xlsx`. This lists the average and confidence interval of the simulation results per state point. The results of the classical force field-based simulations listed are molalities, temperatures, number of water and salt molecules, pressures, densities, *NVT* simulation box sizes, molarities, shear viscosities, self-diffusion coefficients of all components computed from the classical trajectories, electrical conductivities computed with the Nernst-Einstein equation and computed directly using the Onsager coefficients. These tabulated results also contain the properties of the Grotthuss transferring species computed with the post-processing method proposed in the main manuscript. These are the ion lifetimes, Onsager coefficients, and self diffusion coefficients.

1 Detailed Simulation Settings

All simulations were started from random configurations constructed using `fftool` (V1.2.1)^{S1} and `PACKMOL` (V20.3.1).^{S2} Five simulations per state-point were performed with LAMMPS (Aug 2024)^{S3,S4} using the OCTP plugin^{S5} to track the mean squared displacements of the atom positions and the pressure tensor. The LAMMPS compilation was linked to the system-wide FFTW3 for Fourier transforms as to accelerate the computation of long ranged electrostatics.

Table S1: Simulation settings of the classical MD simulations of KOH (aq) at 25 and 60 °C. The force field parameters are listed in Table S6. The equilibration of the configurations was performed in in the *NPT* ensemble, followed by 100 ns of production in the *NVT* ensemble where the density is set to the average density during the *NPT* ensemble.

State points											
Temperature (K)	298.15 and 333.15										
Pressure (atm)	1.00										
Concentration (mol KOH per kg H ₂ O)	0.5	1	2	4	6	8	10	12	14	16	18
Number of K ⁺ and OH ⁻	10	20	40	80	120	160	200	240	280	320	360
Number H ₂ O	1100										
<i>NPT</i> Equilibration Dynamics											
Time step size (fs)	2										
Number of time steps	2500000										
Integrator	<i>NPT</i> Nosé-Hoover Verlet										
Thermostat coupling time (fs)	100										
Barostat coupling time (fs)	1000										
<i>NVT</i> Production Dynamics											
Time step size (fs)	2										
Number of time steps	50000000										
Integrator	<i>NVT</i> Nosé-Hoover Verlet										
Thermostat coupling time (fs)	100										

Table S2: Simulation settings of the classical MD simulations of NaOH (aq) for the adjusted force field at 25 and 60 °C. The force field parameters of the adjusted force field are listed in Table S6. The equilibration of the configurations was performed in in the *NPT* ensemble, followed by 100 ns of production in the *NVT* ensemble where the density is set to the average density during the *NPT* ensemble.

State points											
Temperature (K)	298.15 and 333.15										
Pressure (atm)	1.00										
Concentration (mol NaOH per kg H ₂ O)	0.5	1	2	4	6	8	10	12	14	16	18
Number of Na ⁺ and OH ⁻	10	20	40	80	120	160	200	240	280	320	360
Number H ₂ O	1100										
NPT Equilibration Dynamics											
Time step size (fs)	2										
Number of time steps	2500000										
Integrator	NPT Nosé-Hoover Verlet										
Thermostat coupling time (fs)	100										
Barostat coupling time (fs)	1000										
NVT Production Dynamics											
Time step size (fs)	2										
Number of time steps	50000000										
Integrator	NVT Nosé-Hoover Verlet										
Thermostat coupling time (fs)	100										

Table S3: Simulation settings of the classical MD simulations of NaOH (aq) for the original force field at 25 °C. The force field parameters of the original force field are listed in Table S6. The equilibration of the configurations was performed in in the *NPT* ensemble, followed by 100 ns of production in the *NVT* ensemble for all simulations below 10 mol NaOH per kg H₂O, and 200 ns for all simulations at higher concentrations. The density during the production is set to the average density during the *NPT* ensemble.

State points									
Temperature (K)	298.15								
Pressure (atm)	1.00								
Concentration (mol NaOH per kg H ₂ O)	0.5	1	2	4	6	8	10	12	14
Number of Na ⁺ and OH ⁻	10	20	40	80	120	160	200	240	280
Number H ₂ O	1100								
<i>NPT</i> Equilibration Dynamics									
Time step size (fs)	2								
Number of time steps	2500000 or 5000000								
Integrator	<i>NPT</i> Nosé-Hoover Verlet								
Thermostat coupling time (fs)	100								
Barostat coupling time (fs)	1000								
<i>NVT</i> Production Dynamics									
Time step size (fs)	2								
Number of time steps	50000000 or 100000000								
Integrator	<i>NVT</i> Nosé-Hoover Verlet								
Thermostat coupling time (fs)	100								

Table S4: Simulation settings of the classical MD simulations of HCl (aq) at 25 and 60°C. The force field parameters are listed in Table S6. Because the force field models H_3O^+ instead of the H^+ , a single water molecule is removed for every ion pair in the system. The equilibration of the configurations was performed in the *NPT* ensemble, followed by 100 ns of production in the *NVT* ensemble where the density is set to the average density during the *NPT* ensemble.

State points											
Temperature (K)	298.15 and 333.15										
Pressure (atm)	1.00										
Concentration (mol KOH per kg H ₂ O)	0.5	1	2	4	6	8	10	12	14	16	18
Number of H ₃ O ⁺ and Cl ⁻	10	20	40	80	120	160	200	240	280	320	360
Number of H ₂ O	1090	1080	1060	1020	980	940	900	860	820	780	740
NPT Equilibration Dynamics											
Time step size (fs)	2										
Number of time steps	2500000										
Integrator	NPT Nosé-Hoover Verlet										
Thermostat coupling time (fs)	100										
Barostat coupling time (fs)	1000										
NVT Production Dynamics											
Time step size (fs)	2										
Number of time steps	50000000										
Integrator	NVT Nosé-Hoover Verlet										
Thermostat coupling time (fs)	100										

2 Force field parameters

The sources for the force-field settings (TIP4P/2005, Madrid-Transport, and DFF/OH⁻) are listed in Table S5. The Lennard-Jones pair interaction parameters are tabulated per atom type combination in Table S6. Lennard-Jones tail corrections were applied for both the energy and the pressure. The PPPM method with a relative force error of 10^{-5} is used for long-ranged interactions. Mixing of force-field parameters is performed with the Lorentz-Berthelot mixing rules, unless otherwise stated defined in the ion force fields.

Two NaOH force fields have been used in this study. The original Madrid-Transport force field parameters for aqueous NaOH (aq) resulted in significant overestimation of density and viscosity at high concentrations. This is shown in Fig. 3 of the main manuscript. We adjusted the value of $\sigma_{\text{Na-O}_{\text{water}}}$ from 2.38725 Å to 2.625975 Å, which significantly improved the density, viscosity, and the ion self-diffusion coefficients, also visualized in Fig. 3 of the main manuscript. The resulting Lennard-Jones distance between sodium and the oxygen in a water molecule is closer the value for the Lorentz-Berthelot mixing rules.

Table S5: The force fields used in this study. The order in this table is such that if special (non Lorentz-Berthelot) mixing are applied, this is listed in the later sources (i.e. the mixing between K⁺ and O_{water} is listed in the paper introducing the K⁺ force field). SI in front of the table number in the source indicates that the table is in the Supporting Information and not the main manuscript of the source.

Atom	Name FF	Source	Table in source
O _{water}	TIP4P/2005	Abascal and Vega ^{S6}	Table I.
H _{water}	TIP4P/2005	Abascal and Vega ^{S6}	Table I.
K ⁺	Madrid-Transport	Blazquez et al. ^{S7}	Table X.
Na ⁺	Madrid-Transport	Blazquez et al. ^{S7}	Table II.
Cl ⁺	Madrid-Transport	Blazquez et al. ^{S7}	Table II. and Table X.
O _{hydroxide}	DFF/OH ⁻	Habibi et al. ^{S8}	Table 2. (FF1)
H _{hydroxide}	DFF/OH ⁻	Habibi et al. ^{S8}	Table 2. (FF1)
O _{hydronium}	Madrid-Transport	Blazquez et al. ^{S9}	SI Table II. and Table III.
H _{hydronium}	Madrid-Transport	Blazquez et al. ^{S9}	SI Table II. and Table III.

Table S6: Detailed force field parameters (ϵ and σ) of all Lennard-Jones interactions applied in this study. The last column indicates if the cross-correlation between species uses Lorentz-Berhelot mixing (True) or not (False). The original interaction parameters between O_{water} and Na^+ retrieved from Ref. S7 is shown as well, just as the adjusted O_{water} and Na^+ interactions.

Type 1	Type 2	ϵ/k_B in K	σ in Å	LB-mix
O_{water}	O_{water}	93.19997	3.15890	
O_{water}	H_{water}	0.00000	0.00000	True
O_{water}	K^+	168.43301	2.89040	False
O_{water}	Na^+	95.42268	2.62597	False
O_{water}	Na^+_{original}	95.42268	2.38725	False
O_{water}	$O_{\text{hydronium}}$	94.69644	3.00000	False
O_{water}	$H_{\text{hydronium}}$	0.00000	0.00000	True
O_{water}	Cl^-	7.45490	4.07631	False
O_{water}	$O_{\text{hydroxide}}$	53.04439	3.40445	True
O_{water}	$H_{\text{hydroxide}}$	45.41492	2.30095	True
H_{water}	H_{water}	0.00000	0.00000	
H_{water}	K^+	0.00000	0.00000	True
H_{water}	Na^+	0.00000	0.00000	True
H_{water}	$O_{\text{hydronium}}$	0.00000	0.00000	True
H_{water}	$H_{\text{hydronium}}$	0.00000	0.00000	True
H_{water}	Cl^-	0.00000	0.00000	True
H_{water}	$O_{\text{hydroxide}}$	0.00000	0.00000	True
H_{water}	$H_{\text{hydroxide}}$	0.00000	0.00000	True
K^+	K^+	238.82963	2.30140	
K^+	$O_{\text{hydroxide}}$	78.60289	2.97570	False
K^+	$H_{\text{hydroxide}}$	72.70007	1.87220	True
Na^+	Na^+	177.08370	2.21737	
Na^+	$O_{\text{hydroxide}}$	73.11742	2.93368	True
Na^+	$H_{\text{hydroxide}}$	62.60082	1.83018	True
$O_{\text{hydronium}}$	$O_{\text{hydronium}}$	96.21788	3.10000	
$O_{\text{hydronium}}$	$H_{\text{hydronium}}$	0.00000	0.00000	True
$O_{\text{hydronium}}$	Cl^-	29.82754	3.60000	False
$H_{\text{hydronium}}$	$H_{\text{hydronium}}$	0.00000	0.00000	
$H_{\text{hydronium}}$	Cl^-	0.00000	0.00000	True
Cl^-	Cl^-	9.25172	4.69906	
$O_{\text{hydroxide}}$	$O_{\text{hydroxide}}$	30.19000	3.65000	
$O_{\text{hydroxide}}$	$H_{\text{hydroxide}}$	25.84772	2.54650	True
$H_{\text{hydroxide}}$	$H_{\text{hydroxide}}$	22.13000	1.44300	

References

- (S1) Padua, A.; Goloviznina, K.; Gong, Z. Fftool: XML Force Field Files v1.2.1. 2021; Online available at: <https://doi.org/10.5281/zenodo.4701065>.
- (S2) Martínez, L.; Andrade, R.; Birgin, E. G.; Martínez, J. M. PACKMOL: A package for building initial configurations for molecular dynamics simulations. *Journal of Computational Chemistry* **2009**, *30*, 2157–2164.
- (S3) Plimpton, S. Fast Parallel Algorithms for Short-Range Molecular Dynamics. *Journal of Computational Physics* **1995**, *117*, 1–19.
- (S4) Thompson, A. P.; Aktulga, H. M.; Berger, R.; Bolintineanu, D. S.; Brown, W. M.; Crozier, P. S.; in 't Veld, P. J.; Kohlmeyer, A.; Moore, S. G.; Nguyen, T. D.; Shan, R.; Stevens, M. J.; Tranchida, J.; Trott, C.; Plimpton, S. J. LAMMPS - a Flexible Simulation Tool for Particle-Based Materials Modeling at the Atomic, Meso, and Continuum Scales. *Computer Physics Communications* **2022**, *271*, 108171.
- (S5) Jamali, S. H.; Wolff, L.; Becker, T. M.; M. de Groen; Ramdin, M.; Hartkamp, R.; Bardow, A.; Vlugt, T. J. H.; Moulτος, O. A. OCTP: A Tool for On-the-Fly Calculation of Transport Properties of Fluids with the Order-n Algorithm in LAMMPS. *Journal of Chemical Information and Modeling* **2019**, *59*, 1290–1294.
- (S6) Abascal, J. L. F.; Vega, C. A General Purpose Model for the Condensed Phases of Water: TIP4P/2005. *Journal of Chemical Physics* **2005**, *123*, 234505.
- (S7) Blazquez, S.; Conde, M. M.; Vega, C. Scaled Charges for Ions: An Improvement but Not the Final Word for Modeling Electrolytes in Water. *Journal of Chemical Physics* **2023**, *158*, 054505.
- (S8) Habibi, P.; Rahbari, A.; Blazquez, S.; Vega, C.; Dey, P.; Vlugt, T. J. H.; Moulτος, O. A. A New Force Field for OH⁻ for Computing Thermodynamic and Transport Properties of H₂

57 and O₂ in Aqueous NaOH and KOH Solutions. *Journal of Physical Chemistry B* **2022**, *126*,
58 9376–9387.

59 (S9) Blazquez, S.; de Lucas, M.; Vega, C.; Gámez, F. Acidifying the Madrid-2019 Force Field: A
60 Rigid Model for H₃O⁺ with Scaled Charges. *Journal of Chemical Physics* **2025**, *162*, 171101.