Supporting Information: Temperature effects on the ionic conductivity in concentrated alkaline electrolyte solutions

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Finite-size correction to the Nernst-Einstein conductivity

As is discussed in the main text, the Nernst-Einstein conductivity is computed from the self-diffusion coefficients of cation D_+ and anion D_- (Eq. 1).

$$\sigma_{\text{N-E}} = q^2\rho\beta(D_+ + D_-) \tag{1}$$

The self-diffusion coefficients with periodic boundary conditions are known to have system-size dependence.[S1] The dependence is mainly due to the periodicity-induced hydrodynamic

self-interaction which can be corrected using Eq. 2, where D_0 is corrected self-diffusion coefficient, D_{PBC} is the self-diffusion coefficient obtained under periodic boundary conditions (PBC), $\xi \approx 2.837297$ for cubic simulation boxes is a constant determined by the shape of the simulation box, L is the length of the simulation box, β is the inverse temperature and η is the shear viscosity.

$$D_0 = D_{\mathrm{PBC}} + \frac{\xi}{6\pi\beta\eta L} \tag{2}$$

We estimated the finite size effect for the Nernst-Einstein conductivity using Eq 2 and experimental viscosity from Ref. S2. As is shown in Fig. S1, the finite-size correction is rather small compared to the deviation of $\sigma_{\text{N-E}}$ from $\sigma_{\text{G-K}}$ or $\sigma_{\text{Exp.}}$ because of the relatively large simulation box that we used and high viscosity of NaOH solutions. Therefore, we have neglected the finite-size correction and used the uncorrected self-diffusion coefficient and Nernst-Einstein conductivity in Fig.1 shown in the Main Text.

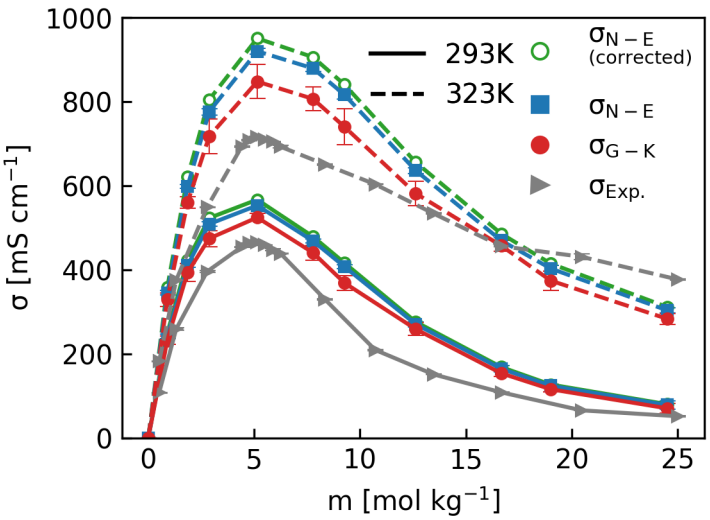

Figure S1: Ionic conductivities of NaOH solutions at 293K and 323K calculated from the Nernst-Einstein formula with and without the finite-size correction, and that obtained from Green-Kubo formula and experimental measurements.

Concentration-dependence of viscosity in NaOH solutions at 293K and 323K from experiments

As seen in Fig. S2a, the viscosity of NaOH solution increases rapidly with the concentration and its value is higher at 293K.

It is interesting to note that deviations from the Nernst-Einstein relation ($\sigma_{\text{N-E}} - \sigma_{\text{G-K}}$) with a maximum around 5m are larger at 323K than those at 293K (Fig. S1). This is in accord with the concentration-weighted inverse viscosity (see Fig. S2b), in the spirit of the Walden's rule.[S3]

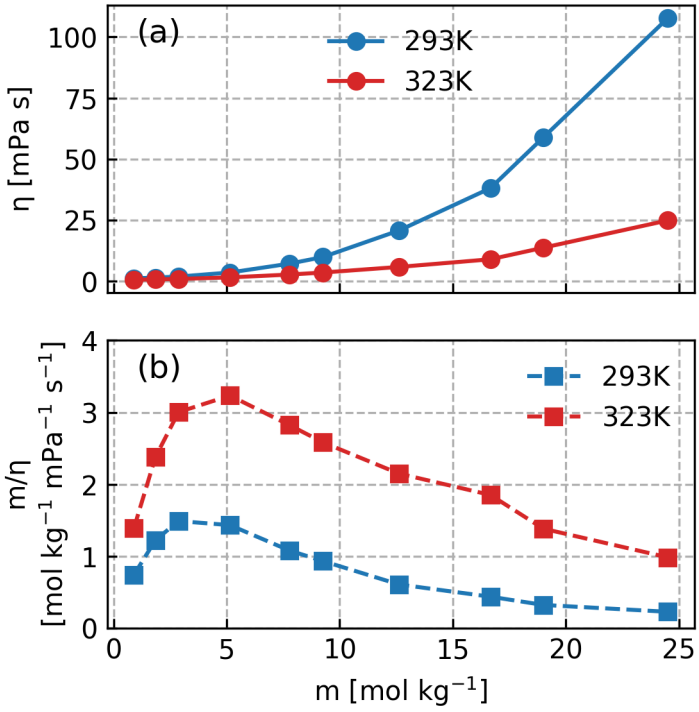

Figure S2: a) Concentration-dependent viscosities of NaOH solutions at 293K and 323K from experimental Ref. S2; b) The corresponding concentration-weighted inverse viscosities at 293K and 323K.

Stoichiometry of simulation boxes

The different molalities of NaOH solutions considered in this work and the actual number of molecules used in the simulations are given in Table S1.

Table S1: Compositions of simulated NaOH solutions in this work: Molality m, number of NaOH and H_2O molecules N_{NaOH} and N_{H_2O}, length of the cubic simulation box L and density ρ at 293K and 323K.

m [mol/kg]	N_{NaOH}	N_{H_2O}	L_{293K} [Å]	ρ_{293K} [g cm^{-3}]	L_{323K} [Å]	ρ_{323K} [g cm^{-3}]
0.896	8	496	24.56	1.04	24.66	1.02
1.852	16	480	24.30	1.07	24.40	1.06
2.874	24	464	24.05	1.11	24.16	1.10
5.144	40	432	23.59	1.19	23.70	1.17
7.778	56	400	23.18	1.26	23.29	1.24
9.259	64	384	22.99	1.30	23.10	1.28
12.626	80	352	22.64	1.36	22.75	1.35
16.667	96	320	22.34	1.43	22.45	1.41
19.006	104	304	22.21	1.46	22.32	1.44
24.509	120	272	21.96	1.52	22.07	1.50

The NaOH neural network potential

The details of the construction and validation of the neural network potential for NaOH solutions using DFT calculations at the dispersion-corrected GGA level (RPBE-D3[S4,S5]) have previously been discussed in detail.[S6–S9] In short, the training data was generated using an iterative procedure;[S6] in the final training set, there were about 16,000 energies and 890,000 force components for water and NaOH solutions with varying concentrations and densities. The root mean square errors on the validation sets (not used during training) were 1.58 meV/atom for the energies and 0.15 eV/Å for the force components.

References

(S1) Yeh, I.-C.; Hummer, G. System-size dependence of diffusion coefficients and viscosities from molecular dynamics simulations with periodic boundary conditions. *J. Phys. Chem. B* **2004**, *108*, 15873–15879.

(S2) Common Fluid – Pumping Sodium Hydroxide with Liquiflo Gear Pumps. 2016; `http://www.liquiflo.com/v2/files/pdf/applicationnotes/AN0101-1-SodiumHydroxide-Jan2016.pdf`.

(S3) Shao, Y.; Shigenobu, K.; Watanabe, M.; Zhang, C. Role of Viscosity in Deviations from the Nernst-Einstein Relation. *DOI:10.26434/chemrxiv.8217152.v2* **2019**,

(S4) Hammer, B.; Hansen, L. B.; Nørskov, J. K. Improved adsorption energetics within density-functional theory using revised Perdew-Burke-Ernzerhof functionals. *Phys. Rev. B* **1999**, *59*, 7413–7321.

(S5) Grimme, S.; Antony, J.; Ehrlich, S.; Krieg, H. A consistent and accurate ab initio parametrization of density functional dispersion correction (DFT-D) for the 94 elements H-Pu. *J. Chem. Phys.* **2010**, *132*, 154104.

(S6) Hellström, M.; Behler, J. Concentration-Dependent Proton Transfer Mechanisms in Aqueous NaOH Solutions: From Acceptor-Driven to Donor-Driven and Back. *J. Phys. Chem. Lett.* **2016**, *7*, 3302–3306.

(S7) Hellström, M.; Behler, J. Proton-Transfer-Driven Water Exchange Mechanism in the Na +Solvation Shell. *J. Phys. Chem. B* **2017**, *121*, 4184–4190.

(S8) Hellström, M.; Behler, J. Structure of aqueous NaOH solutions: insights from neural-network-based molecular dynamics simulations. *Phys. Chem. Chem. Phys.* **2017**, *19*, 82–96.

(S9) Hellström, M.; Ceriotti, M.; Behler, J. Nuclear quantum effects in sodium hydroxide solutions from neural network molecular dynamics simulations. *J. Phys. Chem. B.* **2018**, *122*, 10158–10171.