Supporting Information:
Densities, viscosities and self-diffusion coefficients of aqueous mixtures of NaBH$_4$, NaB(OH)$_4$ and NaOH using the BH$_4^-$ Delft Force Field (DFF/BH$_4^-$)

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The Supporting Information includes the following tables and figures: Force field Parameters (Table S1-S5); Viscosity measurements (Fig. S1 a-g); Computed MD simulations of viscosity for elevated (1-11 m) molalities (mol salt/kg water) of $NaB(OH)_4$ with 1 m $NaBH_4$ and 1 m NaOH at 353 K and 1 bar (Fig. S2); Computed densities and viscosities for the elevated molalities of $NaB(OH)_4$ with 1 m $NaBH_4$ and 1 m NaOH at 353 K and 1 bar (Table S6); Experimental densities (ρ) for different concentrations of NaOH, and $NaBH_4$ concentration in aqueous solution. (Fig. S3); Experimental densities (ρ) and one standard deviation of the experimental densities (ρ_{error}) for different concentrations of $NaBH_4$ and NaOH in aqueous solution, shown in Fig. S3; (Table S7) $\text{MSD}_{D_{i,\text{self}}}$ equation used for Fig. S5 (Eq. S1); $\text{MSD}_{D_{i,\text{self}}}$ equation used for Fig. S5 (Eq. S2); Radial distribution functions g(r) versus radial distance [Å] for different ion and atom combinations with Na^+. (Fig. S4); Mean square displacement curves for calculating self-diffusivity and shear viscosity. (Fig. S5); MD densities and one standard deviation for optimisation of the DFF/BH_4^-. (Table S8)

Table S1: Parameters for TIP4P/2005 [1] force field of water. H and O are the hydrogen and oxygen atom on the water molecule. ϵ and σ are the Lennard-Jones parameters, q is the atomic partial (scaled) charge and l is the bond length.

	TIP4P/2005 [1]	Unit
$\mathrm{H}-\hat{\mathrm{O}}-\mathrm{H}$	104.52	degrees
$l_{\mathrm{O-H}}$	0.9572	Å
σ_{OO}	3.1589	Å
σ_{HH}	0	Å
ϵ_{OO}	0.774908	kJ/mol
ϵ_{HH}	0	kJ/mol
q_{O}	-1.1128	e
q_{H}	+0.5564	e

Table S2: Parameters for the Madrid-2019 [2] force field of Na^+. ϵ and σ are the Lennard-Jones parameters and q is the atomic partial (scaled) charge. The $\mathrm{O_w}$ represents the oxygen atom of water.

	Madrid-2019 [2]	Unit
$\sigma_{\mathrm{Na^+Na^+}}$	2.21737	Å
$\sigma_{\mathrm{Na^+O_w}}$	2.38725	Å
$\epsilon_{\mathrm{Na^+Na^+}}$	1.472356	kJ/mol
$\epsilon_{\mathrm{Na^+O_w}}$	0.793388	kJ/mol
$q_{\mathrm{Na^+}}$	+0.85	e

Table S3: Parameters for the DFF/$\mathrm{OH^-}$. [3] ϵ and σ are the Lennard-Jones parameters, q is the atomic partial (scaled) charge and l is the bond length.

	DFF/$\mathrm{OH^-}$ model	Unit
$l_{\mathrm{O-H}}$	0.98	Å
σ_{OO}	3.85	Å
σ_{HH}	1.443	Å
ϵ_{OO}	0.251	kJ/mol
ϵ_{HH}	0.184	kJ/mol
q_{O}	-1.3805	e
q_{H}	+0.5305	e
q_{OH}	-0.85	e

Table S4: Parameters for the developed BH_4^- force field (DFF/BH_4^-). ϵ and σ are the Lennard-Jones parameters and q is the atomic partial (scaled) charge.

	DFF/BH_4^-	Unit
$\sigma_{BH_4^-BH_4^-}$	4.50	Å
$\epsilon_{BH_4^-BH_4^-}$	1.231	kJ/mol
$q_{BH_4^-}$	-0.85	e

Table S5: Parameters for the $B(OH)_4^-$ force field developed by Habibi et al. [4] ϵ and σ are the Lennard-Jones parameters, q is the atomic partial (scaled) charge and l is the bond length. The O_w represents the oxygen atom of water.

	DFF/$B(OH)_4^-$ [4]	Unit
HO-$\hat{B}$-OH	109.5	degrees
l_{B-OH}	1.49	Å
$\sigma_{(OH)(OH)}$	2.95	Å
$\sigma_{(OH)O_w}$	3.01	Å
$\epsilon_{(OH)(OH)}$	0.418	kJ/mol
q_{OH}	-0.85	e
q_B	2.55	e
$q_{B(OH)_4}$	-0.85	e

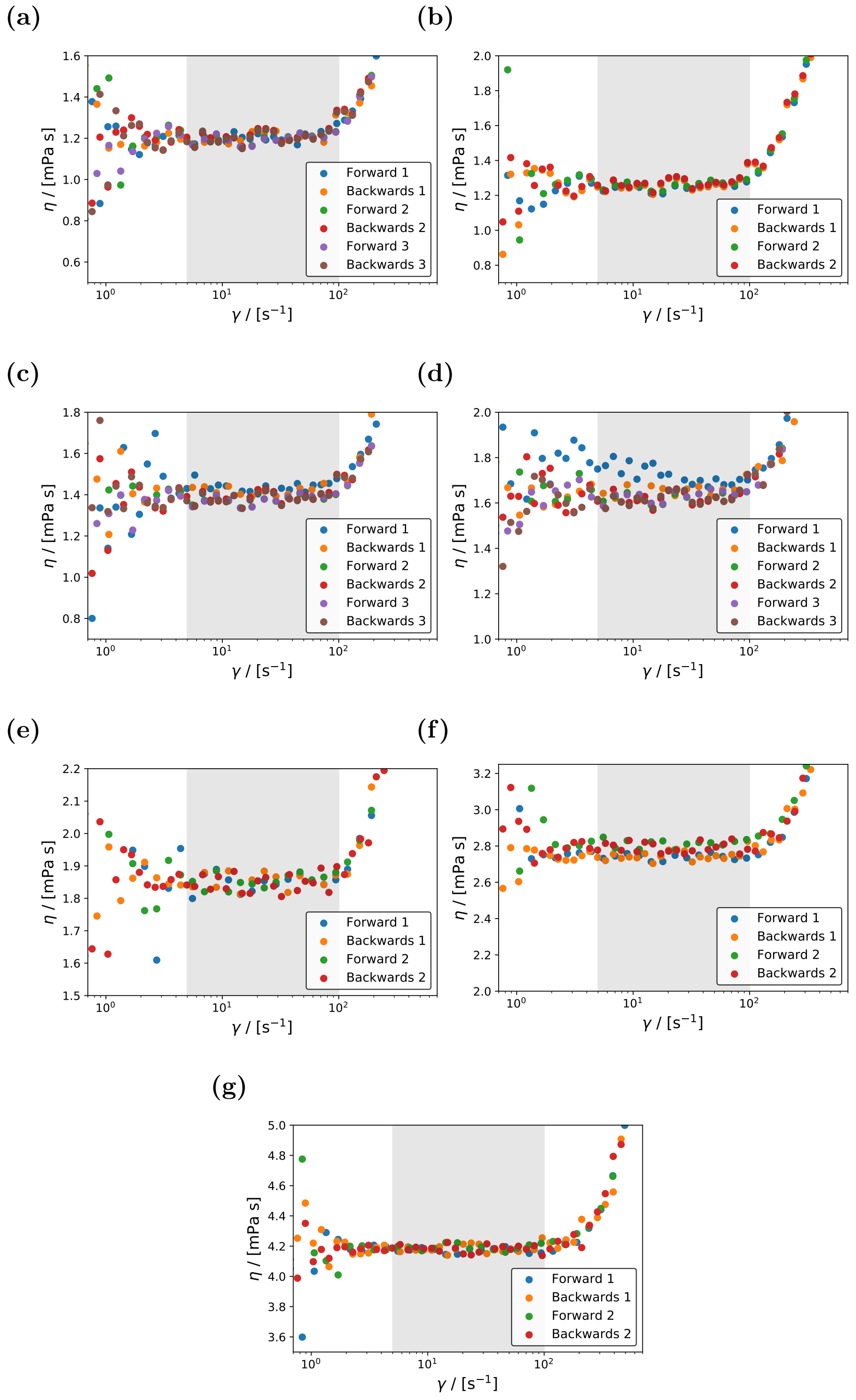

Figure S1: Viscosities (η) measured for aqueous solutions with concentrations of 1 m NaOH and 0, 1, 3 and 5 m $NaBH_4$ concentration (a-d), and 1 m NaOH, 1 m $NaBH_4$ and 1, 2 and 3 m $NaB(OH)_4$ (e-g) versus shear rate (γ). The viscosity is measured with a 1 mm gap between the 50 mm diameter parallel plate and bottom plate to ensure low viscosity (close to 1 mPa s) stability. Four to six measurements are shown: two-three measurements with increasing shear rate as a function of time (i.e. Forward 1, 2 and 3) and two-three measurements with decreasing shear rate (i.e. Backwards 1, 2 and 3). For the forward measurement the shear rate is increased with time and for the backwards measurement the shear rate is decreased with time. The gray area shows the shear rate limits and within these limits the viscosity values are averaged to obtain the viscosity of each solution.

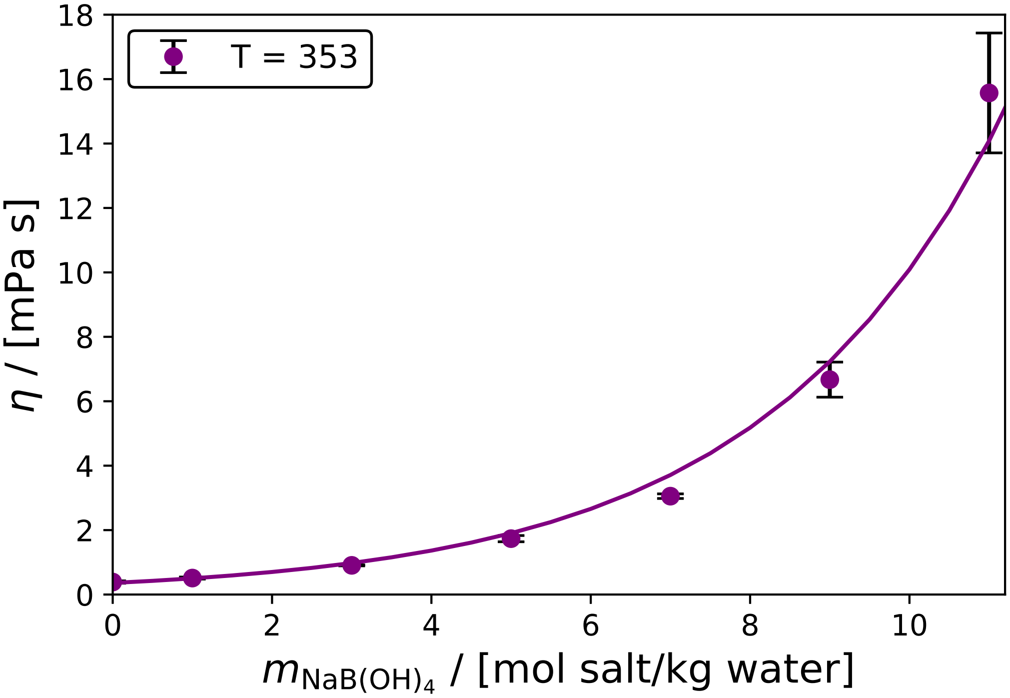

Figure S2: Viscosities (η) are computed for 0 to 11 m (mol salt/kg water) $NaB(OH)_4$ and 1 m $NaBH_4$ in aqueous solutions at 353 K and 1 bar. The empirical correlation is represented by the solid line and follows Eq. 9 with the parameters in Table 9. The empirical correlation fits the MD data even at high concentrations of $NaB(OH)_4$. Computed densities, viscosities and uncertainties of densities and viscosities can be found in Table S6. Note that these are not confirmed experimentally and should not be considered reliable data above the recommended concentration range of the empirical correlations.

Table S6: MD simulations for elevated concentrations of $NaB(OH)_4$ and 1 m $NaBH_4$ aqueous solutions at 1 bar pressure and 353 K. Densities ρ and viscosities η, with uncertainties of the densities (ρ_{error}) and viscosities (η_{error}), are computed for these elevated concentration to verify if the empirical correlation for viscosity (eq. 3) follows the MD simulations at higher concentrations of $NaB(OH)_4$, as shown in Fig. S2. Note that these are not confirmed experimentally and should not be considered reliable data above the recommended concentration range of the empirical correlations.

Molality $NaB(OH)_4$ m [Mol $NaB(OH)_4$/kg water]	Molality $NaBH_4$ m [Mol $NaBH_4$/kg water]	ρ kg/m^3	ρ_{error} kg/m^3	η mPa s	η_{error} mPa s
0	1	972	0.37	0.39	0.037
1	1	1033	0.18	0.51	0.032
3	1	1143	0.40	0.91	0.016
5	1	1240	0.41	1.73	0.097
7	1	1325	0.55	3.05	0.072
9	1	1402	0.82	6.67	0.545
11	1	1467	1.05	15.57	1.861

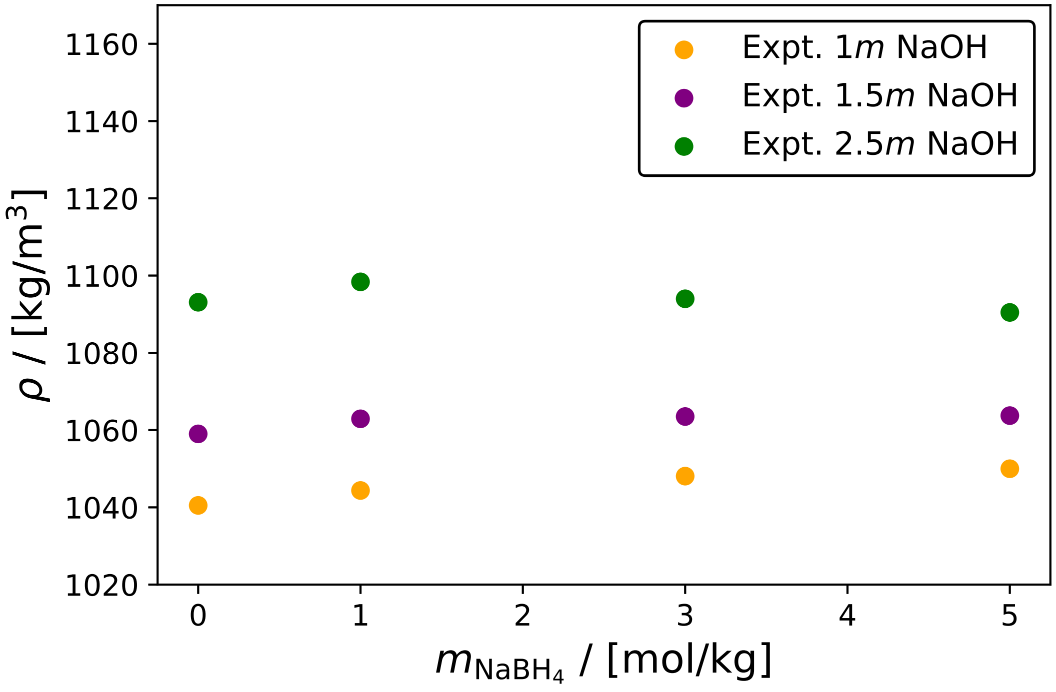

Figure S3: Experimental densities (ρ) for concentrations of 1 (yellow), 1.5 (purple) and 2.5 (green) m NaOH, and 0 to 5 m $NaBH_4$ concentration in aqueous solution at 295 K and 1 bar pressure. The experimental densities aqueous electrolyte solutions are measured using an Anton Paar density meter DMA 5000. All solutions are stabilised using at least 1 m NaOH. The error bars for densities are smaller than the symbol size and have therefore been removed for clarity. The densities and density uncertainties can be found in Table S7.

Table S7: Experimental densities (ρ) and one standard deviation of the experimental densities (ρ_{error}), for different concentrations of $NaBH_4$ and NaOH in aqueous solution at 295 K and 1 bar pressure. Densities are measured using an Anton Paar density meter DMA 5000. All solutions for these measurements are stabilised using at least 1 m of NaOH to prevent any hydrogen bubble formation during the measurements. The uncertainties shown in this table are one standard deviation from the experimental dataset.

Molality NaOH m [mol salt/kg water]	Molality $NaBH_4$ m [mol salt/kg water]	ρ kg/m^3	ρ_{error} kg/m^3
1 m	0 m	1040.5	0.078
1 m	1 m	1044.4	0.43
1 m	3 m	1048.1	0.50
1 m	5 m	1050.0	0.21
1.5 m	0 m	1059.0	0.078
1.5 m	1 m	1062.9	0.43
1.5 m	3 m	1063.5	0.50
1.5 m	5 m	1063.7	0.21
2.5 m	0 m	1093.1	0.3
2.5 m	1 m	1098.4	0.027
2.5 m	3 m	1094.0	0.048
2.5 m	5 m	1090.5	0.032

$$\mathrm{MSD}_{D_{i,\text{self}}} = \frac{1}{6N_i}\left\langle \sum_{j=1}^{N_i} \left(r_{j,i}(t) - r_{j,i}(0)\right)^2 \right\rangle \tag{S1}$$

$$\mathrm{MSD}_{\eta} = \frac{1}{2}\frac{V}{k_B T}\left\langle \left(\int_0^t P_{\alpha\beta}(t^{'})dt^{'}\right)^2 \right\rangle \tag{S2}$$

(a)

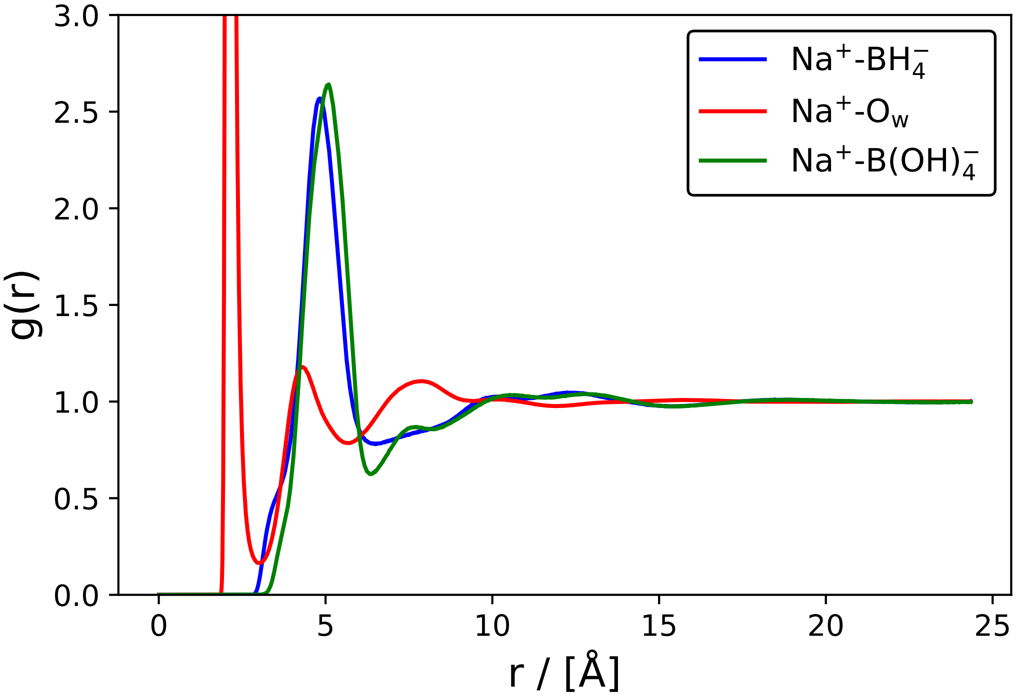

Figure S4: Radial distribution functions (g(r)) for Na^+-O_w, Na^+-$B(OH)_4^-$ and Na^+-BH4$^-$ (O of water) as a function of radial distance (r), at 323 K, 1 bar, and a concentration of 5 *m* $NaBH_4$ and $NaB(OH)_4$. The RDF of Na^+shows the formation of the first hydration layer around 2.5 Å and a second layer around 4.5 Å. The $BH_4^-$and $B(OH)_4^-$ions are primarily present after the second hydration layer, excluding any ion pairing of $Na^+$with the anions. The force field parameters DFF/BH_4^- are used for the MD simulations, combined with the TIP4P/2005 [1] water, Madrid-2019 [2] $Na^+$and DFF/$B(OH)_4^-$ [4] force field.

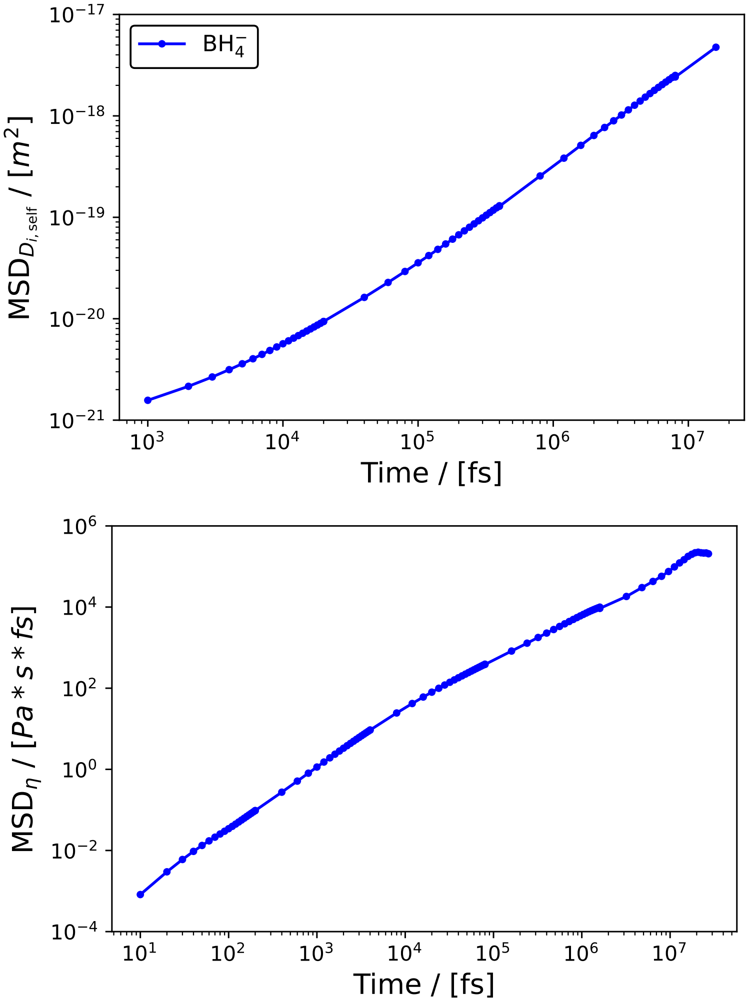

Figure S5: (a) Mean square displacement of the self-diffusivity of BH_4^- ($MSD_{D_{i,self}}$), as a function of simulation time, (b) Mean square displacement of η (MSD_η), as a function of simulation time at 323 K, 1 bar, and a concentration of 5 m $NaBH_4$ and $NaB(OH)_4$, in a log-log plot. The y-axes are based on eq. S1 and S2. These figures are used to calculate the self-diffusivity (a) and shear viscosity (b) by finding where the slope of the $MSD_{D_{i,self}}$ or MSD_η as a function of time is 1 in a log-log plot. The force field parameters DFF/BH_4^- are used for the MD simulations, combined with the TIP4P/2005 [1] water, Madrid-2019 [2] $Na^+$and DFF/$B(OH)_4^-$ [4] force field.

Table S8: MD densities (ρ) and one standard deviation of the MD densities (ρ_{error}), for 5 m of $NaBH_4$ and 1 m NaOH in aqueous solution at 295 K and 1 bar pressure. The densities in this table are used for fitting the σ LJ parameter of the BH_4^-forcefield on density compared with experimental density, shown in Fig. 2. The uncertainties shown in this table are one standard deviation from the MD measurements.

$\sigma_{\mathrm{BH_4^-BH_4^-}}$ Å	ρ kg/m^3	ρ_{error} kg/m^3
4.00	1119.1	0.27
4.05	1112.2	0.13
4.10	1104.7	0.23
4.15	1096.2	0.52
4.20	1089.5	0.41
4.25	1082.1	0.42
4.30	1074.9	0.30
4.35	1066.5	0.19
4.40	1059.9	0.21
4.45	1052.1	0.40
4.50	1044.6	0.18
4.55	1037.0	0.33
4.60	1029.6	0.49
4.65	1021.9	0.16
4.70	1014.5	0.50
4.75	1006.9	0.41
4.80	999.1	0.22
4.85	992.0	0.43
4.90	984.3	0.17
4.95	976.2	0.21
5.00	969.0	0.15

References

(1) Abascal, J. L. F.; Vega, C. A general purpose model for the condensed phases of water: TIP4P/2005. *The Journal of Chemical Physics* **2005**, *123*, 234505.

(2) Zeron, I. M.; Abascal, J. L. F.; Vega, C. A force field of Li^+, Na^+, K^+, Mg^{2+}, Ca^{2+}, Cl^-, and SO_4^{2-} in aqueous solution based on the TIP4P/2005 water model and scaled charges for the ions. *The Journal of Chemical Physics* **2019**, *151*, 134504.

(3) Habibi, P.; Rahbari, A.; Blazquez, S.; Vega, C.; Dey, P.; Vlugt, T. J.; Moultos, O. A. A New Force Field for OH^- for Computing Thermodynamic and Transport Properties of H_2 and O_2 in Aqueous NaOH and KOH Solutions. *Journal of Physical Chemistry B* **2022**, *126*, 9376–9387.

(4) Habibi, P.; Postma, J. R. T.; Padding, J. T.; Dey, P.; Vlugt, T. J. H.; Moultos, O. A. Thermodynamic and Transport Properties of $H_2/H_2O/NaB(OH)_4$ Mixtures Using the Delft Force Field (DFF/$B(OH)_4^-$). *Industrial and Engineering Chemistry Research* **2023**, *62*, 11992–12005.