Molecular Simulation of the Diffusivity of NaOH in Steam

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Molecular dynamics simulation is used to calculate the infinite-dilution diffusivity of sodium hydroxide (NaOH) in steam at conditions of temperature and density typical of steam turbines. These data are needed in order to better understand deposition mechanisms of impurities in steam. An existing polarizable potential was used for water, and a combination of existing potential parameters and molecular parameters based on quantum calculations was used for the NaOH molecule. The diffusivity of NaOH is approximately twice that of NaCl at the same conditions; this appears to be caused by differences in the energetics of the interactions of the two solutes with the water molecule. In contrast to the situation with NaCl, the temperature and density dependence of the diffusivity of NaOH could not be accurately described by a simple kinetic-theory expression.

1. Introduction

Deposition on turbines from impurities in steam is a significant problem in the power industry. A better understanding of the processes involved in deposition could lead to significant improvements in operating reliability and/or to reduction in water treatment costs.

Bellows has suggested [1] that deposition in steam turbines might be diffusion-limited. An obstacle to a thorough analysis of this possibility is the total lack of data for the diffusivities of the relevant solutes in steam. Because of the near impossibility of experimental measurement of this property at the conditions of interest, it is a good candidate for estimation by molecular simulation. Previously [2], we reported simulation results for the diffusivity of NaCl in steam at turbine conditions, along with a simple expression based on kinetic theory that allowed interpolation and limited extrapolation of the results. Here, we extend the work to NaOH, another solute of significant industrial interest, and compare the results to those for NaCl.

2. Intermolecular Potentials, Simulation Details

As in our previous work [2], the water molecules are represented with a potential taken from the literature [3], in which they are rigid, four-site objects. In addition to hydrogen and oxygen sites (with an O-H distance of 0.09572 nm and H-O-H angle of 104.5°), there is an additional site, the M-site, located along the bisector of the H-O-H angle interior to the angle and 0.0215 nm from the O atom. The polarizability is located at the M-site.

The NaOH molecule is represented as a rigid, linear, three-site object. Based on our previous experience with NaCl, consideration of dissocation of NaOH into ions was unnecessary at these low solvent densities because of the extremely low equilibrium probability of such ionized states.

In addition to charges and Lennard-Jones interaction sites located on the Na, O, and H sites, there is a point polarizability located at the center of mass of the molecule, designated as CM. The charges were selected to match the *ab initio* calculated value of the dipole moment of NaOH using the experimental bond lengths quoted by Burk *et al.* [4] (0.195 nm for Na-O and 0.097 nm for O-H). The polarizability at site CM was assigned a value that roughly matched *ab initio* calculated values. The Lennard-Jones parameters for interactions between NaOH and H_2O were adapted from those of Balbuena *et al.* [5] by use of Lorentz-Berthelot combining rules. Table 1 shows the potential parameters used in this work.

Table 1. Interaction parameters. For the NaOH sites, ε and σ are the values for their interactions with the $O(H_2O)$ site. q is in units of the elementary charge e.

Site	ε/k_B (K)	σ (nm)	q	α (nm^3)
$O(H_2O)$	91.56	0.3324	0	0
$H(H_2O)$	0	0	0.519	0
M	0	0	−1.038	0.00144
Na	75.45	0.3007	0.9187	0
O(NaOH)	63.29	0.3279	−1.4252	0
H(NaOH)	51.26	0.2704	0.5065	0
CM	0	0	0	0.002963

The simulation methods were identical to those used previously [2] and will not be discussed at length here. Briefly, molecular dynamics simulations were performed in the NVT ensemble (fixed number of molecules, volume, and temperature) with 215 water molecules and 1 NaOH molecule. The equations of motion were integrated with a time step of 1 fs. Interactions were truncated at 0.9 nm; previous work [2] established that the extra computational effort of Ewald sums was unnecessary in calculating the diffusivity with sufficient accuracy. Polarization interactions were generated by iterative, self-consistent solution for the induced dipole moments.

The diffusivities, D_s, are obtained as the limiting slopes of the mean-square displacements of the particles:

$$D_s = \frac{1}{6} \lim_{t \to \infty} \frac{d}{dt} \left\langle \left| \vec{r}(t) - \vec{r}(0) \right|^2 \right\rangle, \qquad (1)$$

where the brackets indicate an average over time origins and the number of particles. Equilibration, run lengths, and averaging were as described previously [2].

3. Results

Table 2 shows the calculated diffusivities of NaOH for each of the eight state points studied in this work. The simulations were performed at fixed temperature T and density ρ; the pressures p in Table 2 were calculated from water's equation of state [6] at the given T and ρ. We estimate the uncertainty in the simulated diffusivities to be on the order of 30 %.

Table 2 also shows the mean number $<N>$ of hydrating water molecules at each state, calculated as in previous work [2], along with the variance in this number. As expected, $<N>$ decreases with decreasing density and increasing temperature. The relatively large variance is also not unexpected for these relatively low densities, where transient clustering around solutes is likely.

In previous work [2] on the diffusivity of NaCl in steam, it was shown that the results at various state points could be fitted within 15 % by a simple expression suggested by kinetic theory:

$$D_s = AT^{1/2}/n, \qquad (2)$$

where T is the absolute temperature (K) and n is the number density of H_2O molecules (m^{-3}). The value of A derived for NaCl diffusing in steam was 6.9×10^{18} m^{-1}·s^{-1}·K$^{-1/2}$ (note that an incorrect power of 10 was written in [2]). For NaOH, our averaged value of A is 1.7×10^{19} m^{-1}·s^{-1}·K$^{-1/2}$. However, Eq. (2) does not work nearly as well for NaOH as it did for NaCl; the values of A corresponding to different points in Table 2 vary by as much as a factor of 2.

Table 2. Simulated diffusivities for NaOH infinitely dilute in H_2O as a function of temperature T and density ρ. Also tabulated is the mean number of solvating water molecules $<N>$ and its variance σ_N.

T (K)	ρ (kg·m^{-3})	p (MPa)	D_s (10^{-9} m^2·s^{-1})	$<N>$	σ_N
573	25.6	5.65	370	2.6	1.3
573	13.1	3.17	550	1.9	1.1
673	25.6	7.14	450	2.0	1.2
673	13.1	3.86	780	1.2	1.0
673	7.6	2.29	2100	0.8	0.8
773	25.6	8.51	700	1.4	1.1
773	13.1	4.51	1200	0.9	0.9
773	7.6	2.66	2300	0.5	0.7

Therefore, Eq. (2) is of limited value for describing diffusivities for NaOH in steam.

A few calculations were also performed to examine the effect of charge distribution and polarizability of NaOH on the calculated diffusivity. These calculations were performed at the state conditions of the fourth point in Table 2 (673 K, 13.1 kg·m^{-3}). When the charges on the NaOH molecule were reduced by approximately 20 %, the calculated diffusivity increased by about 20 % (to approximately 1000 in the units of Table 2). When the polarizability was removed from the NaOH (with the original charges), the calculated diffusivity increased to approximately 1100. This moderate sensitivity suggests that a fairly accurate model of the solute molecule is required in order to obtain quantitative accuracy. This also suggests that our previous simulated diffusivities for NaCl in steam may be slightly too low, since we used a charge of magnitude 1.0 on both the Na and Cl, when in reality the separation of charge in the neutral NaCl molecule is only about 90 %.

4. Discussion

If one compares the diffusivities in Table 2 with those at the same conditions reported for NaCl [2], it appears that the diffusivity of NaOH is roughly twice as large at identical conditions. One can examine the cause of this difference in an approximate manner by looking at the kinetic-theory expression [7] for a spherically symmetric potential:

$$D_s = \frac{3}{8} \frac{(\pi k_B T / M_{12})^{1/2}}{n \pi \sigma_{12}^2 \, \Omega^{(1,1)\star}}, \qquad (3)$$

where k_B is Boltzmann's constant, M_{12} is the reduced mass of the binary system, σ_{12} is the collision diameter, and $\Omega^{(1,1)\star}$ is the collision integral, which incorporates details of the intermolecular interactions and which has a value of 1 for hard spheres. The smaller molar mass (and therefore smaller M_{12}) for NaOH accounts only for a factor of approximately 1.1 in the diffusivity. Because the solutes are of similar size, the collision diameters should be similar; we note, however, that σ_{12} is squared in Eq. (3) and therefore small differences will be magnified.

In order to estimate the difference in the collision integral $\Omega^{(1,1)\star}$, we calculate a Boltzmann-weighted interaction energy, averaged over all mutual orientations, as a function of separation. The temperature used for the Boltzmann weighting of configurations was 673 K. This averaged interaction energy (in units of $k_B T$) is plotted in Fig. 1 for NaOH-H$_2$O, along with the similar calculation for NaCl-H$_2$O. The minimum of the potential for NaOH-H$_2$O has a strength of approximately 3500 K, producing a reduced temperature of approximately 0.2 at the conditions of our study. Similarly, the reduced temperature for NaCl-H$_2$O is approximately 0.1. Tabulated values for the simpler Lennard-Jones potential [8] yield collision integrals of approximately 3 and 4 for reduced temperatures of 0.2 and 0.1, respectively. On this basis, one would expect the diffusivity of NaOH in steam to be higher by a factor of 4/3. This is still smaller than the factor of 2 difference seen in the simulations, but quantitative agreement is not to be expected since the actual intermolecular potential is far from a Lennard-Jones interaction. We also note that the attractive part of the angle-averaged potential for NaCl extends to much greater distances, which would likely make its collision integral exceed that for NaOH by an amount larger than that predicted by our simple comparison of the minima in the potentials.

The large difference between NaCl and NaOH in their angle-averaged interactions with water (as shown in Fig. 1) might not be intuitively expected. We speculate that this is a consequence of the different arrangement of charge on the solutes; while the NaCl molecule has a positive and a negative end, NaOH has (somewhat smaller) positive charges on both ends with its negative
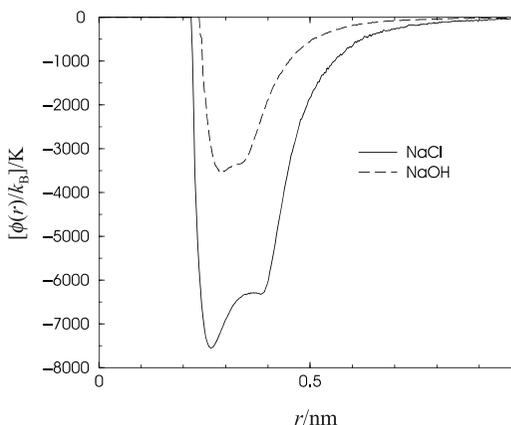

Fig. 1. Boltzmann-weighted angle-averaged interaction energy for NaCl and NaOH with H$_2$O as a function of center-to-center distance r.

charge in the center. This different charge distribution, and therefore different interaction with water molecules, might also be a factor in the inability of simple kinetic theory (Eq. 2) to describe the results.

5. Conclusions

We have used molecular simulation to calculate diffusivities of NaOH in steam at typical turbine conditions. The diffusivity of NaOH in steam is approximately twice that of NaCl at the same conditions; the difference is attributed to the weaker attractive interactions for the NaOH-H_2O binary pair.

References and Notes

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