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Classical simulation of acid and base dissociation constants in supercritical water at constant density

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ABSTRACT

Molecular dynamics simulations were performed to investigate the dissociations of water, NaOH and HCl in water at constant density of 0.9 g cm^{-3} at near-critical and supercritical temperatures. Results were in good qualitative agreement with available data, showing increased temperature favouring all dissociations. The dissociation of water was favoured by more negative values of U/T and an increasing entropy tem, whereas the dissociation of HCl showed both decreasing U/T and entropy. NaOH showed an increasing value of U/T which was dominated by an increasing entropy term. Differences in the energy contributions were attributed to the change in solute charges upon dissociation.

1. Introduction

Over the past few decades, supercritical water (SCW) has been the subject of intense research. Its numerous unusual properties have great potential in industrial applications. For example, it can act as either an acid or base catalyst and can be used as a medium for both organic and polar species, opening up the potential for new reaction mechanisms [1]. Furthermore, it has been found to very promising for environmentally friendly waste destruction, being able to oxidize a variety of waste organic products to carbon dioxide, water and other trace molecules [2–4].

However, serious challenges remain before SCW can see widespread use, the chief of which is the problem of corrosion. At the extreme conditions under which SCW exists, corrosion occurs at a significantly increased rate. This can considerably reduce the lifetime of a reaction vessel and possibly even cause catastrophic failure [5,6]. There are thought to be many factors which contribute to corrosion in SCW vessels including, for example, alloy composition, electrochemical potential, water density and pH [7].

The aim of this work is to investigate the acidity/basicity of an aqueous solute as a function of temperature at constant density by looking at the pK_W of water autoionisation, pK_a of HCl dissociation and pK_b of NaOH. An increase in any would suggest an increased level of corrosion. Previous work has found that, at constant high pressure, the level of acid/base dissociation tends to fall with increasing temperature [8]. Conversely, the pK_W of water first decreases near the critical point, reflecting an increased tendency to form ions, before increasing beyond it [9]. However, corrosion is known to generally increase with increasing temperature at constant densities [7]. So, it is important to understand the causes of the variations in pK_W, pK_a and pK_b with temperature at constant, high density. Furthermore, the behaviour of aqueous electrolytes is not fully understood at supercritical conditions [10].

2. Theory

For a closed isothermal, isochoric system, the Helmholtz free energy of reaction, $\Delta_r A^0$, is connected to the constant volume equilibrium constant, K_V, by

$$\varDelta rA^0 = -RT \ln K_V \tag{1}$$

For an acid or base dissociation, K_V may equivalently be called the dissociation constant and, for a simple dissociation such as $H_2O + HA \rightleftarrows H_3O^+ + A^-$ at the limit of infinite dilution, this is given by the ratio of the concentrations:

$$K_V = \frac{[H_3O^+]\left[A^-\right]}{[HA]\,[H_2O]} \tag{2}$$

At constant volume, the Gibbs-Helmholtz equation may be written as

$$\left(\frac{\partial \ln K_V}{\partial (1/T)}\right)_V = -\frac{\Delta rU^0}{R} \tag{3}$$

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Table 1
Solute geometries.

	Bond length (Å)	Bond angle (rad)
HCl	1.280	
NaOH (O–H)	0.953	
NaOH (Na–O)	3.093	
		3.017
OH	0.965	
H_3O	0.980	
		1.961

Table 3
Number of solvent molecules for each solute system.

Solute	Number of solvent molecules
HCl (molecular)	1024
NaOH (associated)	1024
Cl^-	512
Na^+	512
H_3O^+	511
OH^-	511
Pure (no solute)	1024

The change in internal energy, $\Delta_r U^0$, is relatively straightforward to calculate from molecular simulations and free energy cycles.

$$\Delta rU^0 = \Delta vapU^0(\text{products}) - \Delta vapU^0(\text{reactants}) + \Delta E^{\text{elec}} + \Delta E^{\text{rotation}} + \Delta E^{\text{vibration}} + \Delta E^{\text{kinetic}} + \Delta E^{\text{ZPE}} \quad (4)$$

The values of $\Delta_{\text{vap}} U^0$ can be calculated from classical molecular dynamics (MD) simulations, and ΔE^{elec} can be estimated using gas phase quantum mechanical calculations. Any changes in kinetic energy of the system can be calculated through the kinetic theory. All other contributions will be assumed to be small in comparison and neglected. Thus, Eq. (3) can be numerically integrated to give an estimate of the change in the dissociation constant with temperature and, so, an estimate in the change of the pK_W, pK_a and pK_b.

Having obtained an estimate of ΔK_V, the change in entropy of reaction can be estimated by using Eq. (1) and rearranging $A = U - TS$.

3. Methods

Solute structures were optimized and their energy calculated using density functional theory with the B3LYP exchange-correlation functional [11–14] and the 6–311++G** basis set [15]. The optimized structures are listed in Table 1. Partial charges were calculated from a Mulliken population analysis [16] (Table 2).

MD simulations were performed in the NVT ensemble with the Nosé-Hoover thermostat [17] using infinitely dilute systems containing a single solute molecule, and the number of solvent molecules as listed in Table 3. These systems correspond to an associated gas phase solute species dissociating to give completely separated ions. The volume of each system corresponds to a density of 0.9 g cm^{-3}. This value was chosen due to the fact that corrosion is known to be, in general, higher at higher densities [7,18–20], possibly due to the increased dielectric constant.

Simulations were done at temperatures ranging from 448 K to 898 K, under which conditions only a single fluid phase is ever present. Ewald summation was used to calculate the electrostatic interaction, and OPLS parameters [21,22] were used for the Van der Waals calculation with a cutoff of 10.0 Å (Table 2). The SPC/e model [23] was used to represent the solvent, and this is known to be a robust model which can reproduce the critical point of water well [24,25], and gives good values for thermodynamic the enthalpy of vapourisation in near critical water, though overestimates it slightly at lower temperatures [26,27]. All molecules were kept rigid throughout the MD simulations. This type of simple point charge model does have some well-known limitations, particularly with hydroxide for which there is a tendency to significantly overestimate hydrogen bonding. While improved models have been developed, this work is focused on qualitative reproduction of trend. Furthermore, simple, robust models are preferred due to the extreme conditions being simulated [28–31].

Table 2
Force field details of solutes.

Species	Atom	Charge (e)	σ (Å)	ε (kcal mol^{-1})
Sodium hydroxide	Na	0.774	3.330	0.003
	H	0.229	–	–
	O	−1.003	3.166	0.155
Sodium cation	Na	1.000	3.330	0.003
Hydroxide anion	H	0.118	–	–
	O	−1.118	3.166	0.155
Hydrogen chloride	H	0.164	–	–
	Cl	−0.164	4.417	0.118
Hydronium cation	H	0.380	–	–
	O	−0.140	3.166	0.155
Chloride anion	Cl	−1.000	4.417	0.118

After equilibration, the total time length of each simulation was 5 ns, and information for radial distribution functions and trajectories were collected at 0.5 ps intervals. The data collected was then used to calculate the change in pK_a of HCl acidic dissociation and the change in pK_b for the basic dissociation of NaOH. The pK_a for the autoionisation of water was also calculated in order to compare to other readily available experimental data.

DL_POLY 2 [32] was used for all MD simulations and GAMESS [33] for the DFT calculations.

4. Results and discussion

4.1. Structure

The pair correlation of water (O–H) is in good agreement with similar work. As the temperature increases from 498 K to 898 K, the intensities of the peaks fall and the depth of the well between peaks decreases in magnitude. This represents a loss of water–water ordering as molecules have more kinetic energy, meaning that they are able to overcome hydrogen bonds and move more freely. The trends for both hydronium (H) to water (O) (Fig. 1) and hydroxide (O) to water (H) (Fig. 2) are similar to water (O–H), though the loss of order is more significant, especially for hydroxide which has a high degree of solvent–solute structure at low temperatures. Both the peak positions and intensities are in good agreement with other work at high density [34].

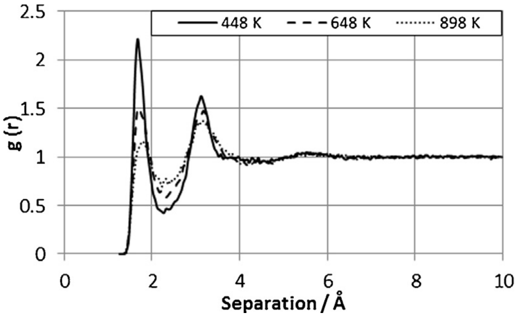

Fig. 1. Pair correlation function for hydronium hydrogen–water oxygen interaction at 0.9 g cm^{-3}.