

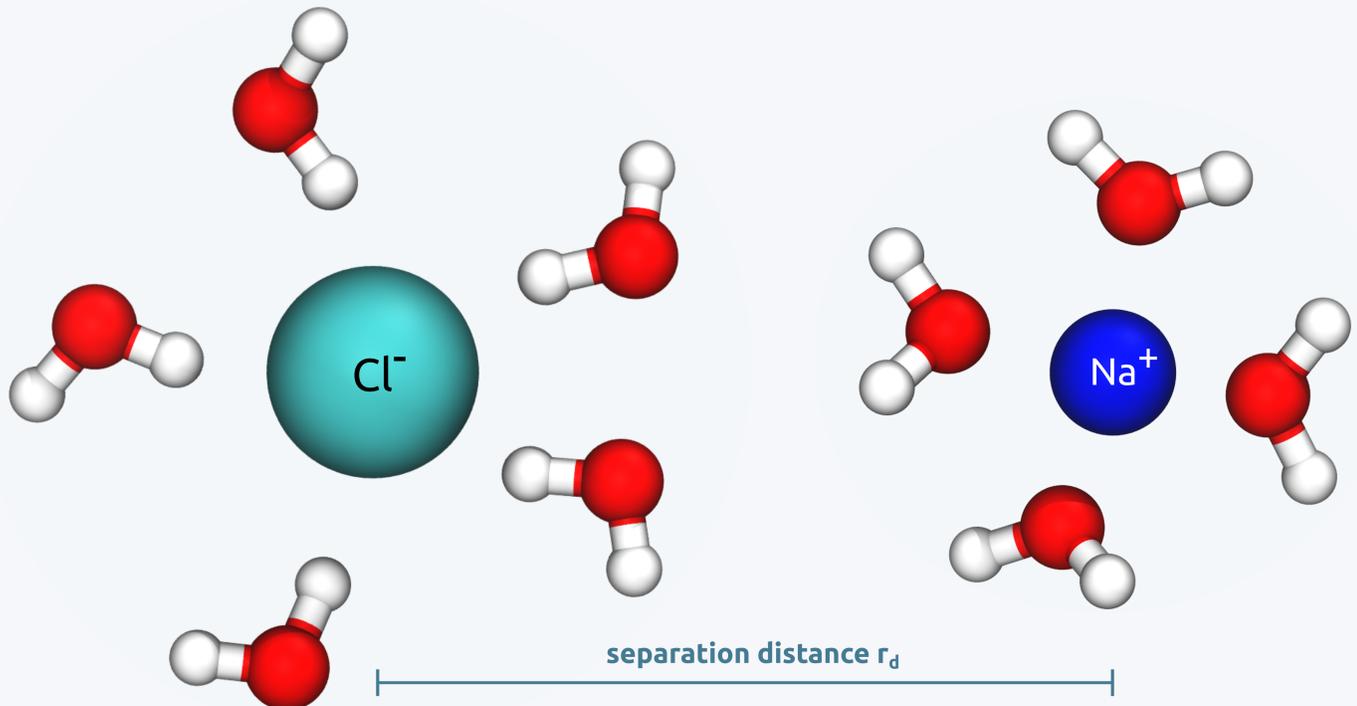
Ion Dissociation in Water Under Supercritical Conditions: A Molecular Perspective on Linear Density Models for Equilibrium Constants

1. Introduction

Experiments have shown a **linear dependence** between the logarithms of the **H₂O density (log(ρ))** and **equilibrium constants (log(K))** at supercritical conditions. This is a promising basis for future thermodynamic models [1]. Here we test the empirically found linearity using the example of **NaCl** with the help of **classical molecular dynamics (MD) simulations**. Our approach is based on the following relationship:

$$k = \frac{\partial \log(K)}{\partial \log(\rho)} = \frac{\Delta V}{\beta RT}$$

where ΔV is the volume of reaction, R is the gas constant, T is the temperature and β is the compressibility of H₂O [2].



2. Methods

Classical MD simulations were carried out with the LAMMPS code [3]. The TIP4P/2005 model [4] and force field parameters from Joung & Cheatham [5] were used to describe H₂O and NaCl. The system consists of 2056 H₂O molecules and one NaCl ion pair. β and ΔV were determined by simulations in the isothermal-isobaric (NPT) ensemble at **673 K** and **pressures from 16 to 1269 MPa**, corresponding to **densities of 0.1 to 1.1 g/cm³**. For comparability, the results are presented as a function of the reduced density $\rho_r = \rho/\rho_c$, where ρ_c is the density of H₂O at the critical point.

4. Discussion

For $r_d = 0.9a$, k is constant at $\rho_r > 1$ (first figure to the right). This **confirms the empirically found linear relationships**. The relatively large separation length $r = 0.9a$ is necessary to account for the long-ranged solute-solvent interactions near the critical point of H₂O. At $\rho_r < 1$, k decreases to smaller values. The resulting values for log(K) form an s-shaped curve with values calculated for the vapour phase as predicted by Pitzer [8] decades ago! Furthermore, the linearity between log(K) and log(ρ) also seems to hold at higher ρ .

3. Volume of Reaction

The question of the **distance r_d** at which a **pair of ions** is considered **dissociated** is not trivial in the case of supercritical aqueous fluids. Therefore, we tested two different cases. First, a series of simulations was performed with r_d set constant at **8.1 Å**, a typical value used in previous studies [6]. In the second series, r_d was set to **0.9a**, where **a is half the length of the simulation cell**. The dependence of ΔV on r_d increases with decreasing ρ_r (left figure). ΔV matches experimental data [7] much better for the higher separation distance $r_d = 0.9a$.

