Two Aspects of the Osmotic Second Virial Coefficient

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Hydrophobic interactions are the effective interaction between hydrophobic molecules or moieties in aqueous solutions. One way to quantify those interactions is to measure the osmotic second virial coefficient B, which is related with the effective solute-solute pair potential $w(r)$ in solution via

$$B = -\frac{1}{2} \int \left[e^{-\frac{w(r)}{kT}} - 1 \right] d\tau$$

where $d\tau$ is the infinitesimal volume element and the integral is over the whole space. Here we report two aspects of the osmotic second virial coefficient for hydrophobic solutes, one concerning salt effects and the other pertaining to length scales of hydrophobic interactions.

The ion-specific effect on the solubility of gases in aqueous solutions is measured by the Setschenow coefficient K_s. Recently the reverse order of lithium and sodium ions in the cation size dependence of K_s has been examined based on molecular simulation [1]. We now introduce an analogous quantity, the salt-enhanced association (SEA) coefficient C_I, which is a measure of the ion-specific effect on the osmotic second virial coefficient [2]. It is shown that the SEA coefficient is explicitly related to the Setschenow coefficient: For ions and solutes that are not very large, the quadratic relation, $C_I \approx \frac{1}{4} K_s$, is derived.

The other aspect of the osmotic second virial coefficient to be discussed is its solute-size dependence. It is known that the second virial coefficient for gases is proportional to the cubic power of the molecular diameter for typical model pair potentials with the well-depth fixed. We evaluated *osmotic B* for hydrophobic molecules of different sizes in water based on molecular simulation [3]. It is found that osmotic B is much more strongly dependent on the molecular size than in vacuum: Specifically, it is proportional to the sixth or higher power of the solute diameter when the solutes are taken to be Lennard-Jones particles with the energy parameter chosen to be that of methane. It is also shown that a similar power law is observed for solutes in a non-polar solvent. Robustness of the power-law dependence of B is discussed from theoretical points of view.

REFERENCES

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