A SEMI-EMPIRICAL MOLECULAR APPROACH TO THE THERMODYNAMIC MODELING OF AQUEOUS SOLUTIONS OF NON-POLAR GASES AT INFINITE DILUTION

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The properties of non-polar substances in aqueous solutions – such as the Henry's law constant (k_H) and hydration parameters ($\Delta_{hyd}H^\infty$, $\Delta_{hyd}V^\infty$, $\Delta_{hyd}C_p^\infty$) – play a key role in thermodynamic calculations of natural and industrial processes involving sparingly soluble gases. Their accurate description is essential for predicting solubility over a wide range of temperatures and pressures, including the supercritical region.

Semi-empirical equations of state for infinitely dilute solutions are commonly used to describe standard properties of dissolved gases. In recent decades, equations of state based on empirical correlations (e.g., SOCW, POCW) have been extensively developed. However, these approaches require complex parameterization and often lack a clear physical foundation. Therefore, the development of molecular models based on physically justified approximations of intermolecular interactions in solution, and capable of ensuring correct limiting behavior, remains an important task.

In a recent study [1], an equation of state was proposed based on the approximation that the interaction energy between water and the dissolved gas can be represented by a square-well potential. This approach makes it possible to describe the Gibbs energy of hydration ($\Delta_{hyd}G^\infty$) explicitly within a unified formalism, without the need to integrate the dependencies of $\Delta_{hyd}V^\infty$ and $\Delta_{hyd}C_p^\infty$, as is done in traditional models.

The model requires only four fitting parameters, which makes the model simpler than its existing counterparts. Despite its simplicity and the small number of adjustable parameters, the model demonstrated high accuracy both in correlating experimental data and in extrapolation [1].

In the present work, a further development of this model is proposed, including an updated expression for the coordination number based on theoretical results reported by Hu et al. [2].

The model was tested on a series of noble gases, light hydrocarbons, and a number of weakly polar gases. The modeling results demonstrate that the model is suitable for describing the Henry's law constant (k_H) and several properties of gases at infinite dilution within experimental error.

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2. Hu J., Duan Z., et al. A general local composition and coordination number model for square-well fluids with variable well width and diameter ratio // Molecular Physics. 2007. Vol. 105. Nr 8. P. 1019–1037. https://doi.org/10.1080/00268970701262900

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