

Theory-based constraints on variations of infinite dilution partial molar volumes of aqueous solutes at various temperatures and water densities

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ABSTRACT

Known theoretical relations provide constraints on variations of the partial molar volume of an infinitely diluted solute at: (1) low solvent densities (as follows from the truncated virial EoS), (2) at the critical point of the solvent (as follows from the near-critical theory of dilute mixtures); and (3) at conditions where repulsive interactions dominate, i.e. at $\rho_{c1} > 1.5$ close to and above the Boyle temperature of a solvent, and $\rho_{c1} > 3$ close to the melting temperature of a solvent (as follows from the theory of mixtures of hard spheres). These constraints are discussed for the case of aqueous solutions at various temperatures and water densities. The constraints provide rigorous checks of the quality of models proposed to correlate or predict V_2^∞ values, and, if applied properly, can significantly improve the reliability of predictions of both V_2^∞ and the fugacity coefficients ϕ_2^∞ .

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1. Introduction

The infinite dilution partial molar volume of a solute, V_2^∞ , if known on an isotherm as a function of the density of a solvent, can be employed to calculate the infinite dilution fugacity coefficient of the solute, ϕ_2^∞ , the most important for the technological and scientific applications thermodynamic property of a solute. Here and below the subscript 2 refers to a solute, 1—to a solvent, the superscript ∞ denotes the property at infinite dilution, and *—the property of a pure compound. The calculation of ϕ_2^∞ can be done [1] with the relation:

$$RT \ln \phi_2^\infty = \int_0^P \left(V_2^\infty - \frac{RT}{P} \right) dP, \quad (1)$$

which however, becomes inconvenient at the near-critical conditions where V_2^∞ diverges (goes to infinite values). O'Connell, with coauthors [2,3], proposed the following expression for calculating ϕ_2^∞ :

$$\ln \phi_2^\infty = \int_0^{\rho_1^*} (A_{12}^\infty - 1) \frac{d\rho_1^*}{\rho_1^*} - \ln \frac{PV_1^*}{RT}, \quad (2)$$

where

$$A_{12}^\infty = \frac{V_2^\infty}{\kappa_T RT}, \quad (3)$$

and $\kappa_T = 1/V_1^*(\partial V_1^*/\partial P)_T$ is the coefficient of the isothermal compressibility of the solvent. The A_{12}^∞ property is a smooth and continuous function everywhere, even at the critical point of a solvent, and thus more convenient for use, especially at low and near-critical densities. It can be shown that Eq. (2) follows from another “textbook” relation to calculate ϕ_2^∞ [1]:

$$RT \ln \phi_2^\infty = \int_V^\infty \left[\lim_{n_i \rightarrow 0} \left(\frac{\partial P}{\partial n_i} \right)_{T,V,n_j \neq i} - \frac{RT}{V_1^*} \right] dV - RT \ln \frac{PV_1^*}{RT}. \quad (4)$$

In many cases V_2^∞ values are measured only in limited $T - P - \rho$ ranges, and need to be predicted. In the literature, there are a number of theoretical relations for values of V_2^∞ , which constrain the variations of V_2^∞ at different temperatures and solvent densities. When properly applied, these constraints significantly improve the reliability of prediction of V_2^∞ and, therefore, of ϕ_2^∞ as well. The goal of the present work is to discuss the theoretical constraints for V_2^∞ values and their applications to aqueous solutions.

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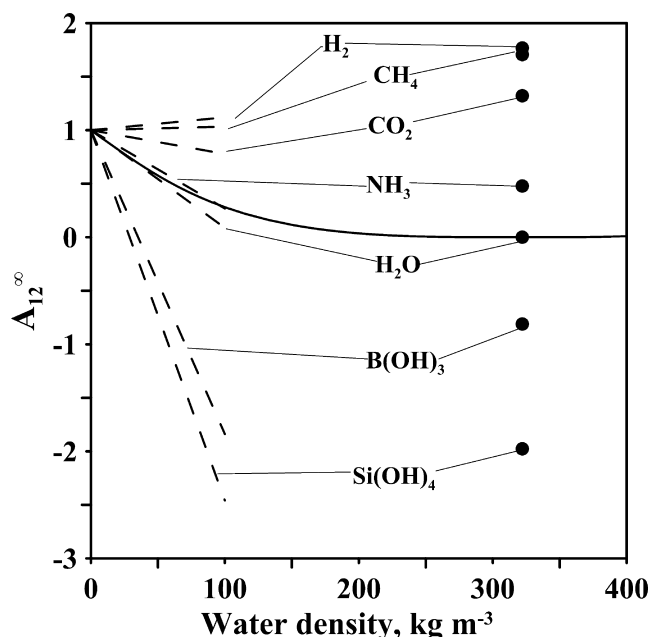


Fig. 1. Values of A_{12}^{∞} at the critical isotherm 647.096 K for a number of aqueous nonelectrolytes, see text.

2. Constraints on the variations of V_2^{∞}

2.1. Constraints in the low-density region of water

At low densities, the virial equation of state is well suited to describe the thermodynamic properties of mixtures. The virial equation of state, which has a strict basis in statistical mechanics, is often represented by the following relation [1]:

$$\frac{PV}{RT} = 1 + \frac{B}{V} + \frac{C}{V^2} + \dots, \quad (5)$$

where B and C are the temperature dependent second and third virial coefficients, accounting for the binary and ternary interparticle interactions. When applied to the A_{12}^{∞} parameter, the following virial relation is held [3]:

$$A_{12}^{\infty} = \frac{V_2^{\infty}}{\kappa_T RT} = 1 + 2\rho_1^* \cdot B_{12} + 3(\rho_1^*)^2 \cdot C_{112} + \dots, \quad (6)$$

where B_{12} is the cross virial coefficient for the binary water–solute interactions, and C_{112} is the cross virial coefficient for the ternary water–water–solute interactions. While values of C_{112} are practically absent, B_{12} for many water–solute interactions are well known from the experimental measurements (see review [4]), high-quality *ab initio* calculations of the last decade [5–7] and others), or can be reliably estimated based on the corresponding-state correlations developed specifically for aqueous mixtures [8–10]. With the known values of B_{12} the density range of applicability of Eq. (6) is expected to be within 1/4–1/3 of the critical density of a mixture [1], i.e. for water up to 80–110 kg m⁻³. It could be that the range of applicability is smaller for bulky solutes [11], and for solutes with very large negative values of B_{12} , see Fig. 1.

2.2. Constraints in the critical point of water

Theory-based estimates of A_{12}^{∞} are possible at low (the virial EoS) and high solvent densities (a theory of a mixture of hard spheres), whereas sound estimations of A_{12}^{∞} at intermediate densities are more difficult. A very useful constraint follows from the theory of diluted near-critical solutions. Thermodynamics of diluted mixtures around the critical point of a solvent is governed by the

Krichevskii parameter A_{Kr} [12,13], defined as $A_{Kr} = \left(\frac{\partial P}{\partial x_2} \right)_{V,T,x_2=0}^c$, where the superscript c means that the evaluation is conducted at a critical point. What is important for this work is the relation between A_{Kr} and the A_{12}^{∞} parameter in the critical point of a solvent:

$$A_{12}^{\infty}(T_{c1}, \rho_{c1}) = A_{Kr} \frac{V_{c1}^*}{RT_{c1}}. \quad (7)$$

The values of the Krichevskii parameter can be evaluated from various types of experimental data and are known for more than 50 aqueous solutes [14] with uncertainties of 10–20 MPa or less. It means that for many aqueous solutes, the values of A_{12}^{∞} at 647.096 K and 322 kg m⁻³ (the critical properties of water [15]) are known with the accuracy of 0.10–0.20 or even better (note that A_{12}^{∞} is a dimensionless property). For experimentally non-studied neutral solutes, the values of the Krichevskii parameter can often be predicted, provided that the thermodynamic functions of hydration (the Gibbs energy, enthalpy, and the heat capacity) for those solutes are known at the reference temperature of 298.15 K [16].

The constraint given by Eq. (7) is particularly useful because the overwhelming majority of methods of predicting thermodynamic properties are based on the so-called “classical” mean-field models and, therefore, will inevitably fail at the critical point.

The challenges of predicting the density dependence of A_{12}^{∞} at low and moderate densities are illustrated in Fig. 1 for the critical isotherm. The dashed lines show the initial density slopes of A_{12}^{∞} evaluated from the known B_{12} data (H_2 [5], CH_4 [6], CO_2 [7], NH_3 [17], H_2O [18], $B(OH)_3$ and $Si(OH)_4$ [19]), and the black circles show A_{12}^{∞} at the critical density (322 kg m⁻³) calculated with Eq. (7) from recommended [14] values of the Krichevskii parameter. For each solute, the line starts with the value of 1 at a zero density, changes initially as indicated by a dashed line, and comes at the critical density to the value indicated by a black circle. Water (a solid line) may serve as a model for other dissolved species. Generally, initial slopes and the values at the critical point provide useful constraints for density variations of A_{12}^{∞} at $\rho_1^* \leq \rho_{c1}$. Another point to note is that for H_2O , $B(OH)_3$, and $Si(OH)_4$, purely geometric considerations suggest that the density range of the applicability of Eq. (6) may be less than 1/4 of the critical density.

2.3. Constraints suggested by the relations from the hard-sphere EoS

Lee [20] derived from the Mansoori–Carnahan–Starling–Leland [21] equation of state an expression for the partial molar volume of the solute in infinitely dilute hard-sphere binary mixtures. For the case of a constant average packing density of a pure solvent (which is a fraction of volume occupied by the molecules of the solvent), the following relation is given:

$$\frac{V_2^{\infty}}{V_1^*} = N, \quad (8)$$

where N is a constant that has neither temperature nor density dependence.

Eq. (8) is expected to be valid at conditions where repulsive forces dominate. First of all, this is a region of high solvent densities, where interparticle distances are small. While water is a hydrogen-bonded liquid, one still may expect [22] the suppression of the orientation-dependent forces at high densities. Second, at high temperatures due to a growth of the kinetic energy of particles, the relative contribution of the attractive forces decreases. As a result, the second virial coefficients eventually become positive (manifesting the dominance of the repulsive force) above the Boyle temperature, which, for water, equal to approximately 1540 K [18].

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