On the Apparent Molar Volumes of Nonelectrolytes in Water

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Apparent molar volumes of aqueous solutions of argon and xenon have been calculated using a previously developed comprehensive equation of state for nonelectrolyte systems. The equation consists of a virial expansion truncated after the fourth virial coefficient and a closed-form term approximating higher coefficients. Mixing rules are based on the composition dependence of virial coefficients, which is known from statistical mechanics. The equation accurately represents vapor-liquid and gas-gas equilibria for the Ar + H2O and Xe + H2O systems over wide ranges of pressure and temperature using two binary parameters. With the binary parameters determined from phase equilibrium data, the equation accurately predicts apparent molar volumes $V_a$ in the near-critical and far-from-critical regions. Apart from reproducing experimental $V_a$ data, the equation reveals remarkable maxima of $V_a$ as a function of pressure and temperature in the near-critical region. The implications of this equation with respect to the Ar-H2O potential are discussed via the second virial coefficient.

KEY WORDS: Apparent molar volumes; vapor-liquid equilibria; aqueous nonelectrolytes; equations of state; near-critical region.

1. Introduction

Much interest is focused on the volumetric properties of dilute solutions in the near-critical region because of their importance in many geologic phenomena and industrial processes, especially those related to supercritical fluid technology. Experimental data are available for several systems including aqueous solutions of nonpolar gases and solutions of organic molecules in solvents used for supercritical fluid
The partial (or apparent) molar volumes of the solute show very sharp maxima\(^{1}\) or minima\(^{2}\) at pressures above but near the critical pressure of the water or other solvent. According to Wheeler's\(^{3}\) lattice-gas theory, the partial molar volumes of solutes in near-critical dilute solutions are proportional to the isothermal compressibility \(\kappa_T\) of pure water. This relation was used by Biggerstaff and Wood\(^{4}\) to correlate their apparent molar volume data with the product \(p\kappa_T\). Although this relationship makes it possible to estimate roughly the location of the extremum, the sign and magnitude of apparent (or partial) molar volumes strongly depend on solute-solvent interactions.

Empirical and semi-theoretical equations of state are frequently used to represent the properties of aqueous nonelectrolyte solutions. Most equations available in the literature (for a review, see Malanowski and Anderko\(^{5}\)) have been developed primarily for the calculation of vapor-liquid equilibria. Partial molar properties have been predicted by Levelt-Sengers and Gallagher\(^{6}\) using a generalized corresponding-states approach. However, this approach is not accurate for phase equilibrium computations and does not reproduce the correct composition dependence of virial coefficients.\(^{6,7}\) Volumetric properties of aqueous nonelectrolyte mixtures were also modelled by Christoforakos and Franck.\(^{8}\) However, their method has not been applied to apparent molar properties of dilute solutions.

Recently, Anderko and Pitzer\(^{6,7}\) developed an accurate equation of state for the representation of phase equilibria and volumetric properties of pure fluids and mixtures. In particular, the equation proved very useful for the representation of mixtures containing water and nonpolar components over wide ranges of pressure and temperature.

In this study, we examine the applicability of the Anderko-Pitzer EOS to the prediction of apparent molar volumes of inert gases in water. In particular, we will attempt to answer the following questions: (1) Can the apparent molar volumes be adequately predicted in the dilute near-critical region using a mean-field equation of state designed to represent phase equilibria in concentrated systems? And (2) What is the sensitivity of the apparent molar volumes to pressure and temperature in the extended near-critical and far-from-critical regions?

In addition, we discuss the implications of the equation concerning the Ar-H\(_2\)O intermolecular potential. In particular, we calculate the second virial coefficient, which is contained in the general equation and compare the depth of the potential well implied therefrom with that predicted by quantum mechanical calculations or derived from spectroscopic measurements.