Analysis of $\bar{v}_i/\kappa_{Tx}$ in Solvent Mixtures at the Critical Line

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The microscopic density fluctuations in fluids near their critical point can complicate experimental approaches for measuring thermodynamic and transport properties in fluid mixtures in their near-critical regions (Bruno, 1991). For this reason, various experimental techniques have been used to circumvent the direct measurement of these properties in the critical region. A convenient method involves the use of supercritical fluid chromatography (SFC) to measure solute partial molar volumes close to the critical point in a dilute binary mixture (van Wasan et al., 1980; Erkey and Akgerman, 1990; Shim and Johnston, 1991; Srinivasan and McCoy, 1991; Chimowitz and Kelley, 1989; Recasens et al., 1993; Spicka et al., 1994; Afrane and Chimowitz, 1995; Chimowitz and Afrane, 1996). Determination of the required properties from these chromatographic data often depends upon an analysis that appeals to the asymptotic values of specific thermodynamic properties near the critical point. The most important of these properties are the limiting values of the terms $\bar{v}_i/\kappa_{Tx}$, where $\bar{v}_i$ is the partial molar volume of species i and κ_{Tx} the isothermal compressibility of the mixture.

In dilute binary supercritical systems Kumar and Johnston (1988) used a classical analysis of this term for the solute species to analyze the behavior of solubility data with density in supercritical solvents. They showed that the linearity in the data of log solubility vs. log density could be represented in terms of the term $\bar{v}_i/\kappa_{Tx}$ at the limit of the solvent critical point. In a review of the properties of dilute, near-critical solutions, Levelt-Sengers (1991) provided a discussion of this property for solvent and solute species in *binary systems* at the limit of infinite dilution using both classical and nonclassical perspectives. In single solvent systems these properties are finite, both classically and nonclassically, because of the solvent's strongly divergent compressibility at its critical point. The same is not true, however, in higher-order solvent systems, and our purpose here is to discuss the extension of the binary case leading to an equation that we believe should be of practical use in analyzing adsorption data taken in near-critical, multicomponent solvent systems with the solute at extreme dilution. Both classical and nonclassical perspectives are analyzed with the solute's infinite dilution limit used as a reference condition. The experimental data used to focus our discussion are the measurements of solute adsorption coefficients in near-critical solvents from which a variety of important thermodynamic properties can be estimated.

Adsorption-Density Equation

The general expression for the variation of adsorption coefficients with density in a multicomponent mixture at constant temperature was provided by Afrane and Chimowitz (1995) in the following form

$$\left(\frac{\partial \ln k_i}{\partial \ln \rho^m}\right)_{T,x_i,\phi} = \frac{A^i}{\theta_i \kappa_{Tx}}(\bar{v}_i^m - \bar{v}_i^s) + \sum_{j \neq i}^{c} \frac{A^j}{\theta_i \kappa_{Tx}}(\bar{v}_i^m - \bar{v}_i^s) - 1 \tag{1}$$

for component i. In this equation k_i is the adsorption coefficient of species i, ρ^m is the density of the mixture, the A^is are stability matrices defined in the original reference, θ_i is the fractional coverage of species i on the stationary phase, $\bar{v}_i^m$ and $\bar{v}_i^s$ are the partial molar volumes of the species in the mobile and stationary phases respectively, and κ_{Tx} is the isothermal compressibility of the mixture. Note the prevalence of terms of the form $\bar{v}_i/\kappa_{Tx}$ in Eq. 1. In the single solvent case, several studies have used an equation similar to Eq. 1 to measure solute partial molar volume data using chromatographic measurements of capacity factors, quantities related to the adsorption coefficient (van Wasan et al., 1980; Erkey and Akgerman, 1990; Shim and Johnston, 1991; Chimowitz and Kelley, 1989; Recasens et al., 1993; Spicka et al., 1994). Key results in reducing Eq. 1 for this case are the finite value of the solute's property $\bar{v}_i^m/\kappa_{Tx}$ at the solvent's critical point and the fact that the system's isothermal compressibility diverges at this limit. This latter property leads to the elimination of the stationary phase terms in Eq. 1 and the

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respective *solvent* terms for the fluid phase. In addition, the variation of the term $\bar{v}_i^m/\kappa_{Tx}$ over limited density ranges is taken to be small, as appears to be borne out by both data and model calculations (see, for example, the analysis by Kumar and Johnston, 1988). Thus, in principle, Eq. 1 provides a basis from which solute partial molar volume data can be found from the slope of isothermal data of $\ln k_i - \ln(\rho^m)$ over small density ranges in the critical region.

Multicomponent Supercritical Solvent Case

The multicomponent solvent case, however, is complicated by the fact that the isothermal compressibility remains finite or shows a weak divergence, respectively, at the critical line depending on whether the system is viewed from a classical or nonclassical perspective. We pursue this issue adopting a three-component system as our yardstick, although the thrust of the arguments used naturally extend to a system with an arbitrary number of solvent species. For a three-component system (where component 3 is the solute), Eq. 1 becomes

$$\left(\frac{\partial \ln k_3}{\partial \ln \rho^m}\right)_{T,x_i} = \frac{A^3}{\theta_3 \kappa_{Tx}}(\bar{v}_3^m - \bar{v}_3^s) + \frac{A^2}{\theta_3 \kappa_{Tx}}(\bar{v}_2^m - \bar{v}_2^s) + \frac{A^1}{\theta_3 \kappa_{Tx}}(\bar{v}_1^m - \bar{v}_1^s) - 1 \quad (2)$$

From thermodynamic stability theory, the A^i terms that apply to the stationary phase can be shown to be positive and finite (Afrane and Chimowitz, 1995). Central to the task of reducing Eq. 2 further depends on the limiting critical values of the ratios $\bar{v}_i/\kappa_{Tx}$ for both solute and solvent species in both phases. In analyzing these terms, we make use of the following thermodynamic identity for the partial molar volume of component i in a multicomponent mixture (Modell and Reid, 1983)

$$\bar{v}_i = v - \sum_{j \neq i}^{n} x_j \left(\frac{\partial v}{\partial x_j}\right)_{T,P,x_{\kappa \neq i,j}} \quad (3)$$

where n is the number of components of the mixture. We now consider the case where the solvent system does not display a critical azeotrope at the point of interest along the critical line since the nonazeotropic situation will represent the vast majority of cases. [For a discussion of these properties at a critical azeotrope, we refer readers to Munoz and Chimowitz (1993a,b) where this situation was dealt with in some detail.]

Solvent Terms in the Mobile Phase

The partial molar property for the solvent in the three-component system given by Eq. 3, divided by the isothermal compressibility κ_{Tx}, is given by

$$\frac{\bar{v}_1}{\kappa_{Tx}} = \frac{v}{\kappa_{Tx}} - x_3 \frac{\left(\frac{\partial v}{\partial x_3}\right)_{T,P,x_2}}{\kappa_{Tx}} - x_2 \frac{\left(\frac{\partial v}{\partial x_2}\right)_{T,P,x_3}}{\kappa_{Tx}} \quad (4)$$

where component 1 and 2 are solvents, and 3 a solute. We make use of the solute's infinite dilution limit and the following identity (Munoz and Chimowitz, 1993a)

$$\frac{\left(\frac{\partial v}{\partial x_3}\right)^{\infty}_{T,P,x_2}}{\kappa_{Tx}} = v \left(\frac{\partial P}{\partial x_3}\right)^{\infty}_{T,v,x_2} \quad (5)$$

to analyze the terms in Eq. 4. In the limit $x_3 \to 0$, classically both κ_{Tx} and $(\partial P/\partial x_3)^{\infty}_{T,v,x_2}$ are finite. Nonclassically, however, κ_{Tx} shows a weak divergence (Levelt-Sengers, 1991), while the term $(\partial P/\partial x_3)^{\infty}_{T,v,x_2}$ is finite. We base this latter result either on the Griffiths-Wheeler (1970) theory of nonclassical behavior or thermodynamic arguments similar to those used by Chang et al. (1984) in the single solvent case. These considerations imply that at the limit of the critical point, the term

$$\lim_{x_3 \to 0} x_3 \frac{\left(\frac{\partial v}{\partial x_3}\right)^{\infty}_{T,P,x_2}}{\kappa_{Tx}} = 0$$

both classically and nonclassically. The first and third terms in Eq. 4 are finite classically, but zero nonclassically as a consequence of the finiteness and weak divergence of κ_{Tx} in these respective cases.

The net result of this analysis is that $\bar{v}_1/\kappa_{Tx}$, $\bar{v}_2/\kappa_{Tx}$ in the mobile phase (for the two solvent components) are finite classically, but zero nonclassically at the critical point. The stationary phase terms in Eq. 2 remain finite classically (since the compressibility is finite) but approach zero in the nonclassical case. The only remaining term to consider in Eq. 2 is the solute term.

Solute Term in the Mobile Phase

The $\bar{v}_i/\kappa_{Tx}$ ratio for the solute, component 3, is given by

$$\frac{\bar{v}_3}{\kappa_{Tx}} = \frac{v}{\kappa_{Tx}} - x_1 \frac{\left(\frac{\partial v}{\partial x_1}\right)_{T,P,x_2}}{\kappa_{Tx}} - x_2 \frac{\left(\frac{\partial v}{\partial x_2}\right)_{T,P,x_1}}{\kappa_{Tx}} \quad (6)$$

In the limit as $x_3 \to 0$, v/κ_{Tx} is finite classically and zero nonclassically. However, the terms

$$\lim_{x_3 \to 0} x_2 \frac{\left(\frac{\partial v}{\partial x_2}\right)^{\infty}_{T,P,x_1}}{\kappa_{Tx}}$$

and

$$\lim_{x_3 \to 0} x_1 \frac{\left(\frac{\partial v}{\partial x_1}\right)^{\infty}_{T,P,x_2}}{\kappa_{Tx}}$$

are both finite classically and nonclassically since

$$\lim_{x_3 \to 0} \frac{\left(\frac{\partial v}{\partial x_2}\right)_{T,P,x_1}}{\kappa_{Tx}} = - \frac{\left(\frac{\partial v}{\partial x_3}\right)^{\infty}_{T,P,x_1}}{\kappa_{Tx}} \tag{7}$$

and

$$\lim_{x_3 \to 0} \frac{\left(\frac{\partial v}{\partial x_1}\right)_{T,P,x_2}}{\kappa_{Tx}} = - \frac{\left(\frac{\partial v}{\partial x_3}\right)^{\infty}_{T,P,x_2}}{\kappa_{Tx}} \tag{8}$$

are both finite from Eq. 5. Therefore in the limit of $x_3 \to 0$ the term $\bar{v}_3/\kappa_{Tx}$ in Eq. 6 is finite in both the classical and nonclassical cases, albeit this finiteness arising for different reasons as discussed above. The net result is that only by invoking nonclassical results do we arrive at a useful (from an experimental standpoint) approximation to Eq. 2. This approximation is given as

$$\left(\frac{\partial \ln k_3}{\partial \ln \rho^m}\right)_{T,x_i} \approx \frac{A^3}{\theta_3 \kappa_{Tx}} \bar{v}_3^m - 1 \tag{9}$$

If a partition function is used for the adsorbed stationary phase, the term A^3 can then be explicitly obtained. Using the Langmuir partition function for adsorption by way of an example, the working equation for the three-component case discussed here (but more generally for any number of solvent components) is obtained as

$$\left(\frac{\partial \ln k_3}{\partial \ln \rho^m}\right)^{\infty}_{T,x_i} = \frac{\bar{v}_3^m}{RT\kappa_{Tx}} - 1 \tag{10}$$

This equation is remarkably similar to the single solvent case (Chimowitz and Kelley, 1989), although it requires closer arguments to develop and the necessity of invoking nonclassical results. Since the nonclassical divergence of the compressibility for mixtures is weak, unlike the single solvent case, this suggests that data analysis using Eq. 10 may require experiments to be done in closer proximity to the critical point (region) than the pure solvent case. Thermodynamics does not provide an answer as to how far this equation can be extrapolated—this of necessity requires details of the intermolecular interactions to be considered (that is, model calculations). Nevertheless, given the value of this scaling approach with solubility data in single solvent supercritical systems we believe that use of Eq. 10 may prove to be useful in analyzing supercritical adsorption data in binary (and higher-order) solvent systems.

A comparison of data taken using this approach with independently acquired data using, for example, the densitometer approach described by Eckert et al. (1986) would provide better insight into this point. However, in binary and higher-order supercritical solvent systems we are not aware of such data currently available in the literature. With this in mind, we recently did adsorption experiments using the ethane-carbon dioxide solvent system in its near-critical region and used Eq. 10 to analyze the data. A representative set of results is shown in Figure 1 for benzene, toluene, and *o*-xylene in a nonazeotropic mixture of ethane (70%) and carbon dioxide at 308 K. The abscissa of the plot of Figure 1 is the molar volume-assuming constancy of the solute term $\bar{v}_3/\kappa_{Tx}$ the linearity predicted by Eq. 10 is quite evident.

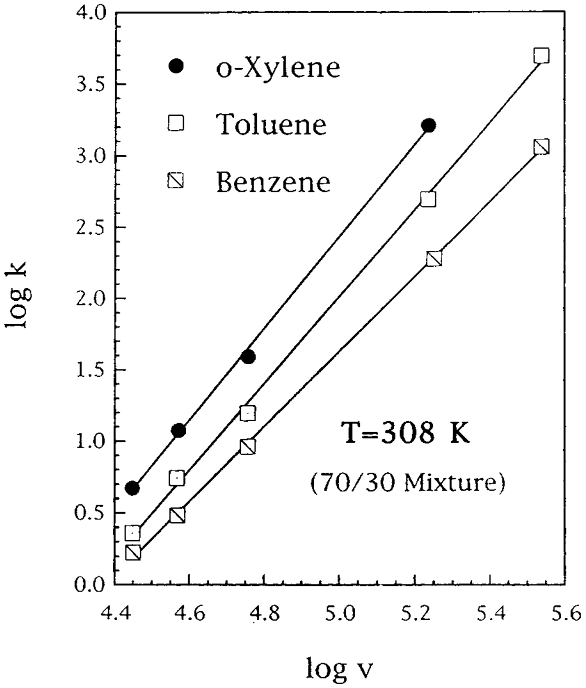

Figure 1. Test of Eq. 10 with capacity factor data for three solutes in ethane (70%) carbon dioxide mixtures at 308 K.

Critical constants: $T_c = 295.3$ K, $P_c = 53$ bar, $V_c = 0.00143$ m³/mol.

Given data for the isothermal compressibility in this system, it would be useful to compare partial molar volume data using this approach (with slopes obtained from a plot similar to that shown in Figure 1) with densitometer measurements if these measurements become available.

Acknowledgment

The authors would like to acknowledge the National Science Foundation for partial financial support for this work through grant no. CBT-9213276.

Notation

P = gas-phase pressure, bars
R = gas constant
T = temperature, K
v = molar volume of mobile phase
x_i = mole fraction of component i in the mixture
∞ = infinite dilution

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Manuscript received Sept. 28, 1995, and revision received June 3, 1996.