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THEORETICAL MODELS OF THERMODYNAMIC PROPERTIES OF SUPERCRITICAL SOLUTIONS

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ABSTRACT

Several separation processes, including supercritical extraction and supercritical fluid chromatography, take advantage of the striking solubility behavior of supercritical fluids. A general theoretical framework is presented for modeling thermodynamic properties of supercritical solutions based on the theory of Kirkwood and Buff. The theory is expressed in terms of the Kirkwood fluctuation integral from statistical mechanics and permits introduction of appropriate molecular solution approximations. Thus, the solute-solvent interaction may be expressed using a local composition approximation, for example, with an accurate equation of state for the pure solvent. This approach is illustrated for two molecular solution approximations and is compared with solubility and partial molecular volume data.

INTRODUCTION

In recent years there has been considerable research interest in the use of supercritical fluids as separations media (1), reaction media (2), etc. The striking solubility behavior of supercritical fluids is illustrated in Fig. 1. The solubility of naphthalene is seen to rise by two orders of magnitude as the reduced pressure, P/P_c, of carbon dioxide is increased from 0.8

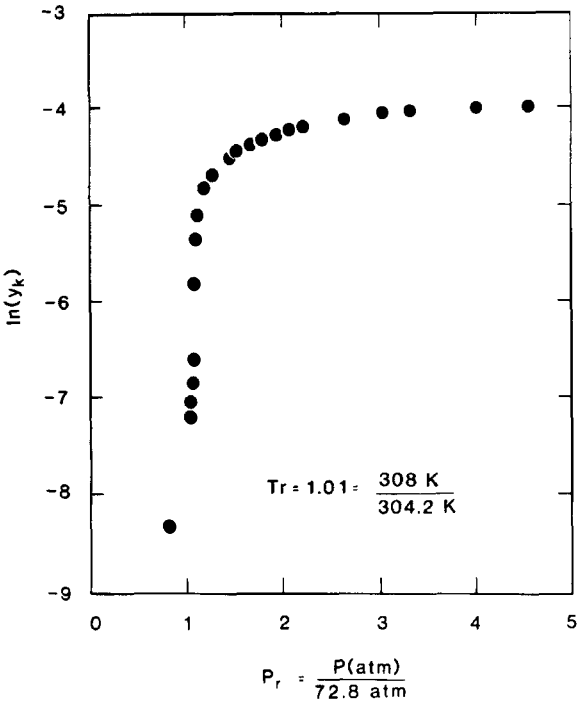

Fig. 1. Natural logarithm of the mole fraction of naphthalene in carbon dioxide vs. reduced pressure at reduced temperature equal to 1.01. Data of Tsekhanskaya, et al. (27)

to 4.5 at a reduced temperature, T/T_c, of 1.01. The strong non-ideality of the solvent enhances its solvent power by four orders of magnitude compared with the solubility that would be expected in an ideal gas mixture. Furthermore, the solvent power may be controlled over this wide range of variation by small changes in solvent pressure or temperature.

There have been a number of approaches proposed to modeling thermodynamic properties of supercritical solutions including the use of empirical equations of state (3) and empirical activity coefficient models (4). Theoretical modeling of thermodynamic properties of supercritical solutions has included computer simulations (5), perturbation theories (6), integral equation theories (7), and various thermodynamic (8) or statistical mechanical (9)

formalisms. To be of practical use, either thermodynamic or statistical mechanical formalisms must be coupled with approximations which permit the introduction of component parameters. In some cases, these approximations may be based upon molecular theory.

Empirical methods do not offer any hope of predictive capability and should be considered as useful interpolation methods. Simulations, perturbation theories, and integral equation theories require excessive computational effort in their use for practical calculations. However, these methods may be considered theoretically sound and may be used to develop or test more approximate methods.

Recently, we have shown (10-13) that the Kirkwood-Buff theory of solutions, based on fluctuation theory, provides a rigorous statistical mechanical formalism within which useful models of supercritical solutions may be developed. O'Connell and coworkers have explored related modeling possibilities based on fluctuation theory for isothermal compressibility and solute partial molar volume in dilute liquid solutions (14) and for PVT and phase behavior (15) of supercritical gases dissolved in liquids. Debenedetti (16, 17) has also explored the application of fluctuation theory to supercritical solutions and has developed a number of theoretical derivations within this formalism.

In this paper we shall present some general theoretical expressions, developed within the Kirkwood-Buff formalism, for describing thermodynamic properties of supercritical solutions and shall consider these expressions from a phenomenological point of view in an effort to gain some physical insights. Then we shall show how molecular solution approximations may be incorporated into the Kirkwood-Buff formalism to yield models that may be useful for practical applications. And, finally, we shall illustrate a few such applications with examples.

KIRKWOOD-BUFF THEORY FOR SUPERCRITICAL SOLUTIONS

A complete and general theory of solutions was developed from statistical mechanics by Kirkwood and Buff (18) based on the fluctuation theory of Kirkwood and expressed in terms of the Kirkwood fluctuation integral, $G_{\alpha\beta}$:

$$G_{\alpha\beta} = \int_0^\infty \left[g_{\alpha\beta}(r) - 1\right] \cdot 4\pi r^2 \cdot dr \quad , \tag{1}$$

where $g_{\alpha\beta}(r)$ is the spatial (averaged over all orientations) pair correlation function for interaction between species α and β and r is the spatial separation between α and β. When multiplied by the number density of a fluid, $G_{\alpha\beta}$ represents the excess of α molecules surrounding a β molecule and has been called the affin-

ity of α for β. Statistical mechanical definitions (12, 19, and 20) of local composition have been expressed in terms of the fluctuation integral. At high temperature the fluctuation integral is approximated by the spatial integral of the potential of mean force.

It has been shown (10, 12) that the isothermal variation of number density of a solute k, ρ_k, with pressure, P, in a solvent j at equilibrium with a second phase of constant composition (e.g., a solid) is given by

$$\left(\frac{kT}{\rho_k}\right)\cdot d\rho_k = \left(G_{jk} + \bar{v}_k\right)\cdot dP + \sum_{i\neq j}\left\{\rho_i\,\bar{v}_i\left(G_{ik} - G_{jk}\right)\cdot dP\right\} , \quad (2)$$

where kT is Boltzmann's constant times temperature and $\bar{v}$ is the partial molecular volume. The first term on the righthand side of (2) contains only the solvent-solute affinity and the solute partial molecular volume. The second term contains the difference between solute-solute and solvent-solute affinity and becomes important only at higher solute concentrations except, perhaps, in the vicinity of a critical point where the fluctuation integrals diverge. Note also that the enhancement of solubility by dilute second solutes, added co-solvents, or entrainers in supercritical solvents arises when the second term on the right hand side in (2) is large.

Equation (2) may be expanded about the infinite dilution limit to yield a simple expression applicable to dilute solutions:

$$\left(\frac{kT}{\rho_k}\right)\cdot d\rho_k = \left(G^{o}_{jk} + \bar{v}_k\right)\cdot dP , \quad (3)$$

where here and after the superscript zero indicates the value of the variable at the limit of infinite solute dilution.

The divergence of the slope of the solubility vs. pressure curve in the vicinity of a critical point (as seen, for example, in Fig. 1) was illuminated within a purely formal thermodynamic expression by Gitterman and Procaccia (8). Equation (3) may be rearranged to illustrate the same phenomenon within the framework of the Kirkwood-Buff formalism:

$$\left(\partial \ln y_k/\partial P\right)_{T,eq} = \frac{1}{kT}\left(G^{o}_{jk} + \bar{v}_k\right) - \left(1 + \rho^{o}_{j}G^{o}_{jj}\right)/\rho^{o}_{j}kT , \quad (4)$$

where y_k is the solute mole fraction and use has been made of the compressibility equation. It is known (21) that the fluctuation integral diverges at a critical point. Let us replace the par-

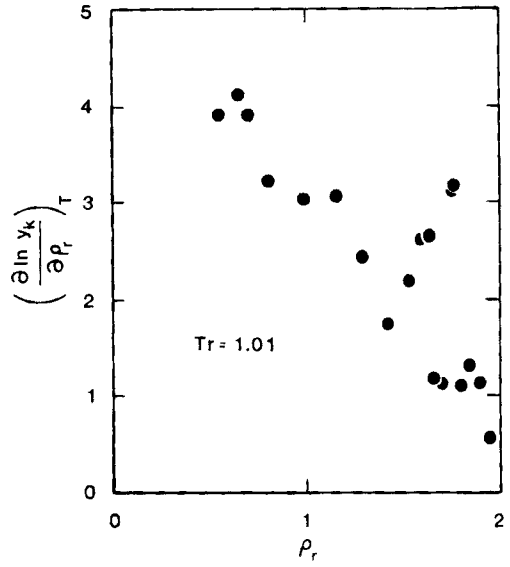

Fig. 2. Slope of solubility curve vs. reduced density for naphthalene in carbon dioxide at reduced temperature equal to 1.01. Data of Tsekhanskaya, et al. (27)

tial derivative with respect to pressure in (4) by a partial derivative with respect to density using the compressibility equation. Then, in the Kirkwood-Buff notation

$$\left(\partial \ln y_k / \partial \rho_j\right)_{T,eq} = \left(G^o_{jk} + \bar{v}_k\right) / \left(1 + \rho^o_j G^o_{jj}\right) - 1/\rho^o_j \quad . \tag{5}$$

One might expect the ratio of fluctuation integrals in (5) to be well-behaved at a critical point. Indeed, the curve of slope vs. density (see Fig. 2) shows approximately a linear decrease in slope for the same data shown in Fig. 1.

Debenedetti and Kumar (17) have expressed the variation of solute fugacity coefficient, ϕ_k, for dilute, binary supercritical solutions with solute concentration in the following form:

$$\ln\left(\phi_k/\phi^o_k\right) = K \cdot y_k \quad , \tag{6}$$

where ϕ^o_k is the infinite dilution fugacity coefficient and K is

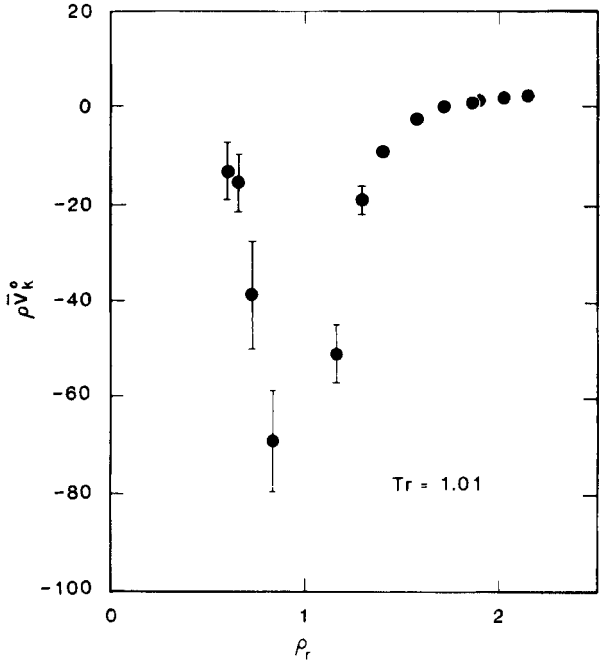

Fig. 3. Dimensionless partial molar volume of naphthalene in carbon dioxide vs. reduced density at reduced temperature equal to 1.01. Data of Eckert et al. (22)

a constant. Application of the Kirkwood-Buff theory of solutions (11) leads to identification of the Debenedetti-Kumar constant as follows:

$$K = \rho\left[\left(G_{kk}^{o} - G_{jk}^{o}\right) + \left(G_{jj}^{o} - G_{jk}^{o}\right)\right] . \qquad (7)$$

Debenedetti (16) has used the Kirkwood-Buff (18) expression for the solute partial molar volume in dilute, binary, supercritical solutions as follows:

$$\bar{v}_k = \left[1 + \rho_j^{o}\left(G_{jj}^{o} - G_{jk}^{o}\right)\right]/\rho_j^{o} , \qquad (8)$$

and has inferred the magnitude of the fluctuation integral from the partial molar volume data of Eckert and coworkers (22) as shown in Fig. 3 for the same carbon dioxide/naphthalene system shown previously in Figs. 1 and 2.

Table 1. Expressions from the excluded volume model for isothermal thermodynamic properties of a dilute supercritical solution at equilibrium with a pure incompressible solid

SOLUBILITY.

$$\ln(y_k)^\circ = \ln\left(\frac{p_k^\circ}{P}\right) + (v_k^* + \alpha_{jk}V_{jj} - V_{jk})\frac{(P - p_k^\circ)}{kT} + \ln(Z_j^\circ) - \alpha_{jk}\ln\left(\frac{f_j^\circ}{\rho_j^\circ kT}\right)$$

SLOPE.

$$\left(\frac{\partial \ln y_k}{\partial \rho_j^\circ}\right)^\circ_{T,eq} = \frac{1}{\rho_j^\circ kT\chi_j^\circ}\left[\frac{\alpha_{jk}}{\rho_j^\circ}(\rho_j^\circ kT\chi_j^\circ - 1) + \alpha_{jk}V_{jj} - V_{jk} + v_k^* - \rho_j^\circ kT\chi_j^\circ\right]$$

PARTIAL MOLECULAR VOLUME.

$$\bar{v}_k^\circ = kT\chi_j^\circ - \frac{\alpha_{jk}}{\rho_j^\circ}(\rho_j^\circ kT\chi_j^\circ - 1) - \alpha_{jk}V_{jj} + V_{jk}$$

Table 2. Expressions from the local composition model for isothermal thermodynamic properties of a dilute supercritical solution at equilibrium with a pure incompressible solid

SOLUBILITY.

$$\ln(y_k)^\circ = \ln\left(\frac{p_k^\circ}{P}\right) + \left[v_k^S + V_{jk}\exp\left(b_0 + \frac{b_1}{T}\right) - V_{jk}\right]\frac{(P - p_k^\circ)}{kT} + \ln(Z_j^\circ) - \alpha_{jk}\ln\left(\frac{f_j^\circ}{\rho_j^\circ kT}\right)$$

SLOPE.

$$\left(\frac{\partial \ln y_k}{\partial \rho_j^\circ}\right)^\circ_{T,eq} = \frac{1}{\rho_j^\circ kT\chi_j^\circ}\left[\frac{\alpha_{jk}}{\rho_j^\circ}(\rho_j^\circ kT\chi_j^\circ - 1) + V_{jk}\exp\left(b_0 + \frac{b_1}{T}\right) - V_{jk} + v_k^* - \rho_j^\circ kT\chi_j^\circ\right]$$

PARTIAL MOLECULAR VOLUME.

$$\bar{v}_k^\circ = kT\chi_j^\circ - \frac{\alpha_{jk}}{\rho_j^\circ}(\rho_j^\circ kT\chi_j^\circ - 1) - V_{jk}\exp\left(b_0 + \frac{b_1}{T}\right) + V_{jk}$$

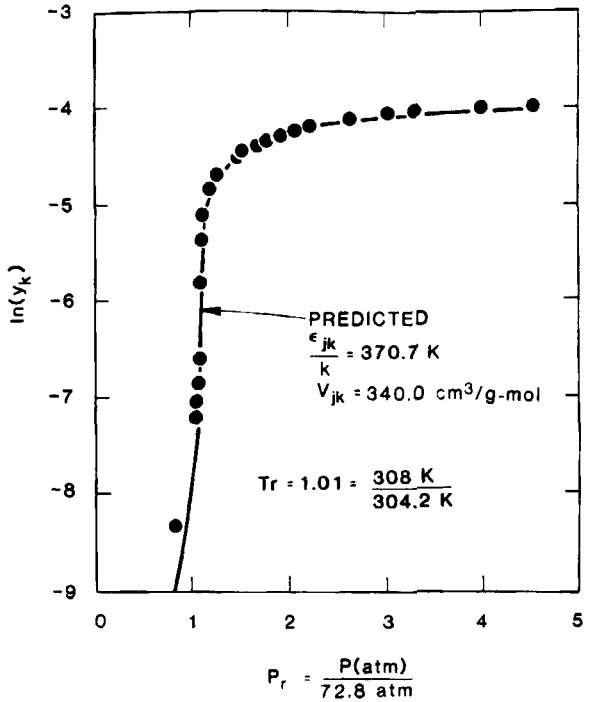

Fig. 4. Naphthalene solubility in carbon dioxide predicted by excluded volume model with temperature-dependent parameters.

We have seen, then, that the Kirkwood-Buff solution theory provides a formalism which may be used to describe the thermodynamic properties of supercritical solutions. In the next section, we shall explore the possibility of developing useful models for quantitative calculations within this formalism.

MOLECULAR SOLUTION APPROXIMATIONS

The expressions for thermodynamic properties of supercritical solutions would remain of largely formal interest unless it were possible to develop means to calculate the fluctuation integrals that appear in them. Toward this goal we shall seek methods to estimate infinite dilution fluctuation integrals, $G^{\infty}_{\alpha\beta}$, from the pure solvent fluctuation integral, G^{∞}_{jj}, by using various molecular solution approximations. Thus, our basic strategy is to assume that the qualitative behavior of the fluctuation

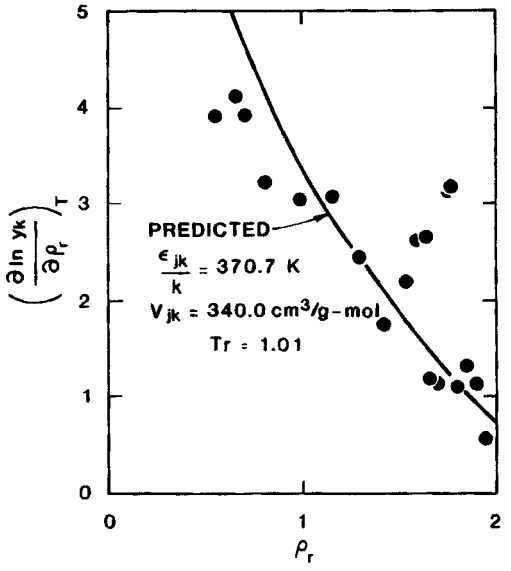

Fig. 5. Slope of solubility curve for naphthalene in carbon dioxide predicted by excluded volume model with temperature-dependent parameters.

integrals at the infinite dilution limit is reflected by the behavior of the pure solvent and then to use molecular solution approximations for quantitative adjustment. The solvent-solvent fluctuation integral may be calculated from an appropriate equation of state for the pure solvent.

$$G_{jj}^{\infty} = \left(kT\rho_j^{\circ}\chi_j^{\circ} - 1\right)/\rho_j^{\circ} = \left[kT\left(\partial\rho j/\partial P\right)_T^{\circ} - 1\right]/\rho_j^{\circ} \quad , \tag{9}$$

where χ_j° is the isothermal compressibility of the pure solvent.

It is our hope that relatively crude approximations may lead to useful results because of the information concerning fluid structure which is captured by the pure solvent equation of state. For the common supercritical solvents, e.g., CO_2 and C_2H_4, very accurate equations of state are available (23, 24).

Excluded Volume Model with Scaled Long-Range Correlations

One very simple model (10, 12) for the fluctuation integral would be to assume that the spatial pair correlation function,

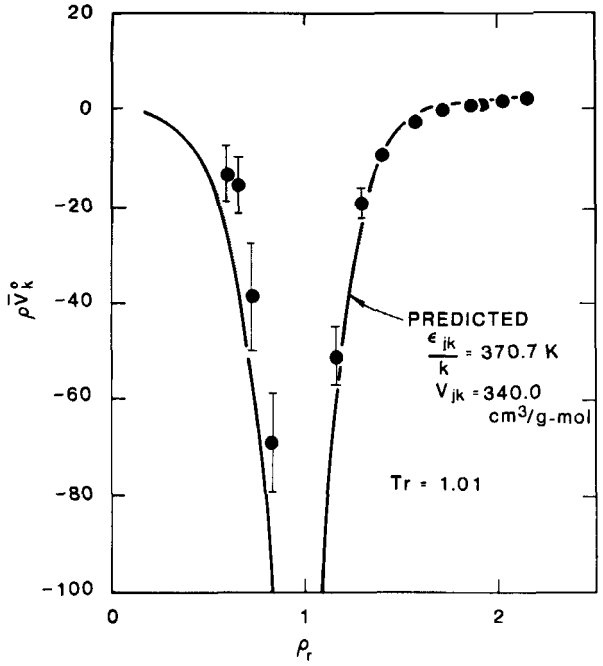

Fig. 6. Partial molar volume of naphthalene in carbon dioxide predicted by excluded volume model with temperature-dependent parameters.

$g_{\alpha\beta}$ (r), is zero within the radius, $\sigma_{\alpha\beta}$, of the impenetrable molecular cores and that the long-range part of the correlation scales, in dimensionless distance, $r^* = r/\sigma_{\alpha\beta}$, with the depth of the attractive energy well, $\varepsilon_{\alpha\beta}$. This approximation for scaling the attractive part of the pair correlation function was presented by Mansoori and Leland (25).

$$g_{\alpha\beta}(r^*) = 0.0 \qquad r^* < 1.0$$

$$= (\varepsilon_{\alpha\beta}/kT)\cdot g_0(r^*) \qquad r^* > 1.0 \quad , \tag{10}$$

where g_0 is a universal function. Then,

$$G^\circ_{jk} + V_{jk} = \left(\varepsilon_{jk}\sigma^3_{jk}/\varepsilon_{jj}\sigma^3_{jj}\right)\cdot\left(G^\circ_{jj} + V_{jj}\right) \quad , \tag{11a}$$

$$= \alpha_{jk}\cdot\left(G^\circ_{jj} + V_{jj}\right) \quad , \tag{11b}$$

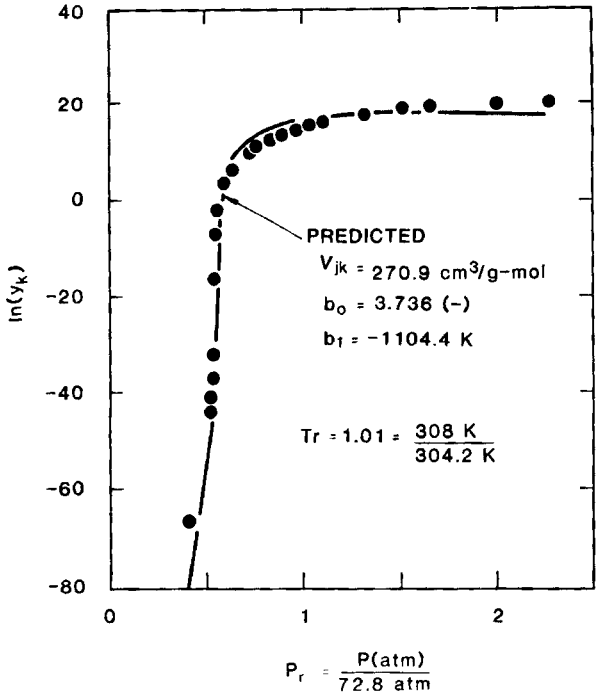

Fig. 7. Naphthalene solubility in carbon dioxide predicted by local composition model.

where V is the volume excluded by the molecular cores. Using (11), we can write expressions for solubility in dilute solution, slope of the solubility vs pressure curve, slope of the solubility vs. density curve, Debenedetti-Kumar constant, and partial molecular volume. Furthermore, using (9) we may write these expressions in terms of the equation of state for the pure solvent. Expressions for thermodynamic properties of supercritical solutions from the excluded volume model with scaled long-range correlations have been developed within the Kirkwood-Buff formalism and are presented in Table 1, where all variables are as previously defined and f_j^o is the fugacity of the pure solvent at the given temperature and pressure.

Local Composition Model with Scaled Long-Range Correlations

When the excluded volume model with scaled long-range correlations was tested against supercritical solubililty data (12),

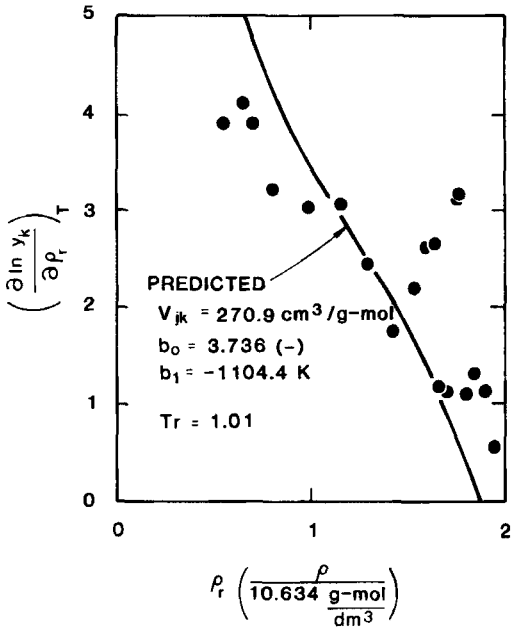

Fig. 8. Slope of solubility curve for naphthalene in carbon dioxide predicted by local composition model.

it was found that the simple scaling constant used, α_{jk}, had to be treated as a temperature-dependent parameter for the most accurate modeling. An alternate approach would be to incorporate improved temperature dependence into the model.

To this end, a local composition model was developed (12) following the form of the Renon-Prausnitz (26) local composition expression. The resulting expression for the fluctuation integral is as follows:

$$G^o_{jk} + V_{jk} = \alpha_{jk}\left[G^o_{jj} + V_{jk}\left(-1/\alpha_{jk}\right) \exp\left(b_0 + b_1/T\right)\right] , \quad (12)$$

where in the local composition model $V_{\alpha\beta}$ is the volume of the solvation sphere rather than the excluded volume used previously and b_0 and b_1 are model parameters.

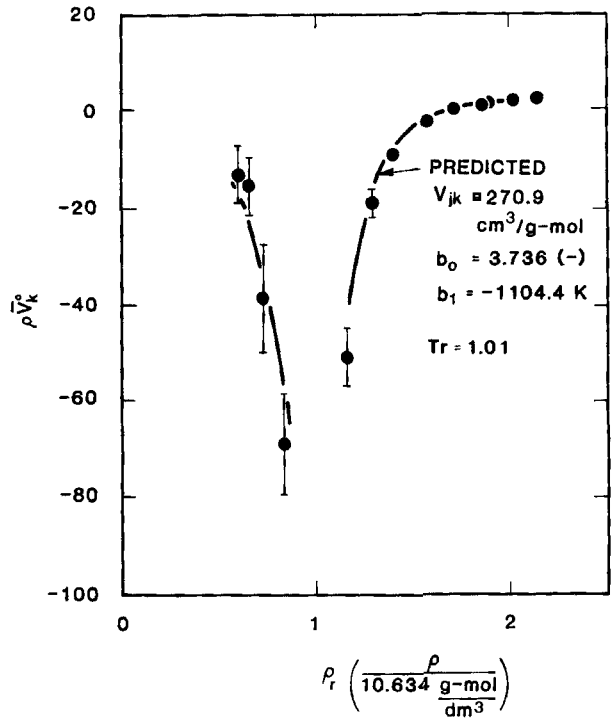

Fig. 9. Partial molar volume of naphthalene in carbon dioxide predicted by local composition model.

Then, using (12) we can write expressions for thermodynamic properties as before, and again, using (9) we may write these expressions in terms of the equation of state for the pure solvent. Expressions for thermodynamic properties of supercritical solutions from the local composition model with scaled long-range correlations have been developed within the Kirkwood-Buff formalism and are presented in Table 2.

ILLUSTRATIVE EXAMPLES

Figures 4, 5, and 6 show solubility of naphthalene vs pressure, slope of solubility curve vs density, and naphthalene partial molecular volume in carbon dioxide calculated using the excluded volume model with scaled long-range correlations. For these calculations temperature-dependent parameters -- $V_{jk(T)}$

and $\alpha_{jk(T)}$ -- were regressed from solubility data then used to predict partial molecular volume data. The accurate equation of state of Huang et al. (23) for carbon dioxide was used to calculate G_{jj} at all state conditions. The agreement with data is gratifying even in the vicinity of the critical point.

In a similar fashion, the performance of the local composition model with scaled long-range correlations is illustrated in Figs. 7, 8, and 9. For these calculations, only three constant parameters — V_{jk}, b_0, and b_1 — were regressed from solubility data. Again, the Huang equation was used for pure carbon dioxide. Again, the agreement with data is satisfactory.

CONCLUDING REMARKS

We have illustrated how the solution theory of Kirkwood and Buff may be used to provide a framework within which models may be developed for the thermodynamic properties of supercritical solutions. The strategy for modeling rests upon our assumption that the qualitative behavior of the fluctuation integrals at infinite dilution may be represented by the pure solvent-solvent fluctuation integral which can be calculated from an appropriate equation of state. Solution properties, then, are estimated by using molecular solution approximations, such as the excluded volume and local composition approximations, to relate the solvent-solute fluctuation integral to the solvent-solvent fluctuation integral. In spite of the divergence of the fluctuation integrals in the vicinity of a critical point, this strategy appears to be successful. This observation suggests that, in the vicinity of a critical point, the fluctuation integrals may diverge together in constant proportion to one another.

NOTATION

b_0, b_1	constants defined in Eq. (12)
f	fugacity
g	spatial pair correlation function
G	fluctuation integral
k	Boltzmann's constant
K	constant defined by Debenedetti and Kumar (17)
P	pressure
r	intermolecular separation
T	temperature
v	molecular volume
V	excluded volume
y	mole fraction
α	constant defined in Eq. (11)
ϵ	intermolecular energy constant
χ	isothermal compressibility
ρ	number density
σ	intermolecular size constant

Subscripts

c	critical point property
j	solvent index
k	solute index
o	universal function
r	reduced property
α,β	arbitrary species indices

Superscripts

◦	pure solvent quantity
—	partial molecular quantity
*	reduced dimension

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