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Thermodynamic Behavior of Supercritical Fluid Mixtures[1]

J. M. H. Levelt Sengers,[2] G. Morrison,[2] G. Nielson,[2] R. F. Chang,[2] and C. M. Everhart[2]

The recent surge of interest in supercritical extraction has brought the unusual properties of supercritical mixtures into the focus of attention. We discuss some of the properties of binary mixtures in a range around the gas–liquid critical line from the point of view of supercritical solubility. The general thermodynamic relationships that govern the enhancement of supercritical solubility are readily derived by a mathematical method introduced by Ehrenfest. The enhancement is governed by a strong divergence centered at a critical end point. We give the classical and nonclassical power-law behavior of the solubility along the experimental paths of constant temperature or pressure. The factor multiplying the strong divergence contains the partial molar volume or enthalpy of the solute in the supercritical phase. These partials are quite anomalous, especially if the mole fraction of the solute is small. They diverge at the solvent's critical point. We cite experimental evidence of these divergences, especially the results of recent experiments in dilute near-critical salt solutions. The anomalies found in these salt solutions are common to all dilute near-critical mixtures with a nonvolatile second component. We show that on experimentally convenient paths the solubility in a binary liquid mixture near its consolute points is not strongly enhanced. Finally, we sketch a nonclassical model based on the decorated lattice gas that can be used to describe supercritical solubility enhancement at low solubility, with the pure solvent used as a reference.

KEY WORDS: aqueous electrolyte solutions; decorated lattice gas; partial molar properties; power-law behavior; supercritical extraction; supercritical fluid mixtures.

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[2] Thermophysics Division, National Bureau of Standards, Gaithersburg, Maryland 20899, U.S.A.

1. SUPERCRITICAL ENHANCEMENT

We imagine a binary mixture in which one component, the solvent, is much more volatile that the other and is in a state near its critical point. Suppose that the nonvolatile component is not miscible with the solvent in all proportions and is present in excess in an additional solid or liquid phase. For the sake of simplicity we consider this phase as pure and inert, but this is not an essential limitation. The gas–liquid critical line that begins at the solvent's critical point is interrupted at a critical end point, where the mixture saturates and the additional phase appears. Usually, there is another critical end point marking the end of the critical line that starts at the solute's critical point. Our discussion is limited mostly to the first critical end point. At saturation, and on an isothermal path, it is found that the mole fraction of the solute in the supercritical phase increases rapidly with pressure in the vicinity of the critical end point. Conversely, the mole fraction decreases rapidly with temperature along an isobar. For the critical end point near the solvent's critical point, the reason is clear: a small change in pressure or temperature will cause large changes in the density and, therefore, in the solvent power of a near-critical fluid. There is, however, a more fundamental reason for the enhancement of supercritical solubility, a reason that is valid for both critical end points. The changes in solubility are governed by two thermodynamic relationships:

$$\left.\frac{dx_2}{dT}\right|_{P\sigma} = \frac{\bar{H}_2 - H_s}{T(1-x_2)(\partial^2 G/\partial x_2^2)_{PT}} \tag{1}$$

$$\left.\frac{dx_2}{dP}\right|_{T\sigma} = \frac{V_s - \bar{V}_2}{(1-x_2)(\partial^2 G/\partial x_2^2)_{PT}} \tag{2}$$

Here 2 refers to the solute, V_s is the molar volume, H_s is the molar enthalpy of the solute component as the inert phase, $\bar{H}_2$ is the partial molar enthalpy, $\bar{V}_2$ is the partial molar volume of the solute in the supercritical phase, and $G(P, T, x)$ is the Gibbs free energy as a function of pressure P, temperature T, and mole fraction x. The symbol σ denotes that a second phase is present in excess.

Equations (1) and (2) can be viewed as information on the slope of a phase boundary in $T-x$ or $P-x$ space. As Ehrenfest showed [1], such slopes can be related to changes in thermodynamic properties as the phase boundary is crossed. Let $C(X, Y)$ be a function which is continuous across a phase boundary but whose derivatives are not. The boundary curve separates regions I and II, each of which, in principle, may be a multiphase region.

Along this boundary curve, we have

$$dC^{I} = \left(\frac{\partial C}{\partial X}\right)_Y^{\mathrm{I}} dX + \left(\frac{\partial C}{\partial Y}\right)_X^{\mathrm{I}} dY \tag{3}$$

and

$$dC^{\mathrm{II}} = \left(\frac{\partial C}{\partial X}\right)_Y^{\mathrm{II}} dX + \left(\frac{\partial C}{\partial Y}\right)_X^{\mathrm{II}} dY \tag{4}$$

Since C is continuous, we have $dC^{\mathrm{I}} = dC^{\mathrm{II}}$ and therefore

$$\delta\left(\frac{\partial C}{\partial X}\right)_Y = -\left.\frac{dY}{dX}\right|_\sigma \delta\left(\frac{\partial C}{\partial Y}\right)_X \tag{5}$$

where σ denotes the boundary curve and δ the difference between derivatives in regions I and II at the boundary curve.

As an example of the usefulness of Eq. (5), consider for a one-component fluid the chemical potential $\mu(P, T)$ as the function C and the vapor pressure curve $P(T)$ as the boundary curve. Then

$$\delta\left(\frac{\partial \mu}{\partial P}\right)_T = -\left.\frac{dT}{dP}\right|_\sigma \delta\left(\frac{\partial \mu}{\partial T}\right)_P \tag{6}$$

Since $(\partial\mu/\partial P)_T = V$ and $(\partial\mu/\partial T)_P = -S$, we obtain Clapeyron's equation, $(dP/dT)_\sigma = \Delta S/\Delta V$. We now derive Eq. (1) for the change in solubility by applying Eq. (5) to the case of a supercritical solvent, component 1, and a solute, component 2, in the presence of an inert additional phase of component 2. We consider $\mu_2(T, x_2)/T$ at constant pressure as the continuous function and the locus where the inert phase first appears as the phase boundary.

Then, from Eq. (5),

$$\delta\left(\frac{\partial \mu_2/T}{\partial T}\right)_{Px} = -\left.\frac{dx_2}{dT}\right|_{P\sigma} \delta\left(\frac{\partial \mu_2/T}{\partial x_2}\right)_{PT} \tag{7}$$

since

$$\delta\left(\frac{\partial \mu_2}{\partial x_2}\right)_{PT} = (1 - x_2)(\partial^2 G/\partial x_2^2)_{PT} \tag{8}$$

and

$$\left(\frac{\partial \mu_2/T}{\partial T}\right)_{Px} = -\frac{\bar{H}_2}{T^2} \tag{9}$$

we have

$$\left.\frac{dx_2}{dT}\right|_{P\sigma} = \frac{\bar{H}_2^{\mathrm{I}} - H_{\mathrm{s}}}{T(1-x_2)(\partial^2 G/\partial x_2^2)_{PT}} \tag{10}$$

Here we have presumed that the additional phase is inert: the $H-x$ relation in the region II at constant P, T is linear and terminates at H_{s} for $x_2 = 1$ so that $\bar{H}_2^{\mathrm{II}} = H_{\mathrm{s}}$. We have made use of the fact that $(\partial^2 G/\partial x^2)_{PT} = 0$ in a two-phase, two-component system. Equation (2) is derived in the same way, with $\mu_2(P, x_2)$ at constant T as the continuous function. If the additional phase is not inert, Eqs. (1) and (2) are readily generalized by replacing the molar properties with the appropriate partial molar properties in that phase. Equations (1) and (2) immediately reveal the origin of enhancement of supercritical solubility: the denominator is approaching zero at the critical end point. In fact, the denominator will be zero all along the critical line, but as long as the additional phase is present, the critical end point is the only point on the critical line that the system can actually reach. Thus this end point, rather than the solvent's critical point, is the focus of the critical enhancement, a fact sometimes overlooked in the interpretation of data on the enhanced solubility in fluids [3] (Fig. 4).

The behavior of $(\partial^2 G/\partial x^2)_{PT}$ is strong in the sense of Griffiths and Wheeler [2]. This means that this property goes to zero as $|T - T_{\mathrm{ce}}|^{\gamma}$ or $|P - P_{\mathrm{ce}}|^{\gamma}$ on a path that is along the coexistence surface of the mixture in field space [2]; here γ is the critical exponent characterizing the compressibility of a pure fluid, with the value $\gamma = 1$ for a classical (van der Waals-like) equation of state, while $\gamma = 1.24$ for real fluids. The subscript ce denotes the critical end point. The experimental path is usually a constant-temperature or a constant-pressure path, which intersects the coexistence surface in field space. This leads to an exponent renormalization from γ to $\gamma/\beta\delta$ [2, 4, 5], where β is the critical exponent characterizing the shape of the coexistence curve and δ is the one characterizing the shape of the critical isotherm of the one-component fluid. Consequently, one expects for the enhancement of the supercritical solubility, Eqs. (1) and (2), a power-law behavior as $|T - T_{\mathrm{ce}}|^{-\gamma/\beta\delta}$ along the critical isobar and as $|P - P_{\mathrm{ce}}|^{-\gamma/\beta\delta}$ along the critical isotherm. The exponent $\gamma/\beta\delta$ equals 2/3 for classical equations and 0.8 for real fluids (not 1, as in the caption of Fig. 5 in Ref. 3). This behavior of $(\partial x/\partial T)_{P,\sigma}$ and $(\partial x/\partial T)_{T,\sigma}$ implies that $|x - x_{\mathrm{ce}}| \sim |T - T_{\mathrm{ce}}|^{1/\delta}$ at P_{ce} and $|x - x_{\mathrm{ce}}| \sim |P - P_{\mathrm{ce}}|^{1/\delta}$ at T_{ce}.

So far, we have discussed the origin of the enhancement of supercritical solubility: the fact that the denominator in Eqs. (1) and (2) approaches zero at the critical end points. In the next section, we pay attention to the behavior of the numerator in Eqs. (1) and (2).

2. PARTIAL MOLAR PROPERTIES; DILUTE SALT SOLUTIONS

We now turn to the numerators of Eqs. (1) and (2) and note that, certainly near the solvent's critical point, the molar volume and enthalpy of the inert phase are smooth functions of the temperature and pressure that "ignore" the presence of a critical end point. Any anomalous behavior has to come from $\bar{V}_2$, $\bar{H}_2$, the partials of the solute in the supercritical phase. In the presence of the inert phase, these partials will be finite, even *at* the critical end point. The *only* place where they diverge is at the solvent's critical point, which is never reached when the inert phase is present. The partials, however, can have very large values of either sign, and for nonvolatile solutes they are typically large and negative near the solvent's critical point. The closer the critical end point is to the solvent's critical point (the lower the solubility), the larger the relative enhancement. Figure 1 gives an idea of the behavior of the excess enthalpy of toluene in supercritical carbon dioxide [6, 7]. The excess enthalpy is plotted at a fixed pressure of 7.60 MPa along a number of isotherms. Three of these, at 358.15, 413.15, and 470.15 K, traverse a two-phase region with a straight tie line and large enthalpies of evaporation. The other two, although in a one-phase region, show very large excess enthalpies. In the case of the lowest isotherm, at 308.15 K, near-critical carbon dioxide is being mixed with liquid toluene. In the case of the highest isotherm, near-critical toluene is mixed with low-density carbon dioxide. Thus, the partial molar enthalpy $\bar{H}_2$, which is related to the slope of these curves, undergoes large changes in supercritical mixtures. In particular, we draw attention to the dramatic change in initial slope at the pure-CO_2 side ($x=1$) as the temperature approaches the critical temperature of CO_2 (304 K).

Figure 2 makes clear why the partials of volume and enthalpy of the solute diverge at the solvent's critical point. It shows the $V-x$ relation of a mixture at the critical temperature of the more volatile component. The addition of a nonvolatile causes a two-phase region to open up. The critical isotherm–isobar is indicated. Its slope, at any point, equals $(\partial V/\partial x)_{PT}$. Since

$$\begin{aligned} \bar{V}_1 &= V - x(\partial V/\partial x)_{PT} \\ \bar{V}_2 &= V + (1-x)(\partial V/\partial x)_{PT} \end{aligned} \tag{11}$$

and since the slope $(\partial V/\partial x)_{PT}$ is infinite at the critical point, we conclude that $\bar{V}_2 \rightarrow -\infty$. Russian scientists reached this conclusion on the basis of an analysis of the classical Helmholtz free energy [8, 9]. According to the classical model, the coexistence curve in Fig. 2 is parabolic and the critical isotherm–isobar is cubic [8–10], so that $(\partial V/\partial x)_{PT}$ and $\bar{V}_2$ diverge as $x^{-2/3}$ on the critical isotherm–isobar. Real fluids behave nonclassically. Wheeler

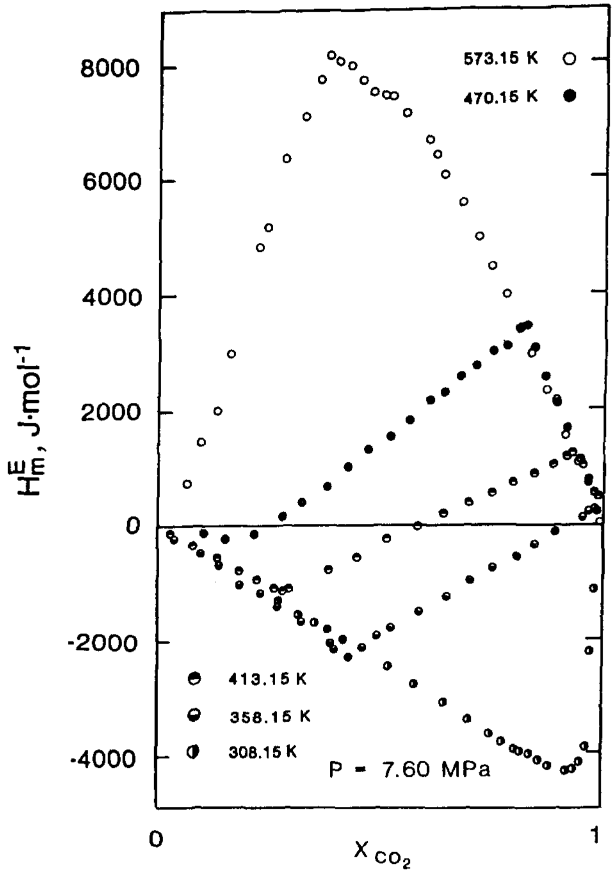

Fig 1. Five $H^E - x$ isotherms at 7.60 MPa for the system toluene ($x = 0$)—carbon dioxide ($x = 1$) [6, 7]. The large values of H^E suggest that a phase transition occurs. In fact, only the isotherms at 358.15, 413.15, and 470.15 K traverse a two-phase region as evidenced by the straight tie line. The signs of the changes in slope as phase boundaries are crossed indicate that the phase boundary in $T - x$ space has a negative slope (Ref. 7). The 308.15 and 573.15 K isotherms, though not traversing two-phase regions, show large H^E values nevertheless. Of interest is the strong downward slope near $x = 1$ on the 308.15 K isotherm, which is near the critical point of CO_2, and the strong upward slope near $x = 0$ on the 573.15 K isotherm, which is near the critical point of toluene.

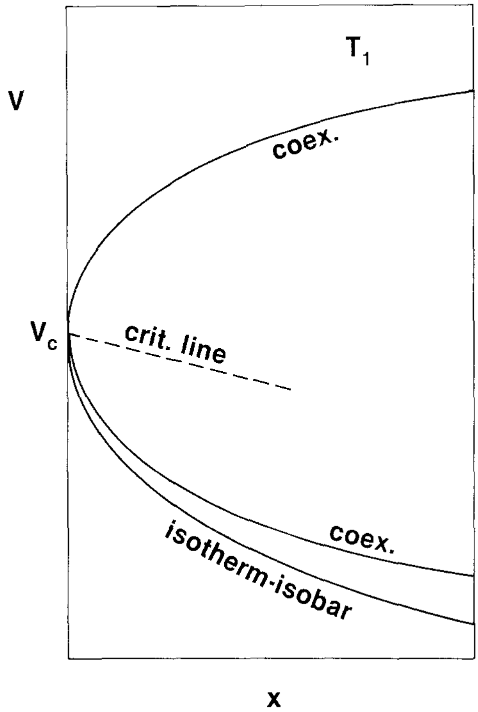

Fig. 2. At the critical pressure and temperature of the solvent, an involatile solute is added. It leads to phase separation. The coexistence curve and critical isotherm–isobar are sketched. The slope of the critical isotherm–isobar approaches $-\infty$ in the limit $x \rightarrow 0$.

[11] used the decorated lattice gas to derive the nonclassical asymptotic behavior of dilute mixtures, while Chang et al. used the Leung-Griffiths model [10]. The exponent of the divergence of $\bar{V}_2$ on the critical isotherm–isobar equals $\gamma/\beta\delta \sim 0.8$. The limiting behavior of the partial molar enthalpy $\bar{H}_2$ can be shown to be the same as that of $\bar{V}_2$ [10]. The partial molar heat capacity, however, diverges much more strongly than the partial molar volume [10]. On the critical isotherm–isobar, it diverges with an exponent $2-1/\delta \sim 1.8$. The strong divergence of the partial molar volume of the solute was recently seen by Eckert et al. [13] in a number of solutions of nonvolatiles in ethylene and carbon dioxide and, also, by van Wasen and Schneider [14]. The ideal place to look for these anomalies, however, is in dilute near-critical salt solutions in which the difference in volatility between the two components is extreme. Large negative apparent molal properties (which are related to the partials as chords are to slopes) have

been reported in a sequence of fine experiments in aqueous sodium chloride solutions at high temperatures and pressures. We refer to apparent molar volumes by Benson et al., [15]; apparent enthalpies of dilution by Busey et al. [16] and by Simonson et al [17], and apparent molar heat capacities by Wood et al. [18]. The large anomalies are to be expected in any dilute near-critical mixture in which the solute is nonvolatile [10, 19, 20].

Supercritical mixtures therefore show a critical anomaly at the solvent's critical point. In supercritical extraction, the solvent's critical point is never reached because of the presence of the additional phase. Nevertheless, if the solubility is small, as it is many applications, the numerator in Eqs. (1) and (2) is strongly anomalous, thus increasing the enhancement. In those cases, one would not expect to see simple power-law behavior due to the denominator alone in any but a very small region around the critical end point.

3. SUPERCRITICAL ENHANCEMENT NEAR A CONSOLUTE POINT

It has been suggested by Procaccia and Gitterman [21] that a binary mixture near a consolute point could be used as a supercritical extractant. The derivative $(\partial x/\partial T)_{P,\sigma}$ indeed diverges strongly in the situation Procaccia and Gitterman describe: a three-component mixture, in three phases, one solid phase of pure component 3, a near-critical ternary liquid phase, and a noncritical low-pressure vapor phase of components 1 and 2. The presence of the constant-pressure vapor phase is crucial; in order to keep the pressure constant while the system is heated, however, a large amount of vapor has to be created. In effect, the fluid's composition is being changed by transforming part of the liquid into a vapor of very different composition. Use is made of the fact that the $T-x$ bubble curve at constant pressure has a horizontal inflection at the ternary-mixture critical end point.

This system when studied other ways, in a constant-volume vessel or at constant pressure but without the vapor, behaves very differently. In either case, the vapor phase is irrelevant and the mathematical isomorphism of the gas–liquid and the liquid–liquid phase transition [5, 22] is achieved by the following transformation of variables.

One-component fluid	Partially miscible binary
P	$-\mu_2$
$\rho-\rho_c$	$x-x_c$
T	T
μ	$\mu_1-\mu_2$

(12)

An observation of these mapping relations reveals immediately that the convenient pressure "knob" that permits the easy variation of the density of the one-component fluid, and therefore of its solvent power, is replaced by a chemical potential knob that usually cannot be turned in the laboratory. This solvent power can be changed only by varying the *composition* of the liquid phase. Chemists have varied solvent power by the use of mixed solvents for over a century; in the Procaccia–Gitterman scheme, the solvent strength is varied by evaporating or condensing a large volume of vapor. In the absence of a vapor phase, however, the use of the temperature knob does not give the desired strong enhancement in the binary liquid, because this knob would be turned at constant composition of the binary liquid mixture. Thus $dx/dT|_\sigma$ is measured at the constant ratio x_A/x_B of the AB mixture (here σ refers to the third component or solute present in excess), which is a constant density in the sense of Griffiths and Wheeler [1]. Thus in the usual experimental situation, one would expect no more than a weak anomaly. If the solubility of the third component in the binary liquid is low, however, we expect that dilute-mixture effects of the same type as discussed in Section 2, may lead to additional enhancement, albeit not an actual divergence, caused by the nearness of the solvent's critical point.

4. A MODEL FOR SUPERCRITICAL SOLUBILITY

Classical thermodynamic functions for mixtures such as proposed by van der Waals, generalized by engineers for the past century, and systematized by van Konynenburg and Scott [23], are capable of qualitatively accounting for the phenomenon of supercritical solubility enhancement in the case that the additional phase is liquid. Since no known equation of state generates the solid along with the fluid phases, the supercritical enhancement in the case of the presence of a solid has to be handled by using a separate formulation for the solid and then equating chemical potentials [24]. Since the nonclassical critical isotherm $x-P$ at T_{ce}, or $x-T$ at P_{ce}, is much flatter than the classical one, it appears desirable to improve the description by using a nonclassical equation of state. Approximate nonclassical expressions have been suggested in the Russian literature [9] and by Gitterman and collaborators [3], which are analogous to those proposed in the 1950s for pure fluids, prior to the development of the scaling laws. These expressions impose the correct asymptotic form on the critical isochore and the critical isotherm and interpolate in between. Although such approximations yield correct answers in certain applications, they lead to nonanalyticities in the one-phase region, and if applied to mixtures, they miss known features of the critical-line behavior [2]. Another suggestion has been to combine an accurate nonclassical description of the pure solvent with the classical idea of corresponding states for a mixture of constant composition [25]. It can be shown that this approach leads to undesirable inconsistencies at the solvent's critical point [12].

Thus there is no choice but to use an internally consistent fully nonclassical formulation. One such formulation is the Leung–Griffiths model and its variants [26, 27]. The drawback of this model is a proliferation of constants and the need for a continuous critical line connecting the critical points of the pure components. An alternative is the decorated lattice gas, introduced by Widom and co-workers [28] and used and reviewed by Wheeler and co-workers for many applications [29, 30]. An ordinary or simple lattice gas is a regular array of cells, each of which can be empty or filled with no more than one molecule. Molecules in nearest-neighbor cells are assigned an attractive energy. It is well known that the simple lattice gas is isomorphic with the Ising model [5, 22, 29]. It is a very rudimentary model for a gas–liquid phase transition with a built-in symmetry with respect to the $\rho = \rho_c$ axis, with ρ_c the critical density, when one-half of the sites are occupied. In the decorated lattice gas (Fig. 3) additional secondary cells are placed in the centers of the line segments that connect centers of the original primary cells. If the molecules are allowed to occupy both types of cells (multiple occupancy still being forbidden), and an assumption is made about the strengths of the interactions between occupied primary–primary and primary–secondary cells, then the resulting partition function can be mapped onto the Ising model by analytic transformation of

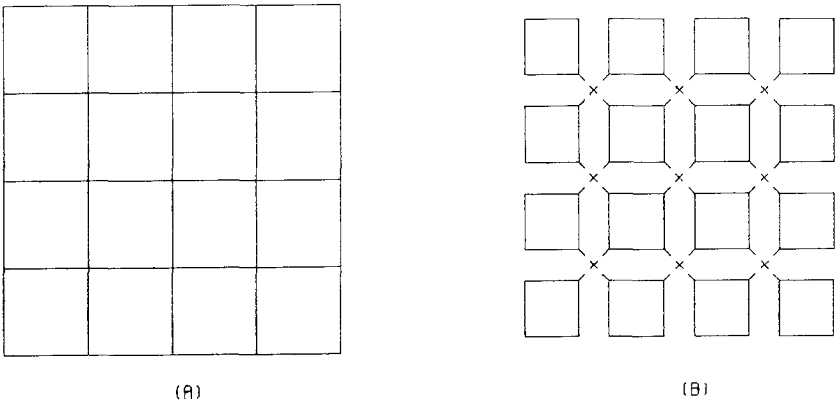

Fig. 3. Cells of the decorated lattice gas [28] as used in our modeling of supercritical solubility. The square cells are on the primary sites and are accessible to solvent molecules or holes. The diamond-shaped interstitial cells are on the secondary sites and are accessible to solvent molecules, solute molecules, and holes.

variables. The one-component decorated lattice gas therefore has the same critical exponents as the simple lattice gas but differs from the latter in that the particle-hole symmetry is broken; the coexistence curve, for instance, shows the asymmetry typical of real fluids. The revised and extended scaled equation that has been developed for describing near-critical fluids [31, 32] is, to leading order in the scaling variables, equivalent to the decorated lattice gas.

In order to describe supercritical solubility, we have to carry the decorated lattice gas one step further. Following Bartis and Hall [33], we allow solvent molecules or holes in primary cells and solvent molecules, solute molecules, or holes in secondary cells. Multiple occupancy is again forbidden. We allow for three types of interaction energies, namely, those between solvent molecules in adjacent primary cells, between solvent molecules in adjacent primary and secondary cells, and between a solvent molecule in a primary and a solute molecule in an adjacent secondary cell. Interactions between molecules in secondary cells cannot be allowed if the mapping onto the Ising model is to be retained. As long as the mixture is dilute, this restriction is acceptable. So the two-component decorated lattice gas can be transformed back to the one-component decorated lattice gas, which in turn maps onto the Ising model.

Since we are interested in the supercritical regime, we have to map onto the Ising model in nonzero field. For this model, however, no thermodynamic potential is available in closed form. We have found an alternative, by mapping only the two-component decorated lattice gas onto the one-component decorated lattice gas. For the latter, we use the revised and extended scaled equation that we have developed for pure fluids. So, in effect, we map the properties of the dilute solution onto those of the pure solvent by a procedure which might be considered the nonclassical equivalent of corresponding states. Since the decorated lattice gas, just as the van der Waals equation, does not allow for the presence of a solid phase, we have to enter this phase by an artifact. In our first attempt, we have set the chemical potential of the solid equal to a constant. We have chosen the constant such that the critical end point falls in the right place. Our model then predicts the supercritical solubility of naphthalene in ethylene as shown in Fig. 4. The range of the solubility curves that we can predict is limited by the range of validity of the scaled equation of ethylene [32]. We are presently working on the incorporation of the pressure dependence of the chemical potential of naphthalene in our prediction of the solubility curve.

We view as the advantages of our work the correctness of the asymptotic behavior, the mapping onto the pure-solvent thermodynamic surface and the use of only two constants for characterizing the solute. This

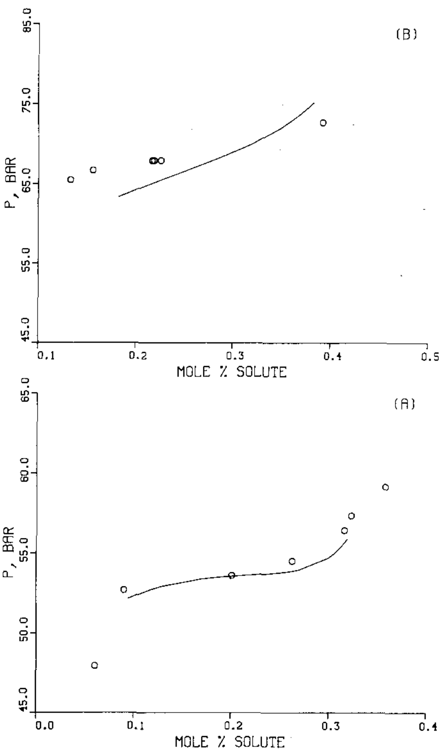

Fig. 4. Prediction of the supercritical solubility of naphthalene in ethylene near the lower one of the two critical end points by means of a two-component decorated lattice gas [29]. The chemical potential of naphthalene has been set equal to a constant. The properties of the solution are mapped onto those of pure ethylene [32].

model will also permit us to distinguish between the effect of the strong anomaly caused by $(\partial^2 G/\partial x^2)_{PT} \rightarrow 0$ at the critical end point and the near-divergence of $\bar{V}_2$ in Eqs. (1) and (2).

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