The Molecular Basis of Temperature Effects in Supercritical Extraction

The behavior of solute partial molar enthalpies in dilute supercritical mixtures gives rise to the well-known phenomenon of retrograde solubility (equilibrium solubility decreasing with increasing temperature at constant pressure). A mechanistic interpretation of this phenomenon in terms of the formation of large clusters of solvent molecules around solute molecules is consistent with experimentally observed retrograde behavior. Cluster formation occurs as a consequence of the unbounded increase in the solvent's compressibility arbitrarily close to the latter's critical point. At infinite dilution, the solute's partial molar volume and enthalpy grow linearly with cluster size. This means that the negative divergence of these quantities is simply a macroscopic manifestation of a "condensation" in which an increasing number of solvent molecules cluster around solute molecules. Arbitrarily close to the solvent's critical point, scaling relationships show that the decay of both solvent-solvent and solute-solvent correlation functions exhibits the same radial dependence. This functionality is thus solute-independent, and is determined exclusively by the proximity to the solvent's critical point. The locus along which thermal effects associated with cluster formation are maximized is arbitrarliy close to the solvent's critical isochore as the latter's critical point is approached.

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Introduction

The thermodynamic behavior of dilute mixtures of nonvolatile solutes in the vicinity of a solvent's critical point is of considerable practical and theoretical importance. The use of supercritical solvents in applications as diverse as coffee decaffeination (Rozelius et al., 1974), enhanced oil recovery (Doscher and El-Arabi, 1982) activated carbon regeneration (De Fillipi et al., 1980), monomer purification (Patrick and Palmer, 1985), precipitation polymerization (Kumar, 1986; Kumar et al., 1986a), supercritical chromatography (Yonker et al., 1987), organic reaction rate modification (Kim and Johnston, 1987), and formation of inorganic films and powders (Matson et al., 1986), frequently involves mixtures in which the solute of interest is present in very low concentrations.

Among the unique features characterizing the thermodynamics of dilute mixtures in the vicinity of a solvent's critical point we mention the divergence of solute partial molar volumes and enthalpies, and the path dependence of the corresponding solvent properties (Rozen, 1976; Chang et al., 1984). Numerous theoretical and experimental studies have been devoted to this topic, pioneered by the work of Krichevskii (1967) and Rozen (1976) in the Soviet Union. Recent experimental work in this country includes measurements of large negative partial molar volumes of nonvolatile organic solutes in supercritical solvents (Eckert et al., 1983, 1986), large negative apparent molar heat capacities and large negative apparent enthalpies of dilution of NaCl in supercritical steam (Smith-Magowan and Wood, 1981; Wood and Quint, 1982; Gates et al., 1982; Busey et al., 1984), and excess enthalpies in hydrocarbon-CO_2 mixtures under conditions including the vicinity of the latter's critical point (Christensen et al., 1984). Theoretical contributions include the work of Levelt Sengers and coworkers (Levelt Sengers et al., 1983, 1986a, b, c; Chang et al., 1984; Sengers and Levelt Sengers, 1986; Chang and Levelt Sengers, 1986; Levelt Sengers, 1986), and the work of Wheeler (1972), Leung and Griffiths (1973), Kim et al. (1985), and Gilbert and Eckert (1986).

Another unusual, and counterintuitive, feature of the thermodynamics of dilute supercritical mixtures, commonly referred to as retrograde solubility, is an isobaric decrease in solubility with increasing temperature occurring in the vicinity of a solvent's critical point—or, equivalently, for low-solubility mixtures of nonvolatile solutes in supercritical fluids, near the mixture's lower critical end point. In this paper we discuss the connection between retrograde solubility and the formation of large clusters of solvent molecules around solute molecules in the vicinity of the solvent's critical point. We start with a brief phenomenological review of temperature effects in dilute supercritical systems, which can be quantified in terms of the solute's partial molar enthalpy in the fluid phase. The strong divergence of this quantity at infinite dilution is shown to be a macroscopic manifestation of the formation of large clusters of solvent molecules around isolated solute molecules. We then show that cluster formation can be explained in terms of the unbounded growth in the correlation length that characterizes near-critical fluids (Landau and Lifshitz, 1980), and derive the corresponding scaling relationships.

The remarkable pressure-dependent isothermal solubility enhancements that underlie many of the technological applications of supercritical solvents have been explained recently from a molecular perspective through the clustering mechanism (Debenedetti, 1987). The present paper shows the important role of clustering in influencing the temperature-dependent macroscopic behavior of dilute supercritical mixtures.

Retrograde Solubility: Phenomenological Review

In order to make the discussion self-contained, we now briefly review the essential phenomenological and macroscopic features associated with retrograde solubility.

Figure 1 shows the experimental (Schmitt, 1984) and calculated solubility of acridine in supercritical carbon dioxide, at three different temperatures. The curves are based on a lattice model, the details of which have been discussed elsewhere (Kumar, 1986, Kumar et al., 1986b). It can be seen that in the approximate range $10 \le P \le 17$ MPa, an isobaric temperature increase can lead to a solubility decrease; this regime is known as the retrograde region, and is characteristic of dilute binary mixtures of nonvolatile solid solutes in supercritical solvents. The phase behavior of such systems exhibits general features that we now summarize. If the solid's triple point temperature exceeds the solvent's critical temperature, the critical locus joining pure-component critical points can be intersected twice by three-phase loci (Kim et al., 1985). Such intersections are called lower and upper critical end points. Between the lower and upper critical end point temperatures a pure solid solute can coexist with a single fluid phase. In low-solubility systems the solvent's critical point is normally very close to the lower critical end point. This means that the behavior of the fluid phase at temperatures close to the lower critical end point is strongly influenced by the proximity to the solvent's critical point (Kim et al., 1985; Morrison et al., 1985).

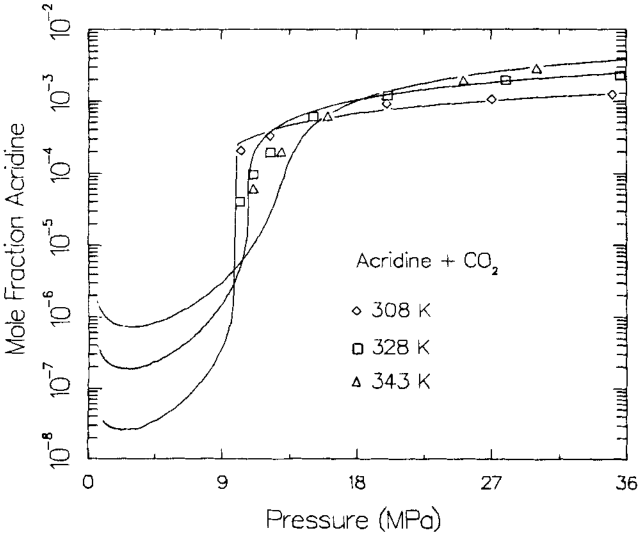

Figure 1. Experimental and calculated solubility of acridine in carbon dioxide.

Data of Schmitt (1984); theoretical curves computed from lattice model of Kumar (1986)

Retrograde solubility has traditionally been "explained" by noting that in the high-compressibility region (i.e., near the solvent's critical point), a temperature increase has a more pronounced effect in decreasing the solvent's density than in increasing the solute's vapor pressure. Mathematically, the solvent density changes with temperature as

$$\left(\frac{\partial \rho}{\partial T}\right)_P = -\rho K_T \left(\frac{\partial P}{\partial T}\right)_\rho \tag{1}$$

Since K_T is arbitrarily large in the vicinity of the solvent's critical point, the solvent's density does change dramatically in this region. This argument presupposes that solubility is related to solvent density—an empirical observation which, although correct, has not yet been explained in molecular terms (Schmitt and Reid, 1985).

The isobaric temperature dependence of the solubility of a pure, condensed solute in a fluid may be expressed by the thermodynamic identity (Kurnik, 1981; Modell and Reid, 1983)

$$kT^2 \left(\frac{\partial \ln x_1^{eq}}{\partial T}\right)_{P,\sigma} = \frac{(\overline{H}_1 - H_1^S)}{1 + \left(\dfrac{\partial \ln \hat{\phi}_1}{\partial \ln x_1}\right)_{T,P}} \tag{2}$$

where x_1^{eq} is the solute's equilibrium mole fraction in the fluid phase, σ denotes differentiation along a phase equilibrium locus, H_1^S is the molecular enthalpy of the pure solute in the condensed phase at the prevailing temperature and pressure, $\overline{H}_1$ is the solute's partial molar enthalpy (per molecule) in the fluid phase, and $\hat{\phi}_1$, its fugacity coefficient in solution.

The righthand side numerator in Eq. 2 is the heat effect (per molecule) associated with the dissolution of the pure solid solute into the supercritical fluid, at the prevailing temperature, pressure, and composition. At the solvent's critical point, the partial molar enthalpy of an infinitely dilute solute diverges (generally, for the systems of interest here, to $-\infty$). As a consequence, the infinite dilution solute partial molar enthalpy is a highly negative number over a wide range of temperatures and pressures. It follows that in low-solubility systems, for which $\overline{H}_1$ is close to $\overline{H}_1^\infty$, retrograde behavior ($\overline{H}_1 < H_1^s$) is exhibited over a wide temperature and pressure "window," and is not confined to the immediate vicinity of the solvent's critical point (or, equivalently, the mixture's lower critical end point). Both the behavior of

$\overline{H}_1^\infty$ and the validity of the assumption $\overline{H}_1^\infty \approx \overline{H}_1$ will be discussed quantitatively in the next section.

The righthand side denominator in Eq. 2, being proportional to a stability coefficient, is everywhere positive except at mixture critical points, where it vanishes. Solute partial molar enthalpies, however, exhibit no singularities at mixture critical points (Modell and Reid, 1983). Consequently, proximity to the lower critical end point simply reinforces retrograde behavior, by increasing the sensitivity of solubility to temperature, but has no influence upon exothermicity (i.e., the righthand side numerator in Eq. 2). Accordingly, retrograde behavior is not found in the vicinity of the upper critical end point of binary mixtures of nonvolatile solids in supercritical fluids (Diepen and Scheffer, 1953).

Retrograde behavior in low-solubility systems, therefore, is a direct consequence of the divergence of $\overline{H}_1^\infty$ at the solvent's critical point. Because of this divergence, the dissolution of a pure solid into a nonreactive fluid is an exothermic process even away from criticality. Although divergent at the solvent's critical point, the magnitude of this exothermicity is otherwise finite. In particular, at the high-pressure limit of the retrograde region—see Figure 1 and Eq. 2—this effect is small. We now address the divergence of $\overline{H}_1^\infty$ from a macroscopic (nonmolecular) viewpoint, as well as the validity of the infinite dilution assumption as a plausible basis for the ensuing molecular arguments.

Behavior of $\overline{H}_1^\infty$: A Macroscopic Analysis

Wheeler (1972) first showed, within the context of a decorated lattice model, that, arbitrarily close to the solvent's critical point,

$$\overline{V}_1^\infty \sim \overline{H}_1^\infty \tag{3}$$

with a positive proportionality constant (throughout this paper, the symbol ~ should be read as "scales as"). Levelt Sengers and her coworkers (Morrison et al., 1985; Levelt Sengers et al., 1986b; Levelt Sengers, 1986) arrived at the same important result for mixtures that display classical behavior. Their argument, however, as we show in Appendix A, is circular. We now show that any system for which $\overline{V}_1^\infty$ diverges as K_T will exhibit proportionality between $\overline{V}_1^\infty$ and $\overline{H}_1^\infty$ (with a positive proportionality constant) in the near-critical region. This conclusion is completely independent, in particular, of the system's classical or nonclassical nature. We first write ($\beta = 1/kT$)

$$\left(\frac{\partial \ln \hat{\phi}_1^\infty}{\partial \beta}\right)_\rho = \left(\frac{\partial \ln \hat{\phi}_1^\infty}{\partial \beta}\right)_P + \left(\frac{\partial P}{\partial \beta}\right)_\rho \left(\frac{\partial \ln \hat{\phi}_1^\infty}{\partial P}\right)_\beta$$
$$= \overline{H}_1^\infty - H_1^* + \left(\frac{\partial P}{\partial \beta}\right)_\rho \left(\beta \overline{V}_1^\infty - \frac{1}{P}\right) \tag{4}$$

where $\hat{\phi}_1^\infty$ is the infinite dilution limit of the solute's fugacity coefficient in the mixture, and H_1^*, the pure solute enthalpy (per molecule) in the ideal gas limit at the prevailing temperature. Noting that $\hat{\phi}_1$ has a well-defined infinite dilution limit

$$\ln \hat{\phi}_1^\infty = -\int_0^\rho \left(1 - \frac{\beta \overline{V}_1^\infty}{K_T}\right)\frac{d\rho}{\rho} - \ln\left(\frac{\beta P}{\rho}\right) \tag{5}$$

where ρ and K_T are now solvent properties, we differentiate and write

$$\left(\frac{\partial \ln \hat{\phi}_1^\infty}{\partial \beta}\right)_\rho = -\int_0^\rho \left\{1 - \frac{\overline{V}_1^\infty}{K_T}\left[1 + \left(\frac{\partial \ln (\overline{V}_1^\infty/K_T)}{\partial \ln \beta}\right)_P\right]\right\}$$
$$\cdot \frac{d\rho}{\rho} - \beta^{-1}\left[1 + \left(\frac{\partial \ln P}{\partial \ln \beta}\right)_\rho\right] \tag{6}$$

It follows from Eq. 6 that any system for which $\overline{V}_1^\infty$ diverges as K_T (i.e., $\overline{V}_1^\infty/K_T$ finite) must have a finite value for $(\partial \ln \hat{\phi}_1^\infty/\partial\beta)_\rho$. From Eq. 4, therefore, it is necessary that $\overline{H}_1^\infty$ be proportional to $\overline{V}_1^\infty$ for such a system, with a positive proportionality constant, related to the limiting slope of the solvent's binodal locus,

$$\overline{H}_1^\infty \rightarrow T\left(\frac{\partial P}{\partial T}\right)_\sigma \overline{V}_1^\infty + \text{const.} \tag{7}$$

If, therefore, $\overline{V}_1^\infty \sim K_T$, the divergence of $\overline{H}_1^\infty$ is mathematically identical to the corresponding $\overline{V}_1^\infty$ divergence, and both quantities have the same sign in the near-critical region.

The divergence of $\overline{V}_1^\infty$ has been studied both experimentally (Eckert et al., 1986) and theoretically (Chang et al., 1984; Kim et al., 1985; Debenedetti, 1987), and follows from writing

$$\overline{V}_1^\infty = \rho^{-1} K_T \left[\left(\frac{\partial P}{\partial N_1}\right)^\infty_{T,V,N_2} N\right] \tag{8}$$

where ρ and K_T are solvent properties. Note that the quantity in bracket, henceforth called δ, is necessarily finite for classical behavior (Kim et al., 1985). Negative divergence ($\partial P/\partial x_1 < 0$, $\overline{V}_1^\infty \rightarrow -\infty$) has been observed for several systems comprising nonvolatile organic solutes and supercritical solvents (Eckert et al., 1983, 1986). The data of Khazanova and Sominskaya (1968) on the ethane-CO_2 system appears to indicate positive divergence ($\partial P/\partial x_1 > 0$, $\overline{V}_1^\infty \rightarrow +\infty$).

The fact that $\overline{H}_1^\infty \sim \overline{V}_1^\infty$ for both classical and nonclassical models means that, except for the calculation of critical exponents, the essential trends which characterize the behavior of $\overline{H}_1^\infty$ in the regions of interest for supercritical extraction can be illustrated by the use of classical equations of state. In order to quantify the behavior of $\overline{H}_1^\infty$ in regions not necessarily restricted to the near-critical regime, we write the thermodynamic identity (see Appendix B)

$$\overline{H}_1^\infty = \frac{5kT}{2} + \int_0^P \left[\overline{V}_1^\infty - T\left(\frac{\partial \overline{V}_1^\infty}{\partial T}\right)_P\right] dP \tag{9}$$

where we have assumed molecules with translational degrees of freedom exclusively. Quantitative estimates of $\overline{H}_1^\infty$ were obtained from Eq. 9 with the use of the van der Waals equation, with van der Waals 1 mixing rules and zero interaction parameter. The results are shown in Figure 2, where the behavior of $\overline{H}_1^\infty/kT_{c2}$ at four supercritical temperatures, over the range $0 < Pr \leq 3$ is illustrated (maximum decreases of 28% in the magnitude of the $\overline{H}_1^\infty$ peaks resulted from using a 0.1 interaction parameter with no change in the basic trends). Each additional degree of freedom (rotational, internal) would shift the curves in Figure 2 by an amount $T/2T_{c2}$ (≈ 0.5 at the temperatures

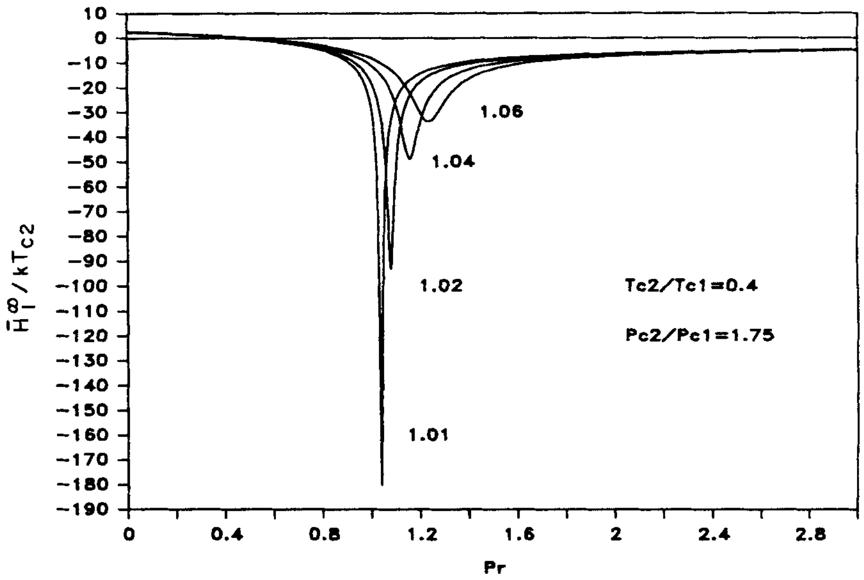

Figure 2. Behavior of the infinite dilution solute partial molar enthalpy at four temperatures, calculated with the van der Waals equation of state.

T/T_{c2} = 1.01, 1.02, 1.04, 1.06

Critical property ratios correspond to the naphthalene-carbon dioxide system

shown). Clearly, this numerical correction will not affect the behavior shown in Figure 2 due to the diverging nature of $\bar{H}_1^\infty$. In this two-parameter model, the ratio of critical temperatures and pressures employed represents the naphthalene-CO_2 system.

In order to interpret Figure 2, it must be remembered that the heat effect associated with the dissolution of a solute molecule into the supercritical fluid (assuming a dilute mixture), is given by $\bar{H}_1^\infty - H_1^S$. This quantity may be rewritten as

$$\bar{H}_1^\infty - H_1^S = (\bar{H}_1^\infty - H_1^*) + (H_1^* - H_1^S)$$
$$\approx (\bar{H}_1^\infty - H_1^*) + \Delta H^{sub} \quad (10)$$

where we have assumed $H_1^S(T,P) \approx H_1^S(T,P \rightarrow 0)$. The heat of sublimation of naphthalene is approximately 31 kJ/mol (Schmitt and Reid, 1985), or 12 kT_{c2} (for CO_2 as solvent). For the naphthalene-CO_2 system, therefore, Eq. 10 may be rewritten as $(\bar{H}_1^\infty - H_1^S)/kT_{c2} \approx \bar{H}_1^\infty/kT_{c2} - 2.5\ Tr + 12$. Adding 12-2.5 T_r to the curves shown in Figure 2, therefore, provides estimates of the heat of dissolution at infinite dilution in the naphthalene-CO_2 system (these estimates are obviously of qualitative significance only, since we are using a zero interaction parameter). This behavior is typical of negatively diverging mixtures ($\bar{V}_1^\infty$, $\bar{H}_1^\infty \rightarrow -\infty$ as $T \rightarrow T_c$, $P \rightarrow P_c$), an example of which is constituted by dilute solutions of nonvolatile organic solids in solvents such as CO_2 at supercritical conditions (Eckert et al., 1983, 1986). The maximum heat effects at $Tr = 1.01$ and 1.02 are an order of magnitude higher than the solute's heat of sublimation and, what is more important, are of the opposite sign (i.e., the process is exothermic). Direct experimental evidence of highly exothermic behavior in dilute, binary supercritical mixtures can be found in the measurements of Christensen and coworkers on hydrocarbon-CO_2 mixtures (Christensen et al., 1984).

The thermal effects discussed above are maximized along the locus of $\bar{H}_1^\infty$ extrema. We will now show that, for a given solvent, the locus of $\bar{H}_1^\infty$ extrema is solute-independent, and becomes indistinguishable from the solvent's critical isochore in the near-critical region. To explain this phenomenon, we assume that the mixture displays classical behavior and write a Taylor series for pressure variations away from the solvent's critical point,

$$p = \alpha t + \beta\eta^3 + \gamma\eta t + \delta' x_1 + \epsilon x_1 t + \lambda x_1 \eta \quad (11)$$

where

$$p \equiv P - P_c \quad (12)$$

$$t \equiv T - T_c \quad (13)$$

$$\eta \equiv \rho - \rho_c \quad (14)$$

$$\alpha \equiv \left(\frac{\partial P}{\partial T}\right)_\rho \quad (15)$$

$$\beta \equiv \frac{1}{3!}\left(\frac{\partial^3 P}{\partial \rho^3}\right)_T \quad (16)$$

$$\gamma \equiv \frac{\partial^2 P}{\partial T \partial \rho} \quad (17)$$

$$\delta' \equiv \left(\frac{\partial P}{\partial x_1}\right)_{T,\rho}^\infty \quad (18)$$

$$\epsilon \equiv \left(\frac{\partial^2 P}{\partial T \partial x_1}\right)^\infty \quad (19)$$

$$\lambda \equiv \left(\frac{\partial^2 P}{\partial \rho \partial x_1}\right)^\infty \quad (20)$$

and where all derivatives are evaluated at the solvent's critical point. For classical behavior and $t \neq 0$, the derivatives $\partial \bar{V}_1^\infty/\partial\eta$ and $(\partial K_T/\partial\eta)^\infty$ are both proportional to $\partial^2 p/\partial\eta^2$. Equation 11 implies that the critical isochore is the locus of $\bar{V}_1^\infty$ and K_T extrema (the relationship between compressibility and solute partial molar volume extrema has been discussed in detail by Kim et al., 1985). Therefore, because $\bar{H}_1^\infty \sim \bar{V}_1^\infty$, the locus of $\bar{H}_1^\infty$ extrema has to approach the solvent's critical isochore as $(t,\eta) \rightarrow 0$. This can be quantified by changing variables in the integrand of Eq. 9,

$$\bar{H}_1^\infty \sim \int \left[\bar{V}_1^\infty - T\left(\frac{\partial \bar{V}_1^\infty}{\partial T}\right)_\rho + \rho T K_T \left(\frac{\partial \bar{V}_1^\infty}{\partial \rho}\right)_T \left(\frac{\partial P}{\partial T}\right)_\rho\right](3\beta\eta^2 + \gamma t)\, d\eta$$

$$\approx \frac{\delta}{\rho_c^2} \int \left[1 - \frac{(6\alpha\beta\eta - \gamma^2 t)T}{(3\beta\eta^2 + \gamma t)^2}\right] d\eta \qquad (21)$$

and noting than an extremum in $\bar{H}_1^\infty$ (η) occurs when the integrand vanishes. This condition is satisfied (for $t \neq 0$) when

$$\eta \approx \frac{\gamma^2}{6\alpha\beta}\left(1 + \frac{t}{T}\right)t \qquad (22)$$

which is solute-independent, and becomes indistinguishable from the critical isochore as $t \rightarrow 0$. As t increases, Eq. 22 overpredicts the density at which $\bar{H}_1^\infty$ extrema occur. This can be seen by adding to the truncated pressure expansion the next terms corresponding to a van der Waals-type equation (i.e., η^4 and $\eta^2 t$). The condition $\partial^2 p/\partial\eta^2$ (and hence the locus of $\bar{V}_1^\infty$ and K_T extrema) now satisfies $\eta = -12\beta\phi t$, where ϕ is the coefficient of $\eta^2 t$. The critical isochore of a van der Waals fluid satisfies $Tr = 4Pr - 3$, which for all practical purposes coincides with the locus of extrema in Figure 2.

From the truncated pressure expansion and Eq. 9 we obtain, along the critical isotherm,

$$K_T \sim \frac{\bar{V}_1^\infty}{\delta} \sim \frac{\bar{H}_1^\infty}{\delta} \sim \frac{\bar{U}_1^\infty}{\delta} \sim |p|^{-2/3} \sim \eta^{-2} \qquad (23)$$

where the $\bar{U}_1^\infty$ relationship is derived in Appendix B. For nonclassical behavior, $p \sim \eta^{4.8}$ along the critical isotherm (Levelt Sengers et al., 1986c). Along this locus, therefore,

$$K_T \sim \frac{\bar{V}_1^\infty}{\delta} \sim \frac{\bar{H}_1^\infty}{\delta} \sim \frac{\bar{U}_1^\infty}{\delta} \sim |p|^{-3.8/4.8} \sim |\eta|^{-3.8} \qquad (24)$$

where $\delta > 0$ for positive divergence, and $\delta < 0$ for negative divergence. The scaling relationships shown in Eqs. 23 and 24 along the critical isotherm are particular cases of the more general asymptotic proportionality between $\bar{H}_1^\infty$, $\bar{U}_1^\infty$, $\bar{V}_1^\infty$, and K_T, first derived by Wheeler (1972) for a decorated lattice model. This scaling is also a characteristic of classical systems, as can be seen by performing the integration, Eq. 9, along different paths in the near-critical region. Results are summarized in Table 1.

Finally, we discuss the validity of the infinite dilution assumption ($\bar{H}_1 \approx \bar{H}_1^\infty$) as applied to low-solubility systems ($x_1 \leq 10^{-3}$). Figure 1 (acridine-CO_2) is typical of dilute binary mixtures in which a nonvolatile organic solid dissolves into a supercritical solvent. Calculations for this system are shown in Figure 3, in which $\bar{H}_1/kT_{c2}$ is plotted against solvent reduced pressure at different mole fractions between infinite dilution and 10^{-3}. Computations were performed using Eq. 9 with $x_1 \neq 0$ and the Peng-Robinson equation of state, with interaction parameters regressed from the equilibrium data of Schmitt and Reid (1985). It is clear that the infinite dilution assumption is virtually exact for $x_1 < 10^{-5}$, and constitutes a very good approximation for $x_1 < 10^{-3}$. Similar conclusions have been reached in recent studies of fugacity coefficients and solubility enhancement in dilute, binary supercritical mixtures (Debenedetti and Kumar, 1986; Debenedetti, 1987). In these cases, as well as in the present paper, the infinite dilution assumption has been used not to predict such things as the actual boundaries of the retrograde region, but to highlight the essential physics underlying the phenomena under consideration.

Central to a mechanistic interpretation of the behavior discussed so far is the idea of cluster formation (Debenedetti, 1987). We introduce the basic concepts and definitions below.

Table 1. Exponents for Partial Molar Enthalpy and Energy

	Classical	Nonclassical*
$\left[\frac{\bar{H}_1^\infty}{\delta}, \frac{\bar{U}_1^\infty}{\delta}\right](t = 0)$	$\sim\lvert p\rvert^{-2/3}$	$\sim\lvert p\rvert^{-3.8/4.8}$
$\left[\frac{\bar{H}_1^\infty}{\delta}, \frac{\bar{U}_1^\infty}{\delta}\right](t = 0)$	$\sim\eta^{-2}$	$\sim\lvert\eta\rvert^{-3.8}$
$\left[\frac{\bar{H}_1^\infty}{\delta}, \frac{\bar{U}_1^\infty}{\delta}\right](\eta = 0)$	$\sim\lvert t\rvert^{-1}$	$\sim\lvert t\rvert^{-1.24}$
$\left[\frac{\bar{H}_1^\infty}{\delta}, \frac{\bar{U}_1^\infty}{\delta}\right](\eta = 0)$	$\sim\lvert p\rvert^{-1}$	$\sim\lvert p\rvert^{-1.24}$
$\left[\frac{\bar{H}_1^\infty}{\delta}, \frac{\bar{U}_1^\infty}{\delta}\right](p = 0)$	$\sim\eta^{-2}$	
$\left[\frac{\bar{H}_1^\infty}{\delta}, \frac{\bar{U}_1^\infty}{\delta}\right](p = 0)$	$\sim\lvert t\rvert^{-2/3}$	

*$K_T(\eta = 0) \sim |t|^{-1.24}$ (Chang et al., 1984)
$p(t = 0) \sim \eta^{4.8}$ (Levelt Sengers et al., 1986c)

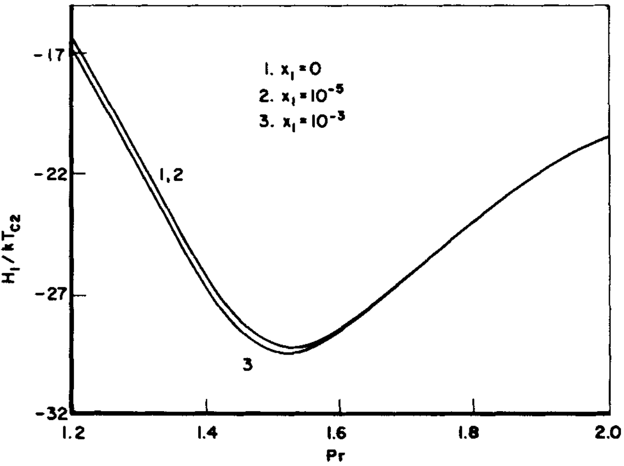

Figure 3. Behavior of acridine partial molar enthalpy in supercritical carbon dioxide at various mole fractions, calculated with the Peng-Robinson equation of state.
$T = 328$ K

The Cluster Concept: Definition and Limitations

That a pure solid can dissolve into a supercritical fluid with an exothermicity arbitrarily higher (in magnitude) than its heat of sublimation is indicative of unusual association effects in the fluid phase. We refer to this phenomenon as clustering.

Given an infinitely dilute binary mixture, the cluster size ξ_c is defined as the excess number of solvent molecules surrounding isolated solute molecules with respect to a uniform distribution at the prevailing density

$$\xi_c = \rho \int (g_{21}^{\infty} - 1)\, d^3r \tag{25}$$

where ρ is the solvent number density and g_{21}^{∞} is the unlike pair correlation function at infinite dilution. Invoking the normalization condition for g in the grand canonical ensemble (Kirkwood and Buff, 1951; Debenedetti, 1987), we can also write

$$\xi_c = \lim_{x_1 \to 0} \frac{\langle \delta N_1 \delta N_2 \rangle}{\langle N_1 \rangle} \tag{26}$$

where δN_i is an instantanous fluctuation in the number of species i molecules within a fixed volume containing, on average, $\langle N_1 \rangle$ solute molecules, and $\langle\ \rangle$ denotes thermodynamic averaging within said volume. Equation 26 therefore expresses the cluster size as a normalized measure of statistical correlations between solute and solvent concentration fluctuations. Similar ideas have recently been invoked by Kim and Johnston (1987) to quantify the difference between local and bulk densities in dilute supercritical systems.

The statistical nature of the cluster concept acquires mechanistic significance in the case of dilute near-critical systems, where $|\xi_c|$ becomes very large. In order to understand the physical basis for this increase in $|\xi_c|$, consider the addition of a solute molecule to a pure solvent in the vicinity of the latter's critical point, at constant temperature and volume (Wheeler, 1972). This addition process will lead to a pressure decrease if solute-solvent interactions are strongly attractive, and to a pressure increase if the interactions are either repulsive or weakly attractive. If the addition is now isobaric, the volume will have to change, decreasing for strongly attractive interactions (pressure decrease upon isochoric solute addition), and increasing for repulsive or weakly attracting interactions (pressure increase upon isochoric solute addition). These volume changes will become progressively larger as the solvent's compressibility increases in the vicinity of the critical point.

The macroscopic manifestation of these volume changes at infinite dilution are the experimentally measurable solute partial molar volumes. Clustering is the physical mechanism through which these volume changes occur. For strongly attractive interactions, the volume contraction occurs through the "collapse" of solvent molecules around each solute molecule, and $\xi_c \to +\infty$ as $\bar{V}_1^{\infty} \to -\infty$ (negative divergence). This is the behavior observed by Eckert et al. (1983, 1986) in their pioneering measurements of partial molar volumes of infinitely dilute nonvolatile organic solutes in supercritical solvents. For repulsive interactions, the volume expansion occurs through the formation of an excluded volume region around solute molecules, and $\bar{V}_1^{\infty} \to +\infty$ (positive divergence). This appears to be the behavior observed by Khazanova and Sominskaya (1968) in their study of the ethane-CO_2 system.

It is possible to endow the preceding arguments with quantitative precision by invoking the relationship between $\bar{V}_1^{\infty}$ and ξ_c (Debenedetti, 1987), the derivation of which we now outline. We first write

$$\bar{V}_1\rho = \left[\frac{\langle(\delta N_2)^2\rangle}{\langle N_2\rangle} - \frac{\langle \delta N_1 \delta N_2\rangle}{\langle N_1\rangle}\right] \cdot \left[x_1\frac{\langle(\delta N_2)^2\rangle}{\langle N_2\rangle} - 2x_1\frac{\langle \delta N_1 \delta N_2\rangle}{\langle N_1\rangle} + (1-x_1)\frac{\langle(\delta N_1)^2\rangle}{\langle N_1\rangle}\right]^{-1} \tag{27}$$

which is simply the fluctuation-explicit form of the Kirkwood-Buff relationship for the partial molar volume of a component in a (binary) mixture (Kirkwood and Buff, 1951). Equation 27 is of general applicability, and is not dependent upon the assumption of pairwise additivity of intermolecular or interatomic potentials. Upon taking the infinite dilution limit, we obtain

$$\bar{V}_1^{\infty}\rho = \rho k T K_T - \xi_c \tag{28}$$

where ρ and K_T are now solvent properties, and we have used the following infinite dilution fluctuation limits (Debenedetti, 1987)

$$\lim_{x_1 \to 0} \frac{\langle(\delta N_2)^2\rangle}{\langle N_2\rangle} = \rho k T K_T \tag{29}$$

$$\lim_{x_1 \to 0} \frac{\langle(\delta N_1)^2\rangle}{\langle N_1\rangle} = 1 \tag{30}$$

$$\lim_{x_1 \to 0} \frac{\langle \delta N_1 \delta N_2\rangle}{\langle N_1\rangle} = \xi_c \tag{26}$$

Equation 29 is a well-known result of the theory of fluctuations (Landau and Lifshitz, 1980), and relates density fluctuations to a substance's compressibility. Equation 30 follows from the fact that fluctuations of noninteracting particles ($x_1 \to 0$) obey Poisson's distribution (Chandrasekhar, 1943; Sciamanna and Prausnitz, 1987; Debenedetti, 1987), which is characterized by the fact that mean and variance are equal to one another; this is precisely what Eq. 30 says. In deriving Eq. 28 from the Kirkwood-Buff expression, we have considered the limit $x_1 \to 0$, $\langle N_1 \rangle$ finite. This corresponds to the limit of noninteracting solute molecules in a macroscopic system (for example, 10^6 solute molecules in 25 cm^3 of an ideal gas mixture at 300 K and 1 bar, in which case $x_1 = 1.66 \times 10^{-15}$, $\langle N_1 \rangle = 10^6$). Because the compressibility term in Eq. 28 is positive, this relationship shows that clustering is necessary for negatively diverging solute partial molar volumes at infinite dilution. Equation 28 has been used recently (Debenedetti, 1987) to calculate cluster sizes from measurements of $\bar{V}_1^{\infty}$ in supercritical mixtures (Eckert et al., 1986), as well as to explain solubility enhancement in such systems from a molecular perspective.

Behavior of $\bar{H}_1^{\infty}$: Molecular Interpretation

It follows from Eq. 28 that

$$\xi_c = K_T(\rho k T - \delta) \tag{31}$$

or, equivalently,

$$\xi_c = \bar{V}_1^\infty \left(\frac{\rho^2 kT}{\delta} - \rho \right) \tag{32}$$

For negatively diverging systems ($\delta < 0$, $\bar{V}_1^\infty \rightarrow -\infty$, $\bar{H}_1^\infty \rightarrow -\infty$), therefore,

$$\xi_c \sim K_T \sim |\bar{V}_1^\infty| \sim |\bar{H}_1^\infty| \tag{33}$$

whereas for positively diverging systems ($\delta > 0$, $\bar{V}_1^\infty \rightarrow +\infty$, $\bar{H}_1^\infty \rightarrow +\infty$),

$$\xi_c \sim K_T \sim \bar{V}_1^\infty \sim \bar{H}_1^\infty \tag{34}$$

but the sign of ξ_c is not prescribed *a priori* for the latter case. The systems of interest in supercritical extraction are all negatively divergent and we focus our attention on this situation of practical interest (if $\bar{V}_1^\infty \rightarrow +\infty$, solubility will be depressed and not enhanced as the pressure is increased at constant temperature.)

Equation 33 means that the divergence of $\bar{H}_1^\infty$ is simply the macroscopically measurable thermal effect associated with cluster formation. For negatively diverging systems, exothermicity occurs as the result of the "condensation" of an arbitrarily large number of solvent molecules around solute molecules, and $\bar{H}_1^\infty$ is necessarily large and negative. Central to these arguments is the fact that the macroscopically measurable diverging quantities ($\bar{V}_1^\infty$, $\bar{H}_1^\infty$) increase as a result of the growth in the correlation length that characterizes strongly fluctuating systems. Consequently, the soundness of the proposed clustering mechanism hinges upon the existence of a strong correlation between diverging observables and cluster size. If, in other words, $\bar{H}_1^\infty$ and $\bar{V}_1^\infty$ are the macroscopic manifestations of the "condensation" of solvent molecules, they should both increase in magnitude in direct proportion to cluster size. Equations 9, 31, and 32 allow the quantitative verification of this picture. We consider classical behavior first.

Figure 4 shows the relationship between $\bar{H}_1^\infty / kT_{c2}$ and ξ_c, calculated by means of the van der Waals equation with van der Waals 1 mixing rules and zero interaction parameter. Arrows indicate the direction of increasing pressure, the low-pressure limit being $(0, 5Tr/2)$. The proportionality between $\bar{H}_1^\infty$ and ξ_c is evident. Note that the cluster size by itself cannot (and does not) determine $\bar{H}_1^\infty$, since a given ξ_c value corresponds to more than one thermodynamic state. Qualitatively identical trends are shown in Figure 5 for the $\bar{V}_1^\infty$ vs. ξ_c relationship. The low-pressure limit is now $(0, +\infty)$, since $\bar{V}_1$ is kT/P in an ideal gas mixture. The loss of linearity along each isotherm is associated with the rapid change in ρ as the pressure changes in the high-compressibility region. Note that along the critical isochore the proportionality factor between ξ_c and $\bar{V}_1^\infty$ approaches the "constant" value $\rho_c^2\, kT_c/\delta - \rho_c + O(t)$. This is why the locus of extrema, Figure 5, lies along a straight line. From this, it follows that the critical isochore is also the locus of ξ_c extrema. Because of the asymptotic proportionality between $\bar{H}_1^\infty$ and $\bar{V}_1^\infty$, we expect the same conclusion to apply to the locus of $\bar{H}_1^\infty$ vs. ξ_c extrema; this is indeed the behavior shown in Figure 4.

Figure 6 shows the ξ_c vs. K_T relationship. The low-pressure limit is now $(+\infty, 0)$, since $K_T = 1/P$ for an ideal gas. All of the essential features shown in Figure 6 follow directly from Eq. 31 and are qualitatively identical to the corresponding $\bar{H}_1^\infty$ vs. ξ_c and $\bar{V}_1^\infty$ vs. ξ_c characteristics discussed above. Note, in particular, the linearity of the extrema locus (critical isochore). Classically, then, the proposed molecular picture is entirely consistent with the linearity in the relationships between macroscopically measurable diverging quantities ($\bar{V}_1^\infty$, $\bar{H}_1^\infty$) and cluster size. We stress the fact that it is only in the near-critical region where cluster size, otherwise a merely statistical concept, acquires mechanistic significance.

In order to analyze entropy effects associated with cluster formation, it is necessary to separate the ideal mixing term, which

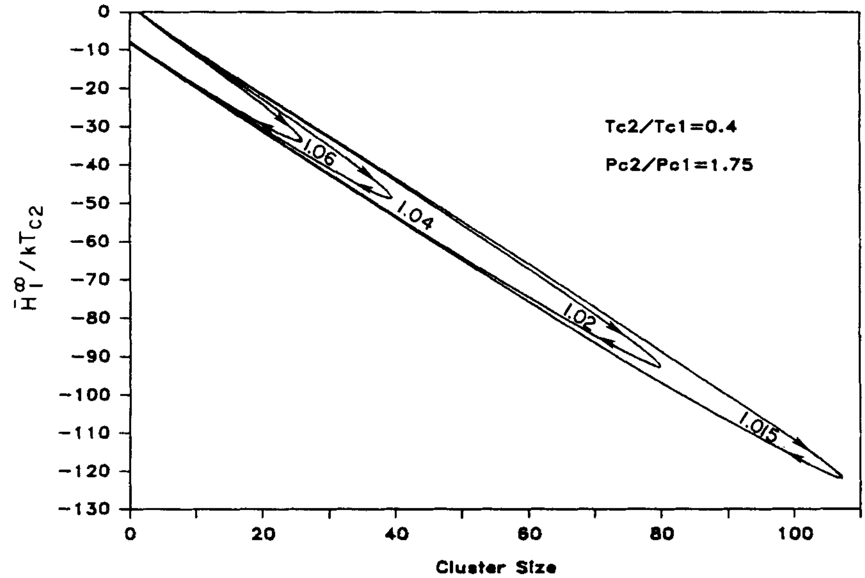

Figure 4. Relationship between infinite dilution solute partial molar enthalpy and cluster size in the supercritical region.

Curve labels are T/T_{c2} values; arrows indicate direction of increasing pressures
Van der Waals solvent, van der Waals 1 mixing rules, zero interaction coefficient

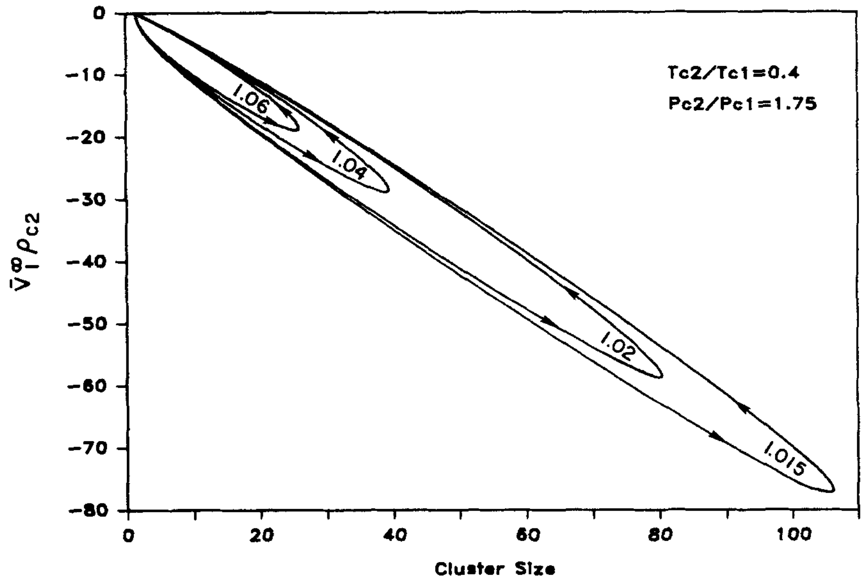

Figure 5. Relationship between infinite dilution solute partial molar volume and cluster size in the supercritical region.
Curve labels are T/T_{c2} values; arrows indicate direction of increasing pressures
Van der Waals solvent, van der Waals 1 mixing rules, zero interaction coefficient

diverges as $x_1 \rightarrow 0$. We thus write

$$\bar{S}_1^\infty - \bar{S}_1^\infty(\rho kT) = -\int_0^P \left[\left(\frac{\partial \bar{V}_1^\infty}{\partial T}\right)_P - \frac{k}{P}\right] dP + k \ln \frac{\rho kT}{P} \tag{35}$$

where $\bar{S}_1^\infty(\rho kT)$ is the solute's partial molar entropy at infinite dilution in an ideal gas mixture at the same temperature and density as the near-critical system, but as a pressure $P^* = \rho kT$. We have already shown that, if $\bar{V}_1^\infty \sim K_T$, then $\bar{V}_1^\infty \sim \bar{H}_1^\infty$. It follows from Eqs. 9 and 35, therefore, that

$$[\bar{S}_1^\infty - \bar{S}_1^\infty(\rho kT)] \sim \bar{V}_1^\infty \sim \bar{H}_1^\infty \sim \bar{U}_1^\infty \sim K_T \tag{36}$$

since it is a necessary condition for the scaling $\bar{H}_1^\infty \sim \bar{V}_1^\infty$ to be true that $(\partial \bar{V}_1^\infty / \partial T)_P$ have a stronger divergence than $\bar{V}_1^\infty$; see Eq. 9.

Equation 36 means that the purely mechanical (i.e., composition-independent) contribution to the solute's partial molar entropy, which is only due to deviations from ideal gas behavior, scales as the diverging mechanical properties. This quantity therefore becomes large (and negative) in the near-critical region, and is the macroscopic manifestation of the ordering arising as the result of the interactions between isolated solute molecules with a solvent, under conditions such that the correlation length is arbitrarily large (i.e., near the latter's critical point).

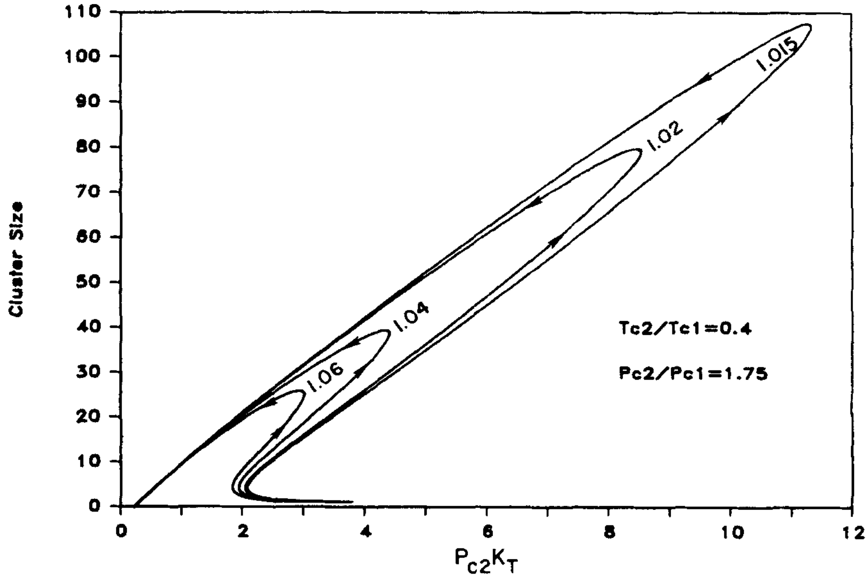

Figure 6. Relationship between cluster size and solvent compressibility in the supercritical region.
Curve labels are T/T_{c2} values; arrows indicate direction of increasing pressures
Van der Waals solvent, van der Waals 1 mixing rules, zero interaction coefficient

Cluster size calculations via classical equations of state—Figures 4, 5, 6—cannot be used arbitrarily close to the critical point, since they fail to take into account long-range density fluctuations, the characteristic wavelength of which (the correlation length r_c) diverges at the critical point. To incorporate this phenomenon into our treatment, we consider (Landau and Lifshitz, 1980) Helmholtz energy changes associated with number density fluctuations within an arbitrary control volume, in the vicinity of the solvent's critical point,

$$\Delta \underline{A} = \int (a - \langle a \rangle)\, d^3 r \tag{37}$$

where a and $\langle a \rangle$ are the instantaneous (fluctuating) and equilibrium Helmholtz energy densities, respectively, and integration is over the control volume. The free energy density expansion reads

$$a - \langle a \rangle = \mu(\rho - \langle \rho \rangle) + \frac{1}{2\langle \rho \rangle}\left(\frac{\partial P}{\partial \rho}\right)_T (\rho - \langle \rho \rangle)^2 + h\left[\frac{\partial(\rho - \langle \rho \rangle)}{\partial \underset{\sim}{r}}\right]^2 + \cdots \tag{38}$$

where the last term ($h > 0$) is the leading contribution to free energy changes associated with long-range density fluctuations (Landau and Lifshitz, 1980). If we now Fourier-analyze the instantaneous density fluctuation, $\Delta\rho$ $(\equiv \rho - \langle \rho \rangle)$,

$$\Delta\rho(\underset{\sim}{r}) = \sum_{\underset{\sim}{k}} \Delta\rho(\underset{\sim}{k})\, e^{i\underset{\sim}{k}\cdot\underset{\sim}{r}} \tag{39}$$

we obtain, upon performing the volume integral,

$$\Delta \underline{A} = \frac{\underline{V}}{2} \sum_{\underset{\sim}{k}} \left[\frac{1}{\langle \rho \rangle}\left(\frac{\partial P}{\partial \rho}\right)_T + 2hk^2\right] |\Delta\rho(\underset{\sim}{k})|^2 \tag{40}$$

or, equivalently,

$$\langle |\Delta\rho(\underset{\sim}{k})|^2 \rangle = \frac{kT}{\underline{V}\left[\frac{1}{\langle \rho \rangle}\left(\frac{\partial P}{\partial \rho}\right)_T + 2hk^2\right]} \tag{41}$$

where $\underline{V}$ is the control volume, and we have used a weighting factor $\exp(-\beta\Delta\underline{A})$ to quantify fluctuation probabilities. We now introduce the density-density correlation function G (Stanley, 1971; $G \sim g_{22}^{\infty} - 1$),

$$G(r) \equiv \langle \Delta\rho(\underset{\sim}{r}_1)\Delta\rho(\underset{\sim}{r}_2)\rangle, \quad r \equiv |\underset{\sim}{r}_1 - \underset{\sim}{r}_2| \tag{42}$$

and obtain, upon substituting Eq. 39 into the above definition,

$$G = \sum_{\underset{\sim}{k}} \langle |\Delta\rho(\underset{\sim}{k})|^2 \rangle e^{i\underset{\sim}{k}\cdot\underset{\sim}{r}} \tag{43}$$

Substituting Eq. 41 into Eq. 43 and Fourier-inverting, we obtain (Landau and Lifshitz, 1980; Debenedetti and D'Antonio, 1986)

$$\beta G(r) = \frac{1}{8\Pi h r} \exp(-r/r_c) \tag{44}$$

where r_c, the correlation length, characterizes the distances over which fluctuations are correlated, and is given by

$$r_c = \left[\frac{2h}{\frac{1}{\langle \rho \rangle}\left(\frac{\partial P}{\partial \rho}\right)_T}\right]^{1/2} = \left(\frac{2h\rho_c}{3\beta\eta^2 + \gamma t}\right)^{1/2} \tag{45}$$

or, equivalently, along the critical isochore,

$$r_c \sim t^{-1/2} \quad (t > 0) \tag{46}$$

Although we have incorporated density fluctuations into the picture, the above treatment is still classical, since we have assumed the validity of the analytical pressure expansion, Eq. 11, close to criticality. In general, then, along the critical isochore we define the critical exponents γ, ν,

$$K_T \sim t^{-\gamma} \tag{47}$$

$$r_c \sim t^{-\nu} \tag{48}$$

where $\gamma = 1$, $\nu = 1/2$ for classical, mean field behavior (Landau and Lifshitz, 1980). It follows from Eq. 44 that, close to criticality ($r_c \rightarrow \infty$)

$$g_{22}^{\infty}(r) \sim r^{-1} \quad \text{(classical)} \tag{49}$$

or, in general, for nonclassical behavior

$$g_{22}^{\infty}(r) \sim r^{-(1+\zeta)} \tag{50}$$

where ζ is the critical exponent characterizing the decay of the correlation function (Landau and Lifshitz, 1980). We now write (Neece, 1967; Clark, 1968; and Eq. 31),

$$\xi_c \sim \langle \delta N_1 \delta N_2 \rangle \sim K_T \tag{51}$$

and, therefore,

$$\xi_c \sim r_c^{\gamma/\nu} \sim r_c^2 \quad \text{(classical)} \tag{52}$$

or, equivalently, for classical behavior,

$$\gamma = 2\nu \tag{53}$$

which is, of course, consistent with the well-known critical exponent relationship (Landau and Lifshitz, 1980)

$$\nu(2 - \zeta) = \gamma \tag{54}$$

It follows from Eq. 52 and the definition of ξ_c, that

$$g_{21}^{\infty}(r) \sim r^{-(1+\zeta)} \sim r^{-1} \quad \text{(classical)} \tag{55}$$

In the near-critical region, therefore, the decay of all correlation functions (g_{21}, g_{22}) shows the same extremely slow radial decay rate characteristic of strongly fluctuating systems. There is, however, a fundamental difference between solvent-solvent and solute-solvent interactions in near-critical systems. The former are necessarily reversible, and the large aggregates that are continuously being formed on every length scale up to r_c are simultaneously disappearing at the same rate. This is equivalent to saying that a substance can exist at its critical point indefinitely, since the latter is a stable limit of stability. Alternately, the reversibility of solvent-solvent aggregates follows from the fact that there can be no net heat effects or volume changes associated with the isobaric, isothermal addition of more solvent molecules to a pure solvent. In the case of solute-solvent interactions, on the other hand, clustering in near-critical systems is an irreversible phenomenon, the macroscopic manifestation of which are $\overline{H}_1^\infty$ and $\overline{V}_1^\infty$. Solute molecules are literally nucleation sites on which an increasing number of solvent molecules condenses as criticality is approached (negative divergence). The arbitrarily large length scale over which this phenomenon occurs (r_c) is solute-independent and is only a function of the proximity to the solvent's critical point.

The particular nature of clustering in near-critical systems, finally, can be seen from the fact that

$$\xi_c \sim r_c^{\gamma/\nu} \sim r_c^2 \quad \text{(classical)} \tag{56}$$

This means that the "condensation" phenomenon described above cannot be pictured as a simple filling of space with an increasing number of molecules (in which case one would expect the cluster size to scale as the cube of a characteristic length). Instead, near-critical clusters exhibit fractal geometry.

Conclusions

The clustering mechanism is consistent with experimentally observed pressure (Debenedetti, 1987) and temperature-dependent behavior in dilute supercritical mixtures. According to this model, retrograde solubility is a macroscopic manifestation of the exothermicity accompanying the condensation of large numbers of solvent molecules around solute molecules. The latter phenomenon occurs as a consequence of the increase in the correlation length in the vicinity of a solvent's critical point. The proportionality between partial molar properties and cluster size is consistent with the "condensation" mechanism. Except for determining the sign of the solute's partial molar volume and enthalpy divergence, differences among solutes become progressively irrelevant in the vicinity of a given solvent's critical point. In this region, the locus along which energy effects associated with cluster formation are maximized approaches the solvent's critical isochore.

The mechanistic interpretation of supercritical behavior addressed in this paper and in a recent publication (Debenedetti, 1987) suggests a number of interesting questions that warrant further investigation. Among these, we mention the spectroscopic determination of cluster sizes, the measurement of solute partial molar enthalpies in highly dilute supercritical mixtures, the calculation of cluster size distributions, and the investigation of cluster formation kinetics and cluster stability. Such studies will contribute toward a more fundamental, molecular-based understanding of the properties of supercritical mixtures.

Acknowledgment

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Notation

A = Helmholtz energy, $ML^2 \cdot t^{-2}$
a = Helmholtz energy density, $ML^{-1} \cdot t^{-2}$
G = density-density correlation function, L^{-6}
g = pair correlation function
H = enthalpy, $ML^2 \cdot t^{-2}$
h = coefficient in Helmholtz energy density expansion, $ML^7 \cdot t^{-2}$
K_T = isothermal compressibility, $M^{-1}t^2L$
k = Boltzmann's constant, $ML^2 \cdot t^{-2} \cdot \theta^{-1}$
$\underset{\sim}{k}$ = reciprocal length, L^{-1}
N = number of molecules
P = pressure, $Mt^{-2} \cdot L^{-1}$
p = pressure difference, $Mt^{-2} \cdot L^{-1}$
r = radial coordiante, L
r_c = correlation length, L
S = entropy, $ML^2 \cdot t^{-2} \cdot \theta^{-1}$
T = temperature, θ
t = temperature difference, θ
U = energy, $ML^2 \cdot t^{-2}$
V = volume, L^3
x = mole fraction
$\langle\,\rangle$ = thermodynamic average

Greek letters

α = coefficient in pressure expansion, $Mt^{-2} \cdot L^{-1} \cdot \theta^{-1}$
α_p = thermal expansion coefficient, θ^{-1}
β = $1/kT$, $M^{-1} \cdot L^{-2} \cdot t^2$, and coefficient in pressure expansion, $ML^8 \cdot t^{-2}$
γ = coefficient in pressure expansion, $ML^2 \cdot t^{-2} \cdot \theta^{-1}$, and compressibility critical exponent
δ' = coefficient in pressure expansion, $ML^{-1} \cdot t^{-2}$
ϵ = coefficient in pressure expansion, $ML^{-1} \cdot t^{-2} \cdot \theta^{-1}$
λ = coefficient in pressure expansion, $ML^2 \cdot t^{-2}$
ζ = pair correlation function critical exponent
η = density difference, L^{-3}
μ = chemical potential, $ML^2 \cdot t^{-2}$
ν = correlation length critical exponent
ξ_c = cluster size
ρ = number density, L^{-3}
ϕ = fugacity coefficient

Subscripts

1 = solute
2 = solvent
c = critical property
r = reduced quantity
σ = phase equilibrium locus
$\_$ = extensive quantity
$\sim$ = vector quantity

Superscripts

eq = equilibrium
i = ideal gas mixture at same temperature and density as mixture
s = solid (or condensed) phase
sub = sublimation
$\hat{}$ = value of a thermodynamic property in a mixture
∞ = solute property at infinite dilution
$\circ$ = solvent property at infinite dilution
$\bar{}$ = partial molar (or molecular) quantity
$*$ = ideal gas property

Appendix A

We first write the thermodynamic identity

$$\left(\frac{\partial H}{\partial x_1}\right)_{T,P} = \left[T\left(\frac{\partial P}{\partial T}\right)_{V,x_1} - \frac{1}{K_T}\right]\left(\frac{\partial V}{\partial x_1}\right)_{T,P} + \left(\frac{\partial H}{\partial x_1}\right)_{T,V} \tag{A1}$$

where H and V are molar (or molecular) quantities. For an infinitely dilute mixture in the vicinity of a solvent's critical point ($K_T^{-1} \rightarrow 0$),

$$\left(\frac{\partial H}{\partial x_1}\right)_{T,P}^{\infty} \approx T\left(\frac{\partial P}{\partial T}\right)_{\sigma}\left(\frac{\partial V}{\partial x_1}\right)_{T,P}^{\infty} + \left(\frac{\partial H}{\partial x_1}\right)_{T,V}^{\infty} \tag{A2}$$

where σ denotes the solvent's coexistence locus. We now introduce the notation

$$\Delta\psi \equiv \psi(\rho, T, x_1) - \psi^i(\rho, T, x_1) \tag{A3}$$

where ψ is any intensive property, and superscript i denotes an ideal gas mixture at the same density, temperature, and composition as the mixture under study ($P^i = \rho k T$). Then,

$$\left[\frac{\partial(\Delta U)}{\partial x_1}\right]_{T,V}^{\infty} = \left[\frac{\partial(\Delta A)}{\partial x_1}\right]_{T,V}^{\infty} + T\left[\frac{\partial(\Delta S)}{\partial x_1}\right]_{T,V}^{\infty} \tag{A4}$$

or, explicitly,

$$\left[\frac{\partial(\Delta U)}{\partial x_1}\right]_{T,V}^{\infty} = (\overline{H}_1^{\infty} - \overline{H}_2^{0}) - (H_1^* - H_2^*) - T\left(\frac{\partial P}{\partial T}\right)_{V,x_1}^{\infty}(\overline{V}_1^{\infty} - \overline{V}_2^{0}) \tag{A5}$$

where superscript 0 denotes the infinite dilution limit ($x_1 \rightarrow 0$) as applied to solvent properties, and H_i^* is species i's ideal-gas enthalpy (per molecule) at the prevailing temperature. Arbitrarily close to the solvent's critical point [$(\partial P/\partial T)_{V,x_1}^{\infty} \rightarrow (\partial P/\partial T)_{\sigma}$],

$$\left(\frac{\partial H}{\partial x_1}\right)_{T,V}^{\infty} = \left(\frac{\partial U^i}{\partial x_1}\right)_{T,V}^{\infty} + V\left(\frac{\partial P}{\partial x_1}\right)_{T,V}^{\infty} + (\overline{H}_1^{\infty} - \overline{H}_2^{0}) - (H_1^* - H_2^*) - T\left(\frac{\partial P}{\partial T}\right)_{\sigma}(\overline{V}_1^{\infty} - \overline{V}_2^{0}) \tag{A6}$$

For classical behavior, ΔA and its derivatives (in particular, $\Delta P = P - \rho k T$) are analytic functions of T, ρ, x_1 in the immediate vicinity of the solvent's critical point. It follows from Eq. 11 that $(\partial P/\partial x_1)_{T,V}^{\infty}$ ($\equiv \delta$) is finite. Thus, the finiteness of $(\partial H/\partial x_1)_{T,V}^{\infty}$, and the scaling $\overline{H}_1^{\infty} \sim \overline{V}_1^{\infty}$ are not independent, since one implies the other and vice versa.

The finiteness of $(\partial H/\partial x_1)_{T,V}^{\infty}$, in the near-critical region, therefore cannot be invoked to prove the scaling $\overline{H}_1^{\infty} \sim \overline{V}_1^{\infty}$ via Eq. A2. This is, however, precisely the argument used by Levelt Sengers et al., (1986a). We have thus shown that their derivation is circular.

Appendix B

The solute's partial molar energy at infinite dilution is given by

$$\overline{U}_1^{\infty}(T, P) = \lim_{x_1 \rightarrow 0} \cdot [\underline{U}(N_2, N_1 + 1, T, P) - \underline{U}(N_2, N_1, T, P)] \tag{B1}$$

and, therefore,

$$\begin{aligned}\overline{\underline{U}}_1^{\infty}(T, P) = \lim_{x_1 \rightarrow 0} & \cdot \{[\underline{U}(N_2, N_1 + 1, T, P) - \underline{U}(N_2, N_1 + 1, T, P^*)] \\ & - [\underline{U}(N_2, N_1, T, P) - \underline{U}(N_2, N_1, T, P^*)] \\ & + [\underline{U}(N_2, N_1 + 1, T, P^*) - \underline{U}(N_2, N_1, T, P^*)]\}\end{aligned} \tag{B2}$$

where P^* is a pressure low enough for the mixture to behave as an ideal gas mixture (the derivation is independent of the value of P^*). Equation B2 can be rewritten as

$$\overline{U}_1^{\infty}(T, P) = \int_{P^*}^{P} \lim_{x_1 \rightarrow 0} \cdot [\underline{V}(PK_T - T\alpha_P)_{N_1+1} - \underline{V}(PK_T - T\alpha_P)_{N_1}]\, dP + \frac{nkT}{2} \tag{B3}$$

where n is the number of degrees of freedom, and we have not included differences in ideal gas energy among chemically distinct species, since they represent additive constants of no consequence in the study of nonreactive mixtures. The compressibility integral can be expressed as ($N = N_1 + N_2$),

$$-\int_{P^*}^{P} P\left(\frac{\partial \underline{V}}{\partial P}\right)_{T,N} dP = -\int_{\underline{V}^*}^{V} P\,d\underline{V} = \int_{P^*}^{P} \underline{V}\,dP + NkT - P\underline{V} \tag{B4}$$

so that, finally,

$$\overline{U}_1^{\infty}(T, P) = \frac{5kT}{2} - P\overline{V}_1^{\infty} + \int_0^P \left[\overline{V}_1^{\infty} - T\left(\frac{\partial \overline{V}_1^{\infty}}{\partial T}\right)_P\right] dP \tag{B5}$$

and, therefore,

$$\overline{H}_1^{\infty}(T, P) = \frac{5kT}{2} + \int_0^P \left[\overline{V}_1^{\infty} - T\left(\frac{\partial \overline{V}_1^{\infty}}{\partial T}\right)_P\right] dP \tag{B6}$$

where we have assumed molecules with translational degrees of freedom only, and we have taken the limit $P^* \rightarrow 0$ (note that since the integrand vanishes for an ideal gas mixture, the actual value of P^* is irrelevant).

We now show that, for classical behavior, $\overline{H}_1^{\infty} \sim \overline{U}_1^{\infty}$ (with a positive proportionality constant). Using the pressure expansion, Eq. 11, and the thermodynamic relationship

$$\left(\frac{\partial \overline{V}_1^{\infty}}{\partial T}\right)_P = \left(\frac{\partial \overline{V}_1^{\infty}}{\partial T}\right)_{\rho} - \rho K_T\left(\frac{\partial \overline{V}_1^{\infty}}{\partial \rho}\right)_T\left(\frac{\partial P}{\partial T}\right)_{\rho}$$

we obtain

$$\overline{V}_1^{\infty} = \frac{\delta\rho_c^{-2}}{3\beta\eta^2 + \gamma t} \tag{B7}$$

$$\left(\frac{\partial \overline{V}_1^{\infty}}{\partial T}\right)_P = \frac{\delta\rho_c^{-2}(6\alpha\beta\eta - \gamma^2 t)}{(3\beta\eta^2 + \gamma t)^3} \tag{B8}$$

Substituting into Eq. B5 we obtain, along the critical isotherm,

$$\bar{U}_1^\infty \sim \frac{\delta \rho_c^{-2}}{3\beta^{1/3}} (\alpha T_c - P)|p|^{-2/3} \tag{B9}$$

For a van der Waals fluid $\alpha T_c - P = 4P_c - P$ (i.e., $\alpha T_c - P > 0$ in the near-critical region). Thus, $\bar{U}_1^\infty/\delta \sim \bar{H}_1^\infty/\delta$, with a positive proportionality constant. Identical considerations apply when other paths (critical isochore, critical isobar, etc.) are considered.

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