Solubility in Binary Mixtures at the Immiscibility Critical Point

It is shown that the solubility of organic solids in binary mixtures of partially miscible liquids is singular at the immiscibility critical point. The theoretically predicted maximum of solubility in the vicinity of the critical point is found experimentally. The effect is similar to the phenomenon observed near the gas-liquid critical point. The similarity of these two critical phenomena may have interesting technical applications and may provide guidelines for identifying promising new solvents for separation processes.

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Introduction

It was realized long ago that the singularities of thermodynamic properties of different media are reflected as anomalies in parameters determining physicochemical properties taking place in these media. For example the Arrhenius plots, characteristic of surface catalyzed reactions (Hedval, 1943) or adsorption-desorption kinetics (Voorhove, 1973) in which the substrate undergoes ferromagnetic transition, demonstrate singularities in the vicinity of the Curie point. Some of the thermodynamic anomalies at the critical point of fluids have been summarized by Greer et al. (1981).

The superior solvent power of fluids in the vicinity of their gas-liquid critical point also was realized long ago. This effect has in recent years received considerable attention, both from theoretical and experimental points of view (Paulaitis et al., 1983a, b). Several chemical processes have been patented that utilize some of the singular thermodynamic properties of those fluids as solvents. The main drawback in using supercritical fluids is, however, the necessity of working under relatively high pressures (Penninger et al., 1985).

It is well known that the singularities of thermodynamic properties of mixtures of partially miscible fluids in the vicinity of the immiscibility critical point are similar to the singularities of the fluids near the gas-liquid critical point. If such solvent pairs have properties at their critical point of immiscibility similar to supercritical fluids, this could lead to a wide range of interesting applications, for example, in separation processes. In this work we present a theoretical and experimental investigation of the effect of the solubility enhancement in critical binary mixtures.

Theory

Consider a solid (solute) in contact with a homogeneous binary mixture (solvent) at temperature $T > T_c$ or $T < T_c$ for the upper and lower critical points, respectively. The number density of a solute in a liquid phase is denoted as n, and N_1 and N_2 stand for the number densities of the components of the binary mixture (solvent). In the present work we consider the case of weak solution so that

$$n \ll N_1 + N_2 = N = \text{constant} \tag{1}$$

The thermodynamic potential Φ of the solution is a homogeneous function of n, N_1, N_2 that satisfies the following homogeneity relation (Landau and Lifshitz, 1983):

$$\Phi(N_1, N_2, n, P, T) = a^{-1}\Phi(aN_1, aN_2, an, P, T)$$

Thus the thermodynamic potential can be written if we set the Boltzmann constant $k_B = 1$:

$$\Phi = \mu_1 N_1 + \mu_2 N_2 + nT \ln\left[\frac{n}{N} f\left(\frac{N_1}{N_2}, P, T\right)\right] \tag{2}$$

where μ_1 and μ_2 are the chemical potentials of pure liquids involved in the critical mixture. In the limit $N_1 \rightarrow 0$ Eq. 2 is equivalent to the formula for the thermodynamic potential of a one-component solvent in contact with the solid (solute) derived in Landau and Lifshitz (1983).

Using the definition

$$T \ln f\left(\frac{N_1}{N_2}, P, T\right) \equiv \Psi(x_1, P, T) \tag{3}$$

where we have introduced a new variable

$$x_1 = \frac{N_1}{N} = \frac{N_1}{N_1 + N_2} \tag{4}$$

the thermodynamic potential of the solution can be represented in a convenient form:

$$\Phi = \mu_1 N_1 + \mu_2 N_2 + nT \ln\left(\frac{n}{eT}\right) + n\Psi(x_1, P, T) \tag{5}$$

and thus the chemical potential of a solute in a liquid phase, which we denote by superscript 1, is:

$$\mu^1 = \frac{\partial\Phi}{\partial n} = T \ln\frac{n}{T} + \Psi(x_1, P, T)$$

The chemical potential of a solid at a temperature much larger than the Debye temperature is (Landau and Lifshitz):

$$\mu^2 = \epsilon_0 - 3\nu T \ln\frac{\omega}{T}$$

where ϵ_0 is the energy of a molecule of a solid in an equilibrium position at $T = 0$, ν denotes the number of molecules per unit cell, and the characteristic frequency ω is defined in Landau and Lifshitz (1983).

In thermodynamic equilibrium $\mu^1 = \mu^2$ and thus we derive readily the relation for the solute concentration in the solution:

$$n(x_1) \approx \exp\left(\frac{\epsilon_0 - \Psi(x_1, P, T)}{T}\right) \tag{6}$$

Equation 6 gives the concentration of the solution as a function of the fluctuating order parameter x_1. Expanding function Ψ in Eq. 6 in powers of fluctuations δ from the mean value $\bar{x}$ and performing the Gaussian averaging over the fluctuating field δ, one readily derives:

$$\bar{n} \approx \exp\left(\frac{\alpha^2\bar{\delta}^2}{4T^2}\right) \tag{7}$$

where

$$\alpha = \frac{\partial\Psi(\bar{x}, P, T)}{\partial x_1}$$

In the vicinity of the critical point the mean square of the order parameter $\bar{\delta}^2$ can be expressed through susceptibility χ and characteristic volume $V_s \approx \xi^3$ where the correlation length $\xi = \xi_0\tau^{-\nu}$:

$$\bar{\delta}^2 = \frac{T_c\chi}{V_s} \approx \tau^{3\nu-\gamma} f\left(\frac{c}{\tau^\beta}\right) \tag{8}$$

where

$$\tau = \left|\frac{T - T_c}{T_c}\right|; \quad c = |\bar{x} - \bar{x}_c|; \quad T_c \approx T_c(c = 0)$$

and $\bar{x}_c$ denotes the critical composition.

In the vicinity of the critical point the critical exponents are: $\gamma \approx 1.23$, $\nu \approx 0.63$, and $\beta \approx 0.33$. The scaling function $f(x)$ in Eq. 8 has a maximum at $x = 0$. It has been shown by Starobinets et al. (1979) that,

$$f(x) = 1 - ax^2 + \cdots \tag{9}$$

where the universal coefficient $a \approx 6$. Far from the critical point where $\tau \geq 1$ the function f rapidly goes to zero.

Substituting Eqs. 8 and 9 into Eq. 7, we find that the solubility has a maximum at the critical composition $c = 0$:

$$\bar{n} \approx \exp\left(\frac{b\tau^{3\nu-\gamma} - 6\alpha^2 c^2 \tau^{3\nu-\gamma-2\beta}}{T^2}\right) \tag{10}$$

where b and α are weak functions of temperature. It should be mentioned that according to the theory of critical phenomena the following identity holds (Landau and Lifshitz, 1983):

$$3\nu - \gamma - 2\beta = 0$$

and thus the coefficient in front of c^2 in Eq. 10 is independent of τ.

Experimental Procedure

Solvent purity was: methanol, 99.9%, with traces of water (0.02%); hexane, 99%; and lutidine (2.6 dimethyl pyridine), 97%. All solvents were purchased from Aldrich Chemical Co. and used without any additional treatment. The solute anthracene was 99.9% gold label (Aldrich) purity, and anthraquinone 1-sodium sulfonate was purified by recrystallization from solution. The solutes were chosen to have little effect on the critical solution temperature (CST). The coexistence curves were determined by visual observation of the cloud point or by the disappearance of the sharp boundary between the phases upon temperature variation. The solubility of organic solids in the binary mixtures was determined as follows: Excess of the solute together with the binary mixture was placed in 20 mL vials sealed off by means of a Teflon septum and shaken for 15–18 h inside a water thermostat. The vials were then transferred to a glass thermostat for an additional 12 h. Samples were then taken inside the glass thermostat, both unfiltered and filtered by means of a 0.45μ Teflon membrane. The concentrations were determined after dilution by means of UV and visible absorption spectrophotometry. It was shown that under the above experimental conditions equilibrium was achieved, and the concentrations measured with and without the filter were in the range of experimental uncertainty. The temperature of the water thermostat was constant within ±0.5°C. The solubility of anthracene, presented in Figure 1 and expressed in units M/L, was not corrected due to the solution volume change upon variation of temperature. Each point on the solubility curve of Figure 1 represents an average of at least three independent measurements. The points of the solubility curve at 35.5°C in the figure repre-

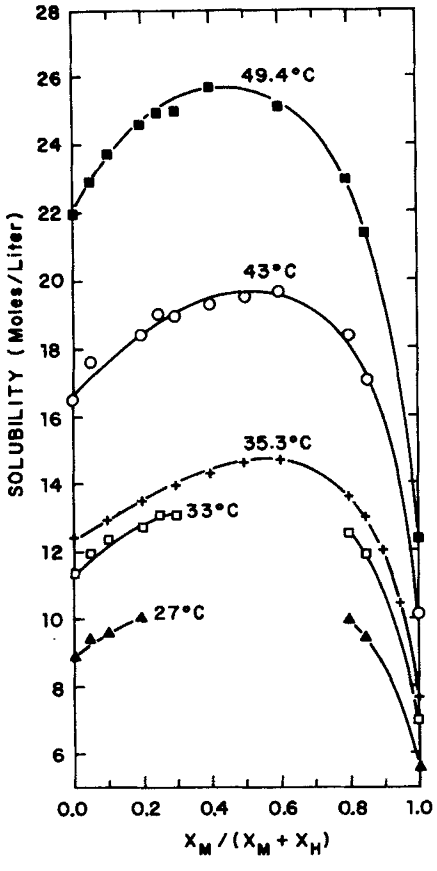

Figure 1. Solubility of anthracene in methanol (X_M)-hexane (X_H) as a function of methanol concentration.

sent an average of about 20 different measurements. The number of experiments performed with the lutidine-water system was minimal due safety considerations.

Results

The coexistence curve of the methanol-hexane mixture used in our experiments is shown in Figure 2. The critical temperature is 34.3 ± 0.2°C. This temperature is higher than that reported by Kiser et al. (1961), 33.2°C, and by Clark et al. (1986), 33.84°C.

Figure 1 describes the solubility of anthracene as a function of methanol concentration in the binary solution mixture of methanol and hexane. The solubility curves show a maximum at all temperatures studied. Similar results (not shown) were observed for phenanthrene in the same binary solution mixture. In Figure 3 we show the solubility of anthraquinone 1-sodium sulfonate in the binary mixture of lutidine (2,6 dimethyl pyridine) and water. This system has a lower immiscibility critical point (the solution mixtures split into two phases above the CST) at approximately $T_c \approx 33$°C.

As shown in Figures 1, 2, and 3, the solubility of the solutes in the two binary solution mixtures, one with an upper CST and the other with a lower CST, exhibits maxima near the corresponding immiscibility critical composition of the pure solvent mixtures. The accuracy of the thermostat used in our experiments did not allow us to test the details of the temperature dependence in the critical region.

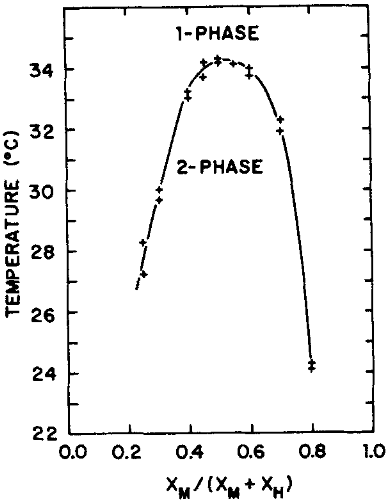

Figure 2. Mutual miscibility of methanol and hexane.

Discussion

Equation 10 explains the maximum of solubility at the critical composition $c = 0$ observed experimentally, Figures 1 and 2. It follows from Eq. 10 that the solubility of a solid in a critical mixture grows with τ as $\bar{n} \approx \exp(b\tau^{0.66})$ in the critical region, where $\tau \ll 1$. It should be mentioned, however, that at the critical point $c = 0$ and $\tau = 0$ the index of the exponent in Eq. 10 is equal to zero. On the other hand, $\bar{\delta}^2$ defined by Eq. 8 goes to zero far from the critical point where $c = O(1)$ and $\tau = O(1)$. This means that there exists a maximum of solubility in the region $0 < \tau < 1$. The phenomenological theory of critical phenomena does not allow quantitative determination of the position of this maxi-

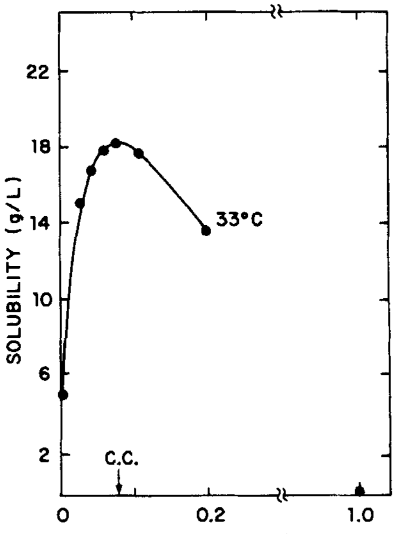

Figure 3. Solubility of anthraquinone 1-sodium sulfonate in lutidine-water as a function of lutidine concentration.

Temperature corresponds to homogeneous one-phase solution
C.C., critical composition of pure binary mixture

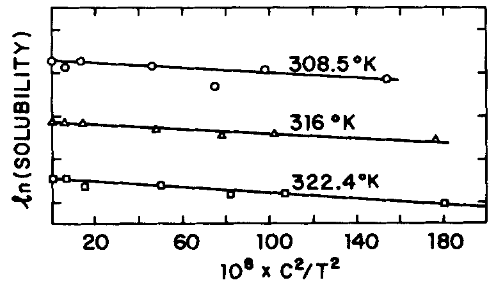

Figure 4. Solubility of anthracene in methanol-hexane as a function of C^2/T^2.

$C = C_{critical} - C$, in units of mole fraction ($C_c = 0.52$)

mum. It follows from Eq. 10 that concentration of the solute in the solvent is singular at the critical point:

$$\frac{\partial \bar{n}}{\partial T} \approx \tau^{-0.33} \tag{11}$$

which diverges when $\tau \rightarrow 0$.

According to Eq. 10,

$$\ln \bar{n} \approx F(T) - 6\alpha^2 Y^2 \tag{12}$$

where $Y = c/T$. Since α is nearly independent of temperature, $\ln \bar{n}$ is a linear function of Y^2. To test Eq. 12 we have plotted in Figure 4 our experimental data on the solubility of anthracene in methanol-hexane binary mixtures as a function of $Y^2 = c^2/T^2$.

Gordon and Scott (1952) have conducted a detailed investigation of phenanthrene solubility in a partially miscible binary mixture (methyl iodide-cyclohexane) with an upper CST at 303 K. According to their findings the maximum of phenanthrene solubility appears to be in the vicinity of the critical composition for the whole range of temperatures studied, Figure 5. We have replotted the above solubility data in Figure 6 in the coordinates of ln n as a function of Y^2. The linear dependence of $\ln \bar{n}$ on Y^2 is observed in a wide interval of variation of both c and T. It should be stressed that all data plotted in Figure 4 and 6 can be expressed in terms of the universal function.

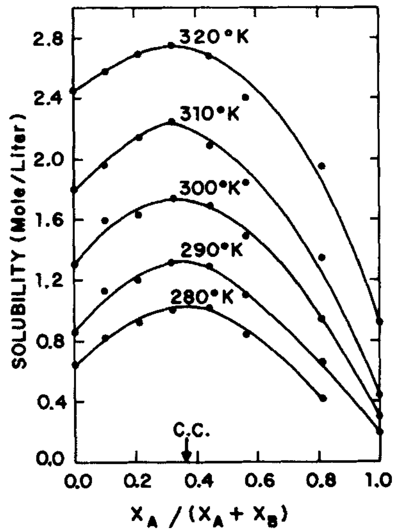

Figure 5. Solubility of phenanthrene in methyleneiodide-cyclohexane.

Temperatures correspond to homogeneous one-phase solutions
C.C., critical composition of pure binary mixture
Data from Gordon and Scott (1952)

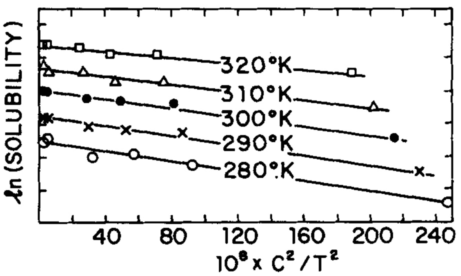

Figure 6. Solubility of phenanthrene in methyleneiodide-cyclohexane as a function of C^2/T^2.

$C = C_{critical} - C$, in units of mole fraction ($C_c = 0.37$)
Data from Gordon and Scott (1952)

$$R = \frac{\ln \bar{n} - F(T)}{6\alpha^2} \approx Y^2 \tag{13}$$

Theoretical considerations presented in this work apply to the critical region of binary mixtures where $\tau \ll 1$. For systems with critical temperature $T_c \approx 300$ K, critical fluctuations are important in a wide range of temperatures; $250 \text{ K} < T < 350\text{–}400$ K. Thus, in testing theoretical predictions of solubility in binary mixtures one must always take into consideration the details of the phase diagram and the role of critical fluctuations in the solubility process.

While these data are in good agreement with the theoretical predictions presented before, we must point out that there are alternative explanations of the maximum observed. The theory of regular solutions of Hildebrand (Hildebrand and Scott; 1964; Hildebrand *et al.*, 1970; Prausnitz et al., 1986) also predicts the existence of a solubility maximum for some solvent pairs. According to this theory the solubility of a solute is maximum if the solubility parameter of the solvent equals that of the solute. Therefore, if for a pair of initially miscible solvents one solvent has a solubility parameter larger than that of the solute, whereas the opposite holds for the second solvent, then there should be a solvent mixture with a composition such that its solubility parameter will equal that of the solute. This applies to one of our cases.

The solubility parameter of anthracene (9.9) in units of (cal/cm^3)$^{1/2}$ is lower than that of methanol (14.5) but higher than that of hexane (7.24) (Burrell, 1975; Fedors, 1974; Hansen, 1971). Thus the observed maximum in anthracene solubility in methanol-hexane can also be interpreted with this approach. However, a methanol-hexane mixture is not a regular solution. Thus the rigorous Hildebrand theory does not apply to it.

Furthermore, the data for the pure solvents and the solute by themselves do not allow reliable prediction of the solvent rate at which the maximum occurs. This was noted by Gordon and Scott (1952) and may be due to the fact that the solubility parameter of the solvent mixture and the solute interactions are hard to predict quantitatively, solely based on the properties of pure components. While there are phenomenological ways of improving the predictions (Prausnitz et al., 1986), the fact remains that the revised predictions lead, for Scott's case, to maximum near the CST. The fact that for many other solvent pairs, the maximum occurs also at the CST indicates (Stephen and Stephen, 1963) that there is no real contradiction between the two approaches and that they are not mutually exclusive. The existence and position of the CST is also a function of solvent.

More detailed studies are required in order to be able to determine the exact role of the critical fluctuations on the solubility and related phenomena. However, the suggested similarity of the singular properties of the binary mixtures and the supercritical fluids can give an impetus to the development of attractive processes such as separation in a way known for the supercritical fluids. In a recent study we have observed that the chromatographic separation of some amino acids by means of binary mixtures exhibits a maximum in separation in the vicinity of the immiscibility critical point of the binary mixture. This will be the subject of a future communication.

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