

Quantitative Analysis of Supercritical Extraction

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In this paper we report some theoretical results concerning the phenomenon of "supercritical fluid extraction" (Worthy, 1981; Gangoli and Thodos, 1977). The effect, which is seen as enhanced solubility of solids in supercritical fluids, has attracted considerable amount of interest due to its technological importance. However, the large amount of data has not been systematically analyzed, and therefore optimization procedures for applications are still lacking.

In our theoretical approach (Gitterman and Procaccia, 1982), the quantities of interest are *slopes* of solubility curves (concentration as functions of pressure for given temperature or vice versa). By considering slopes rather than the concentrations themselves, we obtain universal results which pertain to all systems of interest.

The details of the thermodynamic analysis are given by Gitterman and Procaccia (1982), here we mainly present the typical universal plots that are suggested by the theory.

In view of the typical experiment (Van Leer and Paulaitis, 1980; McHugh and Paulaitis, 1980; Kurnick et al., 1981) in which solid in excess is equilibrated with a supercritical fluid, we considered displacements along an equilibrium line to find the basic relation for the slope of the mole fraction of the solid, X , as a function of the pressure p .

Denoting the chemical potential of the solute in the solid and the supercritical phase by μ_s and μ respectively, we note that along an equilibrium line $\mu_s = \mu$, or $\Delta\mu = 0$. Thus

$$0 = d\Delta\mu(T, p, X) = \left(\frac{\partial\mu_s}{\partial p}\right)_T dp - \left(\frac{\partial\mu}{\partial p}\right)_{T, X} dp - \left(\frac{\partial\mu}{\partial X}\right)_{T, p} dX$$

where the displacement is taken to be isothermal (Van Leer and Paulaitis, 1980; McHugh and Paulaitis, 1980; Kurnick et al., 1981) and use have been made of the fact that $X = 1$ in the solid.

Using the definition of the molar volume of the solid $v^o \equiv (\partial\mu_s/\partial p)_T$ and the partial volume of the solute in the supercritical phase $\bar{v} \equiv (\partial\mu/\partial p)_{X, T}$ we find:

$$\left(\frac{\partial X}{\partial p}\right)_{T, \text{eq. line}} = \frac{v^o - \bar{v}}{\left(\frac{\partial\mu}{\partial X}\right)_{T, p}} \quad (1)$$

We have argued that the denominator $(\partial\mu/\partial X)_{T, p}$ vanishes at two points on the typical phase diagram. These two points are referred to as the "lower" (LCEP) and "upper" critical end points (UCEP) (McHugh and Paulaitis, 1980). The LCEP is typically very close to the critical point of the pure solvent. Since $(\partial\mu/\partial X)_{T, p} \rightarrow 0$ upon approaching these points, the slopes of the solubility curves diverge. An important point is that the way this divergence occurs is universal and for all systems we expect that when $p \sim p_c$,

$$\text{slope} \sim \left(\frac{T - T_c}{T_c}\right)^{-d\gamma/\beta\delta} \quad (2)$$

where p_c and T_c are the critical parameters and $\gamma/\beta\delta$ is a combination of so-called critical indices. The numerical value of $\gamma/\beta\delta$ is ~ 1 . Figure 1 depicts typical experimental results supporting Eq. 2.

Notice that the fact that $(\partial\mu/\partial X)_{T, p} \rightarrow 0$ rationalizes also the increase in solubility itself. Low solubilities mean that μ rises sharply with X , such that increasing the concentration increases the free energy; when $(\partial\mu/\partial X)_{T, p} \rightarrow 0$ the increase in the mole fraction does not cost any free energy.

Most of the available experimental data on supercritical solubility pertains to very dilute solutions of the solid in the fluid phase. We can then use to advantage the proximity to the pure fluid critical point to achieve another universal result. This result relates to the points of maximum solubility changes [i.e., the points p_m, T_m in pressure-temperature plane where $(\partial X/\partial p)_{T, \text{eq. line}}$ is maximal]. We obtain this result (Gitterman and Procaccia, 1982) by first re-writing Eq. 1 in terms that facilitate the use of $p - V - T - X$ data:

$$\left(\frac{\partial X}{\partial p}\right)_{T, \text{eq. line}} = \frac{v^o - v + (1 - X) \left(\frac{\partial p/\partial X}{\partial p/\partial v}\right)_{T, v}}{\frac{RT}{X} + (1 - X) \left(\frac{\partial p/\partial X}{\partial p/\partial v}\right)_{T, X}^2 - (1 - X) \int_{\infty}^v \frac{\partial^2 p}{\partial X^2} dv} \quad (3)$$

where v is the molar volume.

We use now the simplest form of the equation of state near the critical point of pure fluid, which is nothing else but a series expansion in the small parameters $X, \tau \equiv T - T_c/T_c$, $\Phi \equiv v - v_c/v_c$, $\bar{p} \equiv p - p_c/p_c$:

$$\bar{p}(X, \tau, \Phi) = AX + B\tau - (CX + D\tau)\Phi - E\Phi^3 + F\tau^2 \quad (4)$$

We then maximize Eq. 3, substitute Eq. 4, and find that the locus of maxima of solubility changes in $\bar{p} - \bar{\tau}$ plane is given by a universal law, $\bar{p} = B\tau$, which in explicit form is

$$\frac{p_m - p_c}{p_c} = B \frac{T_m - T_c}{T_c} \quad (5)$$

the parameter B , which is $\partial\bar{p}/\partial\tau$ in Eq. 4, is a practically universal number, being 6-8 for most substances. Figure 2 presents data that support Eq. 5.

One practical conclusion of this finding is that one can optimize the effect of supercritical solubility by moving along the line (5) rather than isothermally or isobarically.

The agreement with the theoretical considerations shown in Figures 1 and 2 seem to support our understanding of the phenomenon. However, additional experimental work has to be performed to solidify the theoretical approach and to improve the

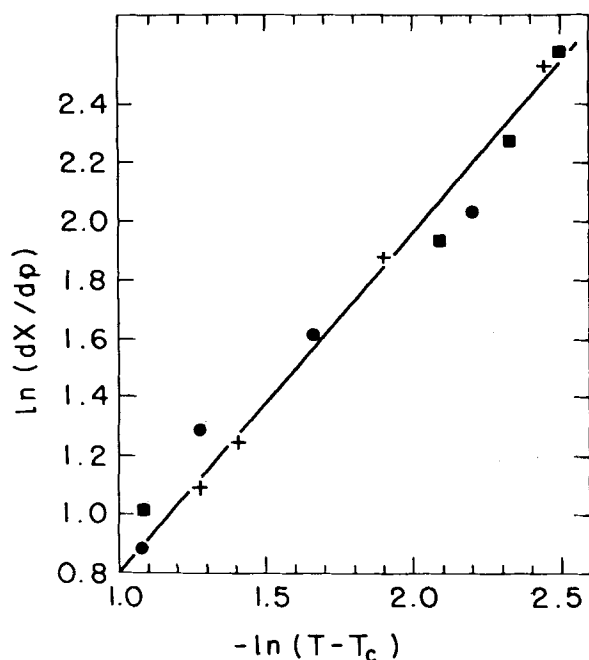


Figure 1. Slopes of isothermal solubility curves for $P \sim P_c$ at various temperatures as a function of $(T - T_c)/T_c$. The intercept in this curve is meaningless. The slope is expected to be ~ 1 . Shown are data on a log-log plot for three different systems: ● Naphthalene in ethylene near UCEP; ■ Naphthalene in ethylene near LCEP; + Naphthalene in CO_2 near LCEP. The solid curve has a slope of ~ 1.05 .

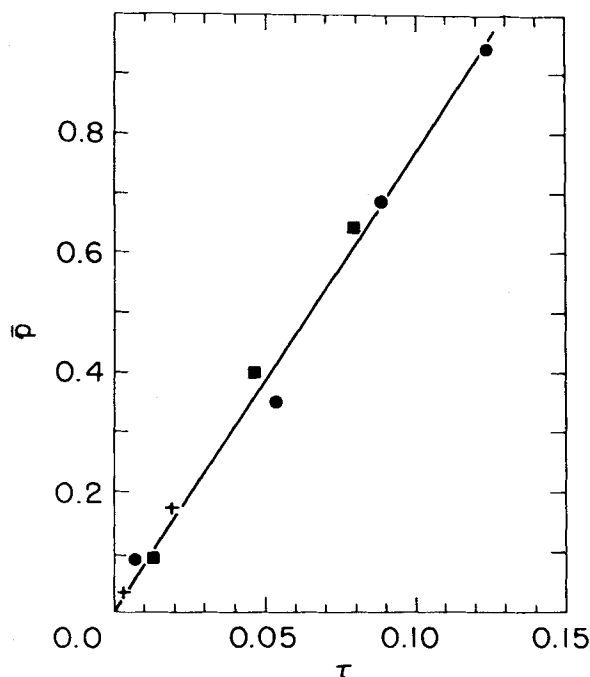


Figure 2. Graph of locus of maxima of differential solubility changes $((\partial X/\partial P)_{T_{eq, max}}^{max})$ in reduced pressure $(P - P_{c,o}/P_{c,o})$ -reduced temperature $(T - T_{c,o}/T_{c,o})$ plane. The theory predicts a universal line with zero intercept and universal slope. Shown are three different systems: ● Naphthalene in ethylene; + Diphenylamine in CO_2 ; ■ Naphthalene in CO_2 . A slope of $B \sim 7.6$ is found.

applicability of the effect. It seems worthwhile to perform experiments on supercritical solubilities in pressure and temperature ranges that are close to both LCEP and UCEP. Both points offer technological advantages. Near the UCEP loading powers are higher, but so are the pressures. Near the LCEP the loading power

is modest, but the effect is achieved at much lower pressures. The location of the UCEP are not known for many systems. Some known examples are the naphthalene-ethylene system and the biphenyl- CO_2 systems; the UCEP are at $T_c = 325.2 \text{ K}$, $p_c = 1.76 \times 10^7 \text{ N/m}^2$ and $T_c = 329.2 \text{ K}$ and $p_c = 4.66 \times 10^7 \text{ N/m}^2$ respectively (McHugh and Paulaitis, 1980). The exact location of the LCEP is not known for many systems as well. However, it is typically very close to the critical point of the pure solvent. For example (Van Gunst et al., 1953), in naphthalene/ethylene $T_c = 283.8 \text{ K}$, $p_c = 5.18 \times 10^6 \text{ N/m}^2$ whereas in pure ethylene $T_c = 282.3 \text{ K}$, $p_c = 5.06 \times 10^6 \text{ N/m}^2$. Thus the deficiency of data for LCEP is not so severe as for UCEP.

Near the LCEP and UCEP, the effects are most pronounced when $T - T_c/T_c \lesssim 10^{-2}$. The data presented in Figure 1 are mostly for $T - T_c/T_c > 10^{-2}$. It would be thus worthwhile to conduct experiments for various isotherms in the close vicinity of the critical point. The data, once analyzed as the slopes for $p \sim p_c$ should conform with Eq. 2. Additional experiments to support Eq. 5 are also called for. Here the coordinates p_m, T_m of the points of maximal slopes for different isotherms should be found and then plotted in reduced form according to Eq. 5. The importance of the effect and its universality as explained above warrants further work for its complete understanding.

ACKNOWLEDGMENT

This work was supported in part by The Fund for Basic Research Administered by the Israel Academy of Sciences and Humanities.

NOTATION

X	= mole fraction of solid component
p	= pressure
T	= temperature
μ	= chemical potential of solute
μ_s	= chemical potential of solute in the solid phase
v^o	= molar volume of solid
\bar{v}	= partial molar volume of solute
T_c	= critical temperature
p_c	= critical pressure
γ, β, δ	= critical exponents
p_m, T_m	= pressure and temperature of point of maximum slope of solubility curve
τ	= $(T - T_c)/T_c$
ϕ	= $(p - p_c)/p_c$
\bar{p}	= $(p - p_c)/p_c$

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Manuscript received May 3, 1982; revision received August 2, and accepted August 30, 1982.