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PARTIAL MOLAR VOLUMES OF NAPHTHALENE DILUTE IN SUPERCRITICAL FLUID SOLVENTS^(*)

Supercritical-fluid extraction is a separation technique with much potential for a variety of industries.

To design and operate a supercritical-fluid extraction process, it is important to understand the behavior of solutes dilute in solvents at conditions close to the solvent's critical point.

In this work, we use Chueh's modification of the Redlich-Kwong equation of state to calculate the pressure dependence of the partial molar volumes of naphthalene infinitely dilute in carbon dioxide (isotherms between -3.15°C and 67°C) and in ethene (isotherms between 0°C and 60°C). These calculations were performed using a binary interaction parameter k_{12} determined from solubility data.

As the solvent's critical point is approached, the solute's partial molar volumes become very large but negative with a sharp minimum at temperatures close to the solvent's critical.

Calculated results compare well with available experimental data. In the critical region the partial molar volume is highly sensitive to temperature and pressure. Therefore, the fugacity coefficient of the solute changes dramatically with small changes in operating conditions. It is this dramatic change which leads to the unique advantages of supercritical-fluid-extraction process.

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INTRODUCTION

Much attention has been given to separation processes using a supercritical fluid (SCF) for extraction. In this separation technique, a fluid at temperatures and pressures slightly exceeding those at its critical point is used to extract a solute (solid or liquid) from a solution.

Compared with conventional extraction methods, SCF extraction is advantageous for energy savings, and for economic recovery of the solvent. Further, a supercritical fluid is often more useful than a liquid solvent because of higher diffusivity, lower density and lower viscosity of the supercritical fluid when compared with those of typical liquid solvents. Carbon dioxide is a popular SCF extractant. It fulfills many of the characteristics for an advantageous extraction agent: good extracting power, non-toxic, chemical stability, inexpensive, readily available and a conveniently low critical temperature (31.1°C).

Several industrial processes using compressed gases for material separation are suggested in the literature (for a review see Paulaitis *et al.* [1]). They include the separation of organic chemicals from water, caffeine from coffee, extraction of hops, spices, tobacco, and extraction of volatile materials from coal and other heavy fossil fuels. While only a few of these applications are as yet used in industry, there is good reason to believe that their number may increase in the near future.

Since the understanding of the behavior of solutes dilute in supercritical fluids is essential for design and operation of SCF extraction equipment, we discuss here the calculation of partial molar volumes of naphthalene infinitely dilute in the supercritical solvents, carbon dioxide and ethene. The partial molar volume is a key quantity for determining optimum operating conditions because it determines the rate at which the fugacity coefficient (and hence the solubility) changes with pressure.

THERMODYNAMIC ANALYSIS

To describe the solubility of a solid in a supercritical fluid, we assume that the solid phase is pure and incompressible.

With these assumptions, it can be shown [2] that at temperature T and pressure P the solubility of a solid (component 2) in a SCF (component 1) is given by

$$y_2 = \frac{P_2^{\text{sat}}}{P} \left\{ \frac{\phi_2^{\text{sat}}}{\phi_2} \exp \left[\frac{v_2^s}{RT} (P - P_2^{\text{sat}}) \right] \right\} \quad (1)$$

where P_2^{sat} is the sublimation pressure of the pure solid, ϕ_2^{sat} is the fugacity coefficient at P_2^{sat} , and the exponential term is the Poynting correction for the fugacity of pure solid, all at system temperature T .

It is the pressure dependence of ϕ_2 which is primarily responsible for the variation of y_2 with pressure. At low pressures, the term set in brackets in Eq. (1) is not far removed from unity. In that case, $y_2 = P_2^{\text{sat}}/P$ which is the ideal solubility of solid 2 in the gas phase. At high pressures, the term in brackets is larger, often very much larger, than unity.

The pressure dependence of fugacity coefficient ϕ_2 can be evaluated from

$$\left(\frac{\partial \ln \phi_2}{\partial P} \right)_{T,y} = \frac{\bar{v}_2}{RT} - \frac{1}{P} \quad (2)$$

where \bar{v}_2 is the partial molar volume of the solute in the fluid phase.

At high pressures, if \bar{v}_2 is negative, $(\partial \ln \phi_2 / \partial P)_T$ may be large and negative. If we raise P , we obtain lower ϕ_2 ; then y_2 must rise because the fugacity of the pure solid is approximately constant and, at equilibrium,

$$\text{constant} \approx f_2^s = f_2^G = \phi_2 y_2 P \quad (3)$$

One convenient way to calculate ϕ_2 is from an equation of state. In this work we use Chueh's modification [3] of the Redlich-Kwong equation of state. From this equation we obtain [2] for ϕ_2 ,

$$\ln \phi_2 = \ln \frac{v}{v-b} + \frac{b_2}{v-b} - \frac{2 \sum_i y_i a_{i2}}{RT^{1.5}b} \ln \frac{v+b}{v} + \frac{ab_2}{RT^{1.5}b^2} \left[\ln \frac{v+b}{v} - \frac{b}{v+b} \right] - \ln \frac{Pv}{RT} \quad (4)$$

For the mixture, parameters a and b are given by the usual mixing rules,

$$a = \sum_i \sum_j y_i y_j a_{ij} \quad b = \sum_i y_i b_i \quad (5)$$

For the pure components, a and b are calculated from

$$a_i = \frac{\Omega_{a_i} R^2 T_{c_i}^{2.5}}{P_{c_i}} \quad b_i = \frac{\Omega_{b_i} R T_{c_i}}{P_{c_i}} \quad (6)$$

where Ω_{a_i} and Ω_{b_i} are dimensionless constants obtained from saturated vapor data.

We evaluate the cross term a_{12} in Eq. (5) from

$$a_{12} = (\Omega_{a_1} + \Omega_{a_2}) R^2 T_{c_{12}}^{2.5} / 2 P_{c_{12}} \quad (7)$$

with

$$P_{c_{12}} = z_{c_{12}} R T_{c_{12}} / v_{c_{12}} \quad (8)$$

$$v_{c_{12}} = \frac{1}{8} (v_{c_1}^{1/3} + v_{c_2}^{1/3})^3 \quad (9)$$

$$z_{c_{12}} = 0.291 - 0.08 \left(\frac{\omega_1 + \omega_2}{2} \right) \quad (10)$$

and

$$T_{c_{12}} = (T_{c_1} T_{c_2})^{1/2} (1 - k_{12}) \quad (11)$$

In these equations, subscript c refers to the critical property, ω_i is the acentric factor for component i and k_{12} is the binary interaction parameter.

Partial molar volumes were also calculated from the Redlich-Kwong equation, through the thermodynamic relation

$$\bar{v}_2 = - \frac{\left(\frac{\partial P}{\partial n_2} \right)_{T, v, n_1}}{\left(\frac{\partial P}{\partial V} \right)_{T, n}} \quad (12)$$

where V is the total volume of the mixture containing n_1 moles of component 1, etc. Since the solubility of the solute in the gas phase is small, we consider the solute infinitely dilute in the supercritical fluid phase. In that case, \bar{v}_2^∞ , the partial molar volume of solute at infinite dilution, is defined by

$$\bar{v}_2^\infty = \lim_{n_2 \rightarrow 0} \left(\frac{\partial V}{\partial n_2} \right)_{P, T, n_1} \quad (13)$$

We obtain \bar{v}_2^∞ by calculating the derivatives in Eq. (12) from Redlich-Kwong equation. The result is

$$\bar{v}_2^\infty = \frac{\frac{RT}{v-b} \left(1 + \frac{b_2}{v-b} \right) - \frac{2a_{12} - \frac{ab_2}{v+b}}{v(v+b)T^{0.5}}}{\frac{RT}{(v-b)^2} - \frac{a}{T^{0.5}} \left\{ \frac{2v+b}{v^2(v+b)^2} \right\}} \quad (14)$$

At infinite dilution, a , b , and v are the corresponding values for the pure solvent.

RESULTS

Using solubility data for naphthalene in CO_2 at 35°C [4, 5] and in ethene at 25°C [5, 6] we used Eq. (1), together with Eqs. (4)-(11) to obtain interaction parameter k_{12} . Data for pure components were taken from IUPAC Tables [7] (CO_2 and C_2H_4) and from reference 8 (naphthalene).

Figure 1 compares experimental with calculated solubilities of naphthalene in supercritical ethene at 25°C .

With $k_{12} = 0$, agreement is good only at low pressures where the gas phase is almost ideal. In the range of pressures studied, calculated solubilities of naphthalene in C_2H_4 agree with experimental data using $k_{12} = -0.0182$, even at higher temperatures as shown in Fig. 2.

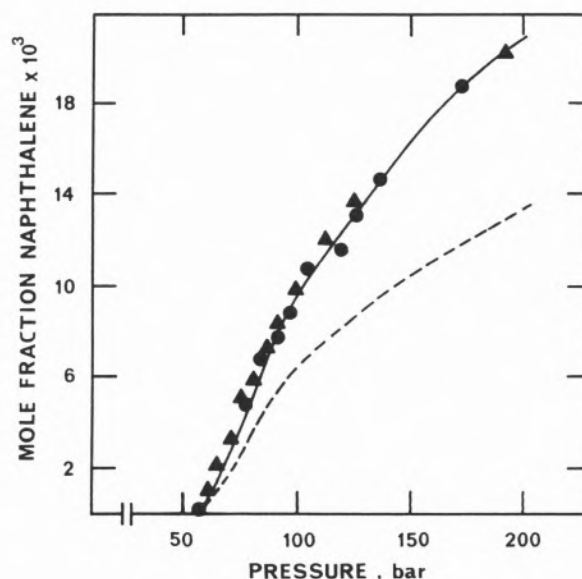


Figure 1

Experimental (▲, ● from ref. 5, 6) and calculated solubilities for naphthalene in supercritical ethene at 25°C . Calculations from Redlich-Kwong equation of state with $k_{12} = 0$ (broken line) and $k_{12} = -0.0182$ (full line)

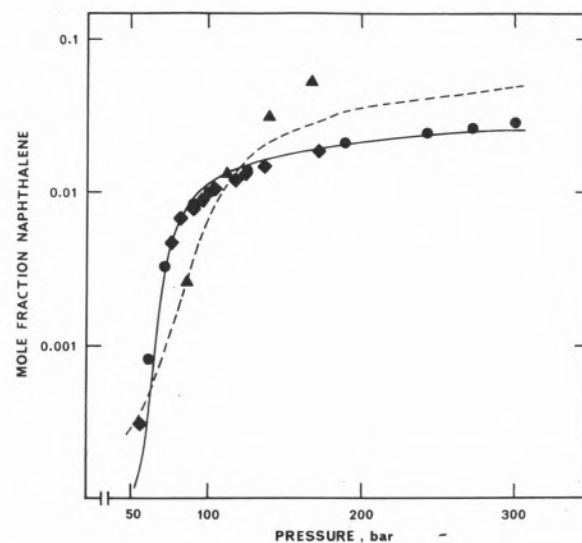


Figure 2

Experimental (● at 25°C , ref. 5; ▲ at 50°C , ◆ at 25°C from ref. 6) and calculated solubilities (with $k_{12} = -0.0182$) for solid naphthalene in supercritical ethene at 25°C (full line) and at 50°C (broken line)

Similar results were obtained for the solubility of naphthalene in supercritical CO_2 . Figure 3 compares calculated solubilities

(using $k_{12} = 0.0626$) with experimental data at 35°C.

Using Eq. (14) with k_{12} obtained from solubility data, we calculated \bar{v}_2^∞ as a function of pressure and temperature. Figure 4 shows isotherms (between 0°C and 60°C) of calculated partial molar volumes as a function of pressure for naphthalene infinitely dilute in ethene.

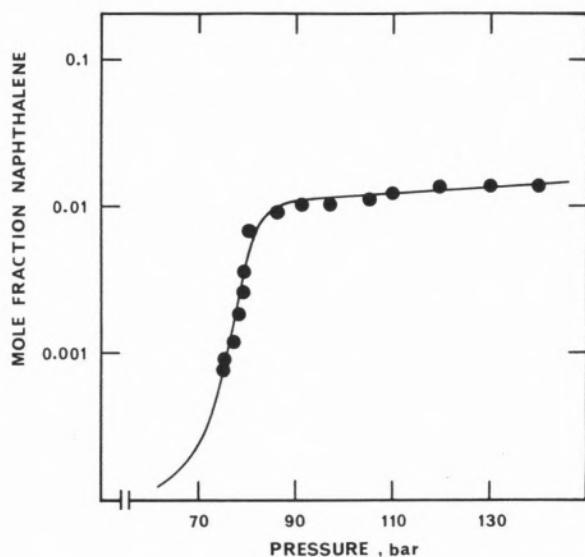


Figure 3

Experimental [4,5] and calculated solubilities (with $k_{12} = 0.0626$) for solid naphthalene in supercritical carbon dioxide at 35°C

Figure 5 shows similar isotherms (between -3.15°C and 67°C) for naphthalene in CO₂.

As shown in Figs. 4 and 5, at low pressures the partial molar volumes of the solute are small and positive. As pressure increases, \bar{v}_2^∞ decreases strongly until a minimum is observed. At higher pressures, \bar{v}_2^∞ increases and eventually become positive again. At conditions of pressure and temperature where the solvent is supercritical, a sharp minimum is observed. This minimum shifts to higher pressures as the temperature rises; the same trend is observed [9] for similar curves showing the dependence of solubility maxima on pressure and temperature.

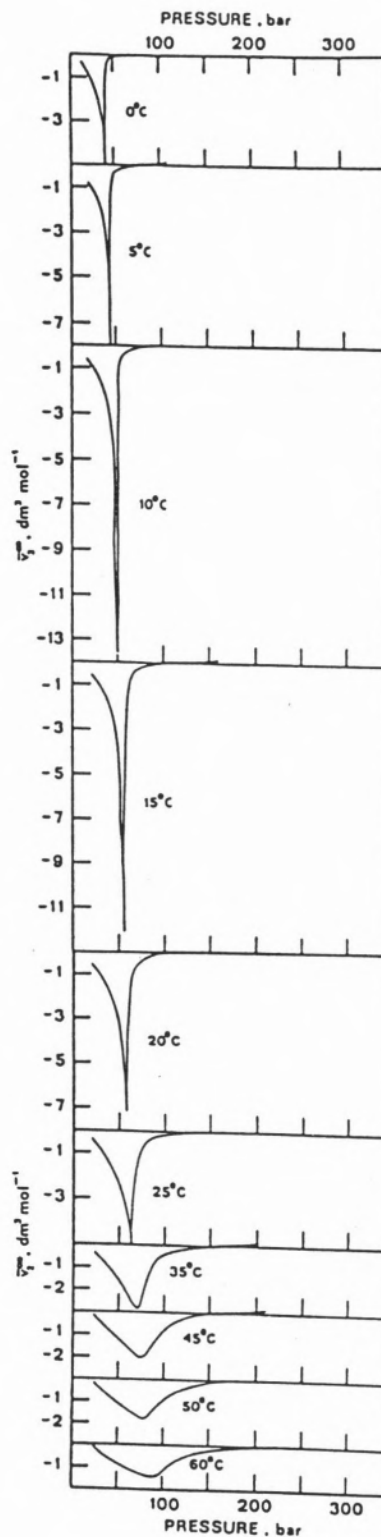


Figure 4

Calculated partial molar volumes of naphthalene infinitely dilute in ethene. Values of \bar{v}_2^∞ are large and negative at temperatures close to the ethene's critical ($t_c = 9.5^\circ\text{C}$)

mental chromatographic data [10] for naphthalene in supercritical carbon dioxide. Agreement is good. The data indicate that \bar{v}_2^∞ may attain negative infinity when approaching the critical point of the solvent. Results shown in Fig. 6 also confirm the strong correlation observed between \bar{v}_2^∞ and the isothermal compressibility of the pure solvent [10].

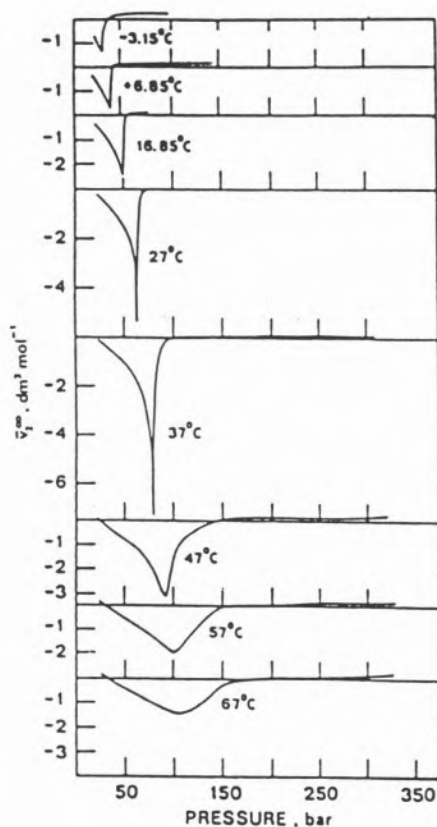


Figure 5

Calculated partial volumes of naphthalene infinitely dilute in carbon dioxide ($t_c = 31.1^\circ\text{C}$)

In addition we point out that an analytic equation of state, such as the Redlich-Kwong we used in this work, cannot describe the behavior of systems very near the critical state. For this reason, Figs. 4 and 5 do not include any calculations at temperatures very near the critical region of the pure solvents.

Figure 6 shows three isotherms which compare \bar{v}_2^∞ calculated from Eq. (14) with experi-

Note that the sharp minima indicate values for \bar{v}_2^∞ which are not only negative but very much larger than the volume of pure condensed naphthalene.

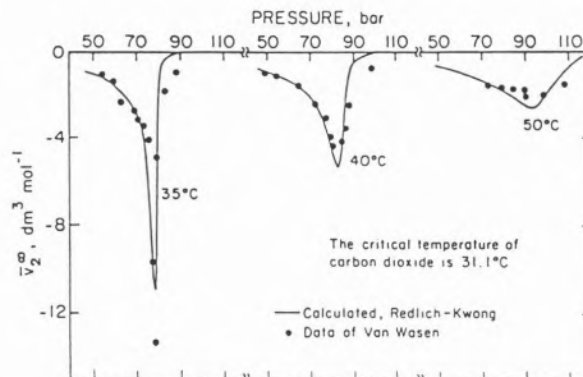


Figure 6

Comparison of calculated partial molar volumes of naphthalene at infinite dilution in supercritical carbon dioxide with experimental chromatographic data [10]. (Prausnitz/Lichtenthaler/Gomes de Azevedo, *MOLECULAR THERMODYNAMICS OF FLUID-PHASE EQUILIBRIA*, 2/E, p. 464, 1986. Reproduced by permission of Prentice-Hall, Inc., Englewood Cliffs, N. J.)

This particular behavior of the solute's partial molar volumes has also been observed for other solute properties. Similar unusual effects are reported for excess enthalpies, apparent molar heat capacities and solubilities of solutes in mixtures near the solvent's critical point [11].

Addition of small quantities of solute to the near-critical solvent acts like a «condensing agent» which is responsible for the large negative partial molar volumes.

As shown, a simple equation of state like the Redlich-Kwong equation (with a binary interaction parameter obtained from other experimental data) is able to predict unusually large and negative partial molar volumes and their sensitivity to small changes in pressure when the solvent is near its critical state.

Very low fugacity coefficients lead to solubilities much larger than those calculated by as-

suming ideal behavior. Large negative molar volumes tell us that a small decrease in pressure can dramatically reduce the solubility. It is precisely this feature which makes SCF extraction attractive because it permits simple and economic solvent recovery.

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RESUMO

Volumes parciais molares de naftaleno em solventes supercríticos

A extração supercrítica é uma técnica de separação com grandes possibilidades de aplicação em várias indústrias.

No projecto e na operação de processos envolvendo a extração supercrítica é importante conhecer o comportamento de solutos diluídos em solventes em condições próximas do ponto crítico do solvente.

Neste trabalho utilizou-se a modificação de Chueh da equação de estado de Redlich-Kwong para calcular a dependência com a pressão dos volumes parciais molares do naftaleno infinitamente diluído em dióxido de carbono (isotérmicas entre -3.15°C e 67°C) e em eteno (isotérmicas entre 0°C e 60°C). Estes cálculos foram efectuados usando um parâmetro de interacção binária k_{12} determinado a partir de dados de solubilidade.

À medida que se aproxima o ponto crítico do solvente, os volumes parciais molares do soluto tornam-se muito grandes e negativos, com um mínimo acentuado para temperaturas próximas da temperatura crítica do solvente.

Os resultados calculados estão em boa concordância com os resultados experimentais existentes.

Na região crítica, o volume parcial molar é muito sensível à temperatura e à pressão. Por isso, o coeficiente de fugacidade do soluto varia acentuadamente com pequenas alterações nas condições de operação. É esta variação apreciável que conduz às vantagens particulares dos processos de extração supercrítica.

NOTATION

a	constant in Redlich-Kwong equation of state
b	constant in Redlich-Kwong equation of state
f	fugacity, bar (1 bar = 10^5 Pa)
k	deviation from geometric mean
n	number of moles
P	pressure, bar
R	gas constant, bar cm ³ mol ⁻¹ K ⁻¹
T	temperature, K
t	temperature, °C
v	molar volume, cm ³ mol ⁻¹
V	total volume, cm ³
x	liquid phase mole fraction
y	gas phase mole fraction
z	compressibility factor
φ	fugacity coefficient
ω	acentric factor
Ω	dimensionless constant in Redlich-Kwong equation of state

Subscripts

1, 2, i, j	components
c	critical property

Superscripts

G	gas phase property
sat	evaluated at saturation
s	solid phase property
—	partial molar property
∞	infinite dilution property