

Calculations of solubilities of aromatic compounds in supercritical carbon dioxide

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of 2000 and was border line with respect to turbulent flow. The jet twisted or flickered at this flow, and slightly higher flow rates gave turbulence. For smaller nozzles, excessive turbulence at the tip was observed at calculated Reynolds numbers of 1000. The TCE flow to the nozzle was cooled to 20 °C and the nozzle discharged into a column of hot TCE for internal gelation of the drops. Useful tests were made with this two-fluid nozzle arrangement. The size distributions showed D_{84}/D_p values of 1.03-1.05. The single-fluid nozzles above the TCE surface were found to give simpler operation, higher capacities, and slightly better size uniformities.

Conclusions

The gel-sphere processes require the formation of liquid drops of controlled and uniform sizes at rates of 10^3 - 10^7 drops/min. The product spheres allow good measurements of the drop size distributions. The basic technique reported here uses an applied vibration to give a controlled and uniform breakup of laminar liquid jets into drops. Controlled alternating current powers the small electro-mechanical vibrators to apply vibrations to liquid jets in several different ways.

A highly regular and reproducible breakup occurs for vibration frequencies that promote a breakup near the natural frequency of breakup for the laminar jet. With optimum conditions, the drop formation is so regular that the motion appears to be completely stopped when observed with a stroboscopic light.

Criteria are given in this paper for selection of jet diameters, jet velocities, vibration frequencies, and the configurations of the drop-formation apparatus. Selection

of these parameters for a specific gel-sphere process involves some compromises to minimize the observed problems by empirical adjustments. Preparation of gel-sphere samples required repeated runs in which the drop formation was controlled and reproduced without difficulty. Examples of these results and conditions are given. The values of $\sigma = D_{84}/D_p$ (the geometric standard deviations for a log-normal distribution) were 1.01-1.05.

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Calculations of Solubilities of Aromatic Compounds in Supercritical Carbon Dioxide

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Solubilities of five aromatic compounds in supercritical carbon dioxide are calculated in this work by using the Patel-Teja equation of state. Unlike the traditional van der Waals mixing rules, the energy parameter of the equation of state is evaluated by equating the excess free energy calculated by the equation of state to that from a UNIFAC group contribution liquid model. New UNIFAC group interaction parameters of carbon dioxide and various hydrocarbon groups are obtained through regression of experimental vapor-liquid equilibrium data. A new mixing rule for the excluded volume parameter of the equation of state is proposed, and a generalized correlation of that parameter is presented. With the new mixing rules, solubilities of aromatic solids in supercritical carbon dioxide can be calculated satisfactorily. The results are comparable to those computed by using the van der Waals mixing rule with multiple best-fitted unlike pair parameters.

Introduction

Supercritical fluid extraction (SCFE) is a new separation technology which has received much interest in the processing of pharmaceuticals, natural products, and many other special applications (McHugh and Krukons, 1986; Brennecke and Eckert, 1989). Carbon dioxide is a promising solvent since it is inexpensive, nontoxic, inflammable, and environmentally acceptable and has a low critical

temperature and a moderate critical pressure. The design and development of supercritical extraction processes also depend on the ability to model and predict the solubilities of solid solutes in supercritical solvents. The prediction is usually difficult because of the large differences in sizes and molecular interactions between the solute and solvent molecules.

Cubic type equations of state (EOS), which have been extensively applied in vapor-liquid equilibrium (VLE) calculations, have also been used in computing the solubilities of solids in supercritical fluids (A review paper on

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modeling supercritical mixtures was given by Johnston et al. (1989)). Haselow et al. (1986) have evaluated nine cubic equations of state regarding their abilities in SCFE calculations. They suggested that there is a need to develop new mixing rules. Otherwise, no existing cubic equations of state with traditional van der Waals mixing rules can yield good solubility results. Eckert et al. (1983, 1986) have examined the behavior of the infinite negative value of the partial molar volume of solutes in supercritical fluids. They also concluded that the EOS model can predict the partial molar volumes accurately only when proper mixing rules are applied.

In this study, we propose that the solubilities of aromatic solids in supercritical carbon dioxide be calculated by using the Patel-Teja EOS. Unlike the traditional van der Waals mixing rules, we evaluate the energy parameter of the EOS with a method suggested by Huron and Vidal (1979). A modification for the mixing rule of the excluded volume parameter has also been presented. Satisfactory calculation results can be obtained by the improved mixing rules, and the results are compared to those using the traditional van der Waals mixing rules.

Solubility of Solid Solute in Supercritical Fluid

The general phase equilibrium equation for a solid-supercritical fluid mixture is

$$f_2 = \hat{f}_2^{\text{scf}} \quad (1)$$

where subscript 2 indicates the heavy solute component. The solid phase is considered to be pure, and the nonideal behavior is entirely in the supercritical phase.

The fugacity of a pure solid at a given temperature and pressure is expressed as

$$f_2 = P_2^{\text{sat}} \phi_2^{\text{sat},s} \exp \left[\frac{V_2^{\text{sat}}(P - P_2^{\text{sat}})}{RT} \right] \quad (2)$$

The fugacity coefficient of a saturated solid, $\phi_2^{\text{sat},s}$, is taken to be 1.0 at low solid vapor pressures.

The fugacity of a solute in the supercritical phase is

$$\hat{f}_2^{\text{scf}} = y_2 \hat{\phi}_2^{\text{scf}} P \quad (3)$$

From the combination of eqs 2 and 3, the solubility of a solid is expressed as

$$y_2 = \frac{P_2^{\text{sat}} \exp[V_2^{\text{sat}}(P - P_2^{\text{sat}})/RT]}{\hat{\phi}_2^{\text{scf}} P} \quad (4)$$

The fugacity coefficient, $\hat{\phi}_2^{\text{scf}}$, is calculated by an EOS. The accuracy of solubility computations depends on the proper mixing rules to evaluate the fugacity coefficient.

Equation of State and the Mixing Rules

In this study, the fugacity coefficient is calculated by the Patel-Teja EOS (Patel and Teja, 1982):

$$P = \frac{RT}{V-b} - \frac{a}{V^2 + (b+c)V - bc} \quad (5)$$

For mixture calculations, the following van der Waals mixing rules are conventionally applied for cubic type equations of state:

$$a_m = \sum_i \sum_j x_i x_j (a_i a_j)^{1/2} k_{ij} \quad (6)$$

$$b_m = \sum_i \sum_j x_i x_j \left(\frac{b_i + b_j}{2} \right) l_{ij} \quad (7)$$

$$c_m = \sum_i \sum_j x_i x_j \left(\frac{c_i + c_j}{2} \right) m_{ij} \quad (8)$$

where k_{ij} , l_{ij} , and m_{ij} are adjustable unlike interaction parameters. These parameters are fitted by using the experimental data. They cannot be predicted or correlated and may have different values at various temperatures. Kwak and Mansoori (1986) have shown these parameters when they applied the Peng-Robinson EOS in supercritical fluid extraction modeling.

Improved methods have been proposed to evaluate the EOS parameters without using empirically adjustable parameters. The model presented by Huron and Vidal (1979) is a good example. They assumed that no excess volume exists at an infinite pressure limit and determined the energy parameter by equating the Gibbs free energy calculated by the EOS to that of a liquid model. This approach is employed by many investigators (e.g., Tochigi et al. (1985), Pandit and Singh (1987), and Huang (1990), etc.) to correlate nonideal mixtures. On the basis of Huron and Vidal's model, Sheng et al. (1989) and Suen et al. (1989) also have applied the Patel-Teja EOS and the UNIFAC group contribution liquid model (Fredenslund et al., 1977; Larsen et al., 1987) to VLE and multiphase equilibrium calculations, respectively. Their method is extended to solid-supercritical fluid mixtures in this study.

In this research, we calculate the excess Helmholtz free energy from the Patel-Teja EOS at an infinite pressure limit:

$$\left(\frac{A^E}{RT} \right)_{P=\infty} = \frac{a_m Q Q_m}{2RTN_m} = \sum_i \frac{x_i a_i Q Q_i}{2RTN_i} \quad (9)$$

where

$$N = \left[bc + \frac{(b+c)^2}{4} \right]^{1/2} \quad (10)$$

$$Q Q = \ln \left[\frac{3b+c-2N}{3b+c+2N} \right] \quad (11)$$

The excess Helmholtz free energy of a group contribution liquid model, like UNIFAC, is assigned to the excess Helmholtz free energy expression in eq 9. The EOS parameter, a_m , can then be determined from eq 9 and the group contribution liquid model. The excess Helmholtz free energy equation from the UNIFAC model is written in a pressure-independent form and is usually taken as equal to the expression of the excess Gibbs free energy.

Huron and Vidal (1979) assumed that no excess volume exists at an infinite pressure limit and determined the volume parameter, b_m , by a simple van der Waals mixing rule. This assumption is good for VLE, liquid-liquid equilibrium, or multiphase equilibrium calculations (Sheng et al., 1989; Suen et al., 1989), but we found in this research that it is not adequate for solid-supercritical fluid mixtures. We propose a modification on the volume parameter by including an excess term beyond the simple van der Waals mixing rule

$$b_m = \sum_i x_i b_i + b^E \quad (12)$$

and we express the composition dependence of the excess term by a three-suffix Margulus-type equation:

$$b^E = x_1 x_2 (K_1 + K_2 x_2) \quad (13)$$

where K_1 and K_2 are two constants, which are to be fitted as functions of the characteristic properties of pure solute.

Following the new mixing rule, we can express the fugacity coefficient of component i in a mixture as

$$RT \ln \hat{\phi}_i^{scf} = (RT\hat{b}_i/(V - b_m)) + (\hat{a}_i \ln(QQ_m)/2N_m) - [a_m[V(b_m\hat{b}_i + c_m\hat{c}_i + 3\hat{b}_i c_m + 3b_m\hat{c}_i) + (b_m^2\hat{b}_i + c_m^2\hat{c}_i + 3b_m b_i c_m + 3b_m c_m \hat{c}_i)]/(4N_m^2[V^2 + (b_m + c_m)V - b_m c_m])^{1/2}] + [(a_m(b_m\hat{b}_i + c_m\hat{c}_i + 3\hat{b}_i c_m + 3b_m\hat{c}_i) \ln(QQ_m))/(4N_m^2)^{2/3}] \quad (14)$$

where

$$\hat{a}_i = n^{-1}(\partial n^2 a_m / \partial n_i)_{T,V,n_j} \quad (15)$$

$$\hat{b}_i = (\partial n b_m / \partial n_i)_{T,V,n_j} \quad (16)$$

$$\hat{c}_i = (\partial n c_m / \partial n_i)_{T,V,n_j} \quad (17)$$

The energy and volume parameters a_m and b_m are expressed by eqs 9, 12, and 13, respectively. c_m is written in a simple van der Waals form as

$$c_m = \sum_i x_i c_i \quad (18)$$

The partial molar volume of the solute can be expressed by

$$\hat{V}_i = - \frac{n(\partial P / \partial n_i)_{T,V,n_j}}{(\partial P / \partial V)_{T,\text{all } n}} \quad (19)$$

where

$$\left(\frac{\partial P}{\partial V}\right)_{T,\text{all } n} = - \frac{RT}{(V - b_m)^2} + \frac{a_m(2V + b_m + c_m)}{[V^2 + (b_m + c_m)V - b_m c_m]^2} \quad (20)$$

$$\frac{n\left(\frac{\partial P}{\partial n_i}\right)_{T,V,n_j}}{\hat{a}_i} = \frac{RT}{V - b_m} + \frac{RT\hat{b}_i}{(V - b_m)^2} + \frac{a_m[V(\hat{b}_i + \hat{c}_i) - b_m\hat{c}_i - \hat{b}_i c_m]}{[V^2 + (b_m + c_m)V - b_m c_m]^2} \quad (21)$$

Modified UNIFAC Group Contribution Liquid Model

We apply a modified UNIFAC group contribution liquid model to calculate the energy parameter of the EOS by eq 9. The modified combinatorial part of the UNIFAC equation suggested by Sheng et al. (1989) is used

$$\frac{G^{E,C}}{RT} = \sum_i x_i \ln \left(\frac{\psi'_i}{x_i}\right) - \frac{z}{2} \sum_i q_i x_i \ln \left(\frac{\psi_i}{\theta_i}\right) \quad (22)$$

where

$$\psi'_i = \frac{x_i(r_i)^{p_i}}{\sum_j x_j(r_j)^{p_j}} \quad (23)$$

$$\psi_i = \frac{x_i r_i}{\sum_j x_j r_j} \quad (24)$$

$$p_i = 1 - \frac{1}{0.8(q_i r_i^{-2/3} - 1)^{1.5} + 1} \quad (25)$$

$$\theta = \frac{x_i q_i}{\sum_j x_j q_j} \quad (26)$$

The residual part employed in this work is similar to the

Table I. Binary Group Interaction Parameters for Carbon Dioxide and Various Hydrocarbon Groups in the UNIFAC Model

group pairs, $i-j^a$	$A_{ij,1}$	$A_{ij,2}$	$A_{ij,3}$
CO ₂ -CH ₄	516.2	9.409	-22.62
CH ₄ -CO ₂	-336.2	-13.89	45.41
CO ₂ -CH ₂	467.2	6.551	10.88
CH ₂ -CO ₂	-2.825	-2.719	-4.085
CO ₂ -ACH	129.3	-0.347	-1.914
ACH-CO ₂	4.162	0.288	-0.358
CO ₂ -ACCH ₂	388.5	-0.48	1.367
ACCH ₂ -CO ₂	-112.2	-0.867	-0.407
CO ₂ -NAC	455.6	-2.317	-3.065
NAC-CO ₂	1304	0.256	0.150
ACH-ACCH ₂	167.0	0	0
ACCH ₂ -ACH	-146.8	0	0
ACH-NAC	372.2	1.340	1.486
NAC-ACH	1.959	1.126	1.142
ACCH ₂ -NAC	697.6	0.542	0.657
NAC-ACCH ₂	582.6	0.829	0.634

^aAbbreviations: CH₄ = methane, CH₂ = aliphatic C, ACH = aromatic CH, ACCH₂ = aromatic CCH₂, NAC = naphthenic C.

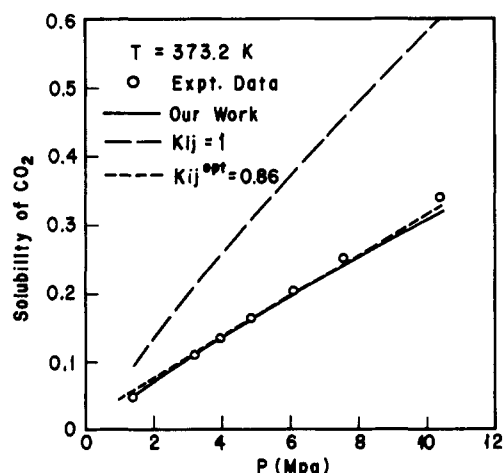


Figure 1. Comparison of solubilities of carbon dioxide in naphthalene calculated by this work and the van der Waals mixing rules at 373.2 K (experimental data: Barrick et al., 1987).

one presented by Larsen et al. (1987), with group interaction parameter A_{ij} in the following temperature-dependent form:

$$A_{ij} = A_{ij,1} + A_{ij,2}(T - T_0) + A_{ij,3} \left(T \ln \left(\frac{T_0}{T} \right) + T - T_0 \right) \quad (27)$$

where the reference temperature, T_0 , is 298.15 K. The UNIFAC group interaction parameters are regressed from experimental phase equilibrium data. Since those parameters involving carbon dioxide are not available in literature, they must be evaluated by fitting VLE or gas solubility data of carbon dioxide and hydrocarbon mixtures.

Results and Discussion

The UNIFAC group interaction parameters for carbon dioxide and hydrocarbons are fitted in this work, and the results are shown in Table I. We use the method suggested by Sheng et al. (1989) to regress those group interaction parameters, and our VLE and gas solubility results on carbon dioxide and hydrocarbon binary systems are shown in Table II. Comparisons of our calculated results with those obtained by traditional van der Waals mixing rules are also shown in Table II and Figures 1 and 2. Good agreement between our results and experimental data is observed. The accuracy of our results is usually

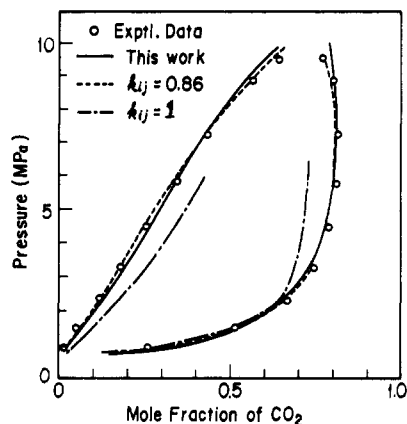


Figure 2. Comparison of the calculated P - x - y curves of carbon dioxide and n -pentane by this work and the van der Waals mixing rules at 377.59 K (experimental data: Besserer and Robinson, 1973).

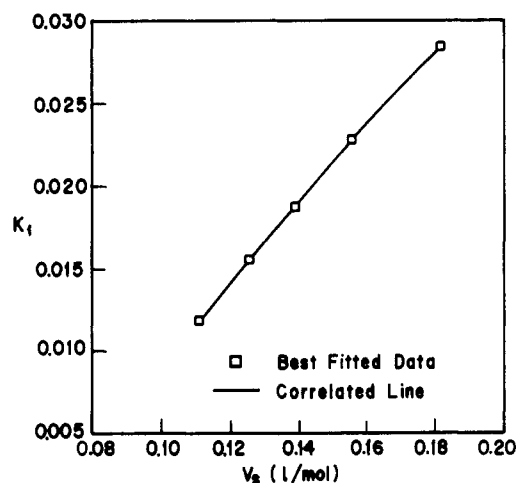


Figure 3. Plot of the parameter K_1 against the solid molar volumes.

better than that of the van der Waals model with its optimally fitted binary interaction parameters.

Table III gives the physical properties of the five aromatic compounds studied in this work. The critical constants and acentric factors for carbon dioxide and naphthalene are taken from Reid et al. (1987), and those values for other components are taken from Haselow et al. (1986). Solid volumes are taken from Weast (1989), and that of 2,6-dimethylnaphthalene is estimated in this work. Experimental solid vapor pressures are taken from Fowler et al. (1968), Schmitt and Reid (1986), and Osborn and Douslin (1975). The solid vapor pressures are fitted by the Antoine equation, and the parameters are given in Table III. We regress the Patel-Teja EOS parameters ζ_c and F for naphthalene from its saturation data (Fowler et al., 1968). EOS parameters for other compounds are calculated by the correlation equation given by Georgeton et al. (1986).

Parameters K_1 and K_2 in the excess volume equation can be fitted in the solubility calculations of the five aromatic compounds in supercritical carbon dioxide. We observe that these parameters are functions of solid molar volumes. The results are shown in Figures 3 and 4, and the functions are expressed as

$$K_1 = -0.0356 + 0.5275V_s - 0.9408(V_s)^2 \quad (28)$$

$$K_2 = 10.72 - 124.135V_s + 248.944(V_s)^2 \quad (29)$$

Table IV shows our calculated solubility results. It is again found that our improved mixing rules, with no ad-

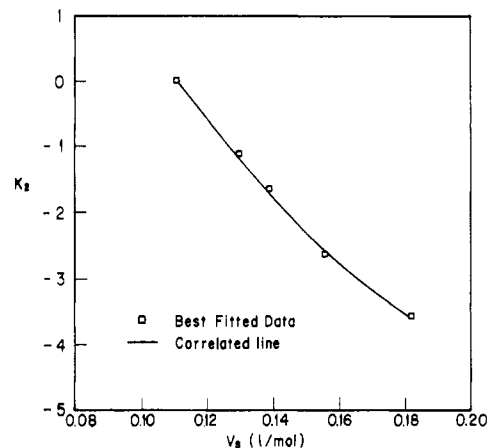


Figure 4. Plot of the parameter K_2 against the solid molar volumes.

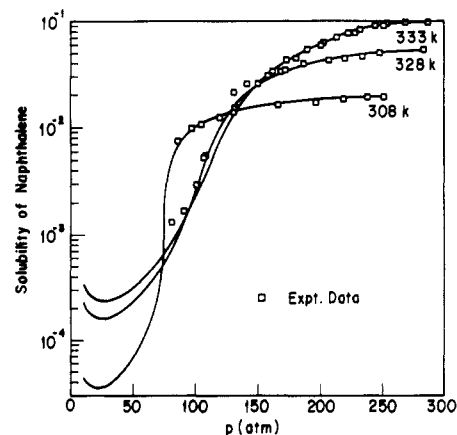


Figure 5. Calculated results of the solubilities of naphthalene in supercritical carbon dioxide by this work (experimental data: McHugh and Paulatis, 1980).

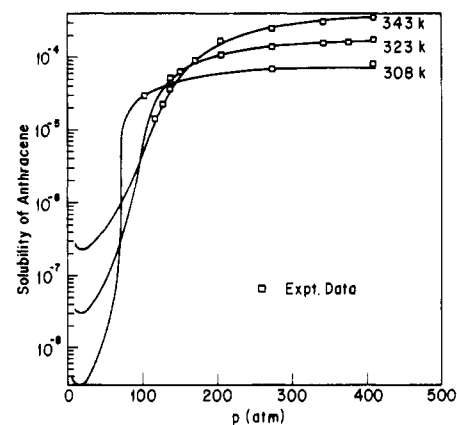


Figure 6. Calculated results of the solubilities of anthracene in supercritical carbon dioxide by this work (experimental data: Johnston et al., 1982).

justable parameters, are superior to the traditional van der Waals mixing rules with optimally fitted unlike pair parameters. Graphical comparisons of experimental and calculated solubilities of naphthalene, anthracene, and phenanthrene at various temperatures are shown in Figures 5-7, respectively.

Figure 8 shows our calculated result of the infinite dilution partial molar volumes of naphthalene in carbon dioxide at 308 K. A sharp negative value is observed close to 78 bar, which is in satisfactory agreement with the experimental data of Eckert et al. (1986), where a negative minimum at near 79.7 bar was found. Eckert et al. (1983) have discussed the importance of using proper mixing rules

Table II. Correlation of Vapor-Liquid Equilibria of Binary Mixtures of Carbon Dioxide and Hydrocarbons

hydrocarbons	no. of data points	temp range, K	press. range, atm	AADP, ^w %		ref
				this work	van der Waals mixing rules ^z	
methane	64	193-270	14-85	3.76	2.10	a-c
n-propane	50	277-344	10-61	3.59	6.72	d, e
n-butane	24	310-377	4-71	3.74	6.78	f, g
n-pentane	38	278-377	2-95	8.20	6.71	h
n-decane	16	463-583	19-50	2.55	3.82	i
n-hexadecane	16	463-663	20-50	5.37	16.7	i
n-eicosane	47	310-373	5-75	5.80	40.9	j
benzene	52	298-393	9-131	2.61	55.9	k-m
toluene	49	311-542	3-150	3.12	4.14	n-p
m-xylene	49	303-543	3-170	3.67	6.28	o, q, r
1-methylnaphthalene	28	353-703	8-142	3.79	3.83	n, s
naphthalene	14 ^v	373-423	14-103	6.61	13.8	t
1-methylnaphthalene	8 ^v	300-475	1	8.28	10.0	u

^aDonnelly and Katz, 1954. ^bSomait and Kidnay, 1978. ^cMraw et al., 1978. ^dReamer et al., 1951. ^eHaman and Lu, 1976. ^fOlds et al., 1949. ^gBesserer and Robinson, 1971. ^hBesserer and Robinson 1973. ⁱSebastian et al., 1980a. ^jHuie et al., 1973. ^kOhgaki and Katayama, 1976. ^lGupta et al., 1982. ^mNagarajan and Robinson, 1987. ⁿMorris and Donohue, 1985. ^oSebastian et al., 1980c. ^pNg and Robinson, 1978. ^qNg et al., 1982. ^rVera and Orbey, 1984. ^sSebastian et al., 1980b. ^tBarrick et al., 1987. ^uTremper and Prausnitz, 1976. ^vGas solubilities are calculated for these systems. ^wA nearly optimal k_{ij} value of 0.9 is used in the van der Waal mixing rule for all systems. ^xAADP = $(100/NP)\sum_i |(P_i^{calc} - P_i^{expt})/P_i^{expt}|$; NP = number of data points.

Table III. Physical Properties of Five Aromatic Compounds Studied in This Work^a

	naphthalene	phenanthracene	anthracene	2,3-dimethylnaphthalene	2,6-dimethylnaphthalene
T_c , K	748.4	890	869.3	785	777
P_c , atm	40	32.5	34.4	31.75	31.8
ω	0.302	0.429	0.532	0.424	0.420
V_c , L/mol	0.111	0.182	0.139	0.1558	0.130
A	9.5810	11.420	12.630	11.910	12.357
B	2619.9	4567.7	5313.7	4292.1	4439.3
C	52.50	0.0	0.0	0.0	0.0
ζ_c	0.307	0.333	0.294	0.3003	0.3005
F	0.82539	0.95986	1.06550	0.95461	0.95047

^aThe solid vapor pressures are fitted to a function of $\log(P^{sat}/\text{mmHg}) = A - B/[(T/K) - C]$.

Table IV. Correlation of Aromatic Solid Solubilities in Supercritical Carbon Dioxide

aromatic compd	no. of data points	temp range, K	press. range, MPa	AADY, ^d %			ref
				this work	(II)	(I)	
naphthalene	44	308-333	9-30	6.12	6.79	40.07	a
2,3-dimethylnaphthalene	14	308-328	10-30	5.40	6.98	8.77	b
2,6-dimethylnaphthalene	15	308-328	10-30	7.04	16.49	23.35	b
anthracene	21	303-343	9-42	7.00	8.72	14.41	c
phenanthrene	15	318-338	8-42	7.82	7.57	15.46	b

^aMcHugh and Paulatis, 1980. ^bKurnik et al., 1981. ^cJohnston et al., 1982. ^dAADY = $(100/NP)|(y_2^{calc} - y_2^{expt})/y_2^{expt}|$; NP = number of data points. AADY(I): van der Waals mixing rules with one optimal adjustable parameter k_{ij}^{opt} . AADY(II): van der Waals mixing rules with two adjustable parameters k_{ij}^{opt} and l_{ij}^{opt} .

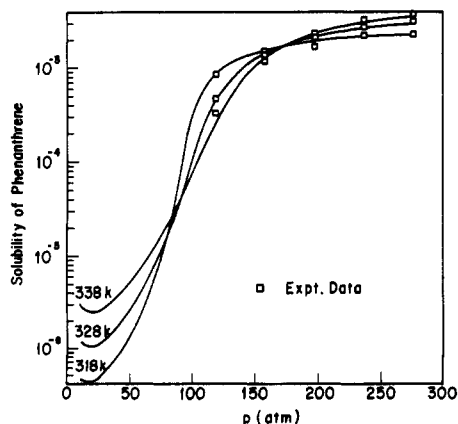


Figure 7. Calculated results of the solubilities of phenanthrene in supercritical carbon dioxide by this work (experimental data: Kurnik et al., 1981).

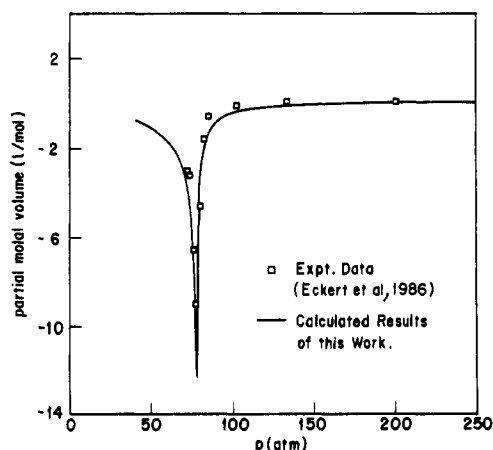


Figure 8. Calculated results of the partial molar volumes of naphthalene in supercritical carbon dioxide at 308 K by this work (experimental data: Eckert et al., 1986).

to correlate the partial molar volume data. The agreement shown in Figure 8 indicates that our improved mixing rules

are suitable in modeling the phase equilibria of solid and supercritical fluid mixtures. Further calculations of the

solubilities of biological compounds in supercritical carbon dioxide are currently undergoing.

Conclusions

Solid solubilities of five aromatic compounds in supercritical carbon dioxide are calculated by using the Patel-Teja EOS and the improved mixing rules. This study suggests a generalized method, with no adjustable parameters for each binary system, to calculate the solid solubilities in supercritical fluids. The results of this work are comparable to those by using the traditional van der Waals mixing rules with multiple best-fitted unlike pair parameters. This improved method can also give satisfactory predictions of partial molar volumes of solute in supercritical solvent.

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Nomenclature

A = temperature coefficient of the UNIFAC group interaction parameters, or the parameter in the vapor pressure equation, or the Helmholtz free energy

B, C = parameters in the vapor pressure equation

a, b, c = equation of state parameters

$\hat{a}, \hat{b}, \hat{c}$ = partial derivatives defined in eqs 15-17

F = parameter in the Patel-Teja equation of state

f = fugacity

G = Gibbs free energy

K_1, K_2 = parameters in eq 13

k, l, m = unlike pair factors defined in eqs 6-8, respectively

n = number of moles

P = pressure

p = exponent defined in eqs 23 and 25

q, r = surface area and volume parameters in the UNIFAC model, respectively

R = gas constant

T = temperature

T_0 = reference temperature of 298.15 K

V = volume

x, y = mole fractions

z = coordination number

Greek Letters

ψ, Ψ = volume fractions defined in eqs 23 and 24, respectively

θ = surface fraction defined in eq 26

ζ_c = parameter in the Patel-Teja equation of state

ϕ = fugacity coefficient

ω = acentric factor

Superscripts

C = combinatorial contribution

E = excess property

s = solid phase

sat. = saturation condition

scf = supercritical phase

Subscripts

2 = solute component

c = critical property

i, j = general component of group indexes

m = mixture property

Registry No. CO₂, 124-38-9; naphthalene, 91-20-3; phenanthrene, 85-01-8; 2,3-dimethylnaphthalene, 581-40-8; 2,6-dimethylnaphthalene, 581-42-0.

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Polymer Solution Properties of a Phenol-Formaldehyde Resol Resin by Gel Permeation Chromatography, Intrinsic Viscosity, Static Light Scattering, and Vapor Pressure Osmometric Methods

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A plywood adhesive-type phenol-formaldehyde (PF) resol resin was shown to have structures generally described as polymeric methylene(hydroxymethyl)phenols as determined by ¹³C NMR, and static light scattering gave molecular weights of up to about 114 000 daltons. The molecular weight and intrinsic viscosity data resulted in a Mark-Houwink exponent of 0.21 in tetrahydrofuran and 0.15 in ethyl acetate, which indicated a compact molecular structure in solution due to branching of the polymer chain. With the molecular weight and intrinsic viscosity data, the gel permeation chromatographic results obtained on a cross-linked polystyrene gel in tetrahydrofuran gave a universal calibration curve that agreed well with a similar curve obtained for linear polystyrene standards. This work determined the molecular weight and extent of branching of a wood adhesive PF resol resin synthesized by sodium hydroxide catalysis.

Introduction

The alkaline phenol-formaldehyde (PF) resol resins used extensively as binders in the wood products industry are polymeric methylene(hydroxymethyl)phenols of varying molecular weights (Figure 1). Molecular properties of these resins greatly depend on the synthesis parameters. In wood binder applications, the PF resins are normally

synthesized at 60-100 °C with a formaldehyde/phenol (F/P) ratio of 1.9-2.5, a sodium hydroxide content of up to 0.8 mol/mole of phenol, and a resin solids range of 40-60%. Since the resin viscosity must lie within a certain range for most applications, the resin solids level in the reaction mixture has been the major synthesis variable in controlling the molecular weight. In North America, the PF resins used in plywood adhesives normally have a solids level of 40-45% including the sodium hydroxide catalyst and are among the highest molecular weight PF resins manufactured.

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