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Density-Based Correlation for Solid Solubility in Supercritical Solvents

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Abstract

The use of solvents at conditions above their critical points is increasing because of their increased dissolving power and enhanced transport properties, as in caffeine extraction, etc. This research sought an improved method for correlating the solubility of materials in light solvents from conditions below the critical point of the solvents to those above it, especially to facilitate prediction, interpolation, and extrapolation of solubility data better than existing equations. Solvent density was recognized early as a factor in solvent dissolving power but not used as a correlating parameter. A density approach based on mass-action equilibrium law employing the solvation concept was used to correlate the data on selected binary mixtures with excellent results. For high pressures the relationship yields a plot of log solute solubility (g/L solution) versus log solvent density (g/L solution) which is sectionwise linear. A simplification of the relationship applies well at lower pressures. For both regions, experimental data are represented more easily and better than by conventional equations of state.

INTRODUCTION

The literature suggests that relatively extensive experimental data are required to develop sound designs for maximizing solute pickup and selecting the best conditions for a supercritical extraction process. A method of representing solubility behavior that would cover a broader range of conditions and be more accurate than current equation of state methods should have value.

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Although experimental work has been carried out on systems above the critical point of the solvent for a number of years, effort to represent the behavior of these systems has not been overly successful. There is a general feeling that it is very difficult to predict, interpolate, and extrapolate supercritical solubilities using conventional equations of state (EOS) such as Peng-Robinson and Redlich-Kwong. Thus, conventional equations of state may not represent the optimum approach.

This research program began with investigation of several ideas for applying supercritical solvents to improvement of industrial processes. Despite the amount of research effort expended in this field in the last two decades, our work was immediately confronted with a shortage of data for industrial systems of interest. Also, the existing methods for correlating data for prediction, interpolation, and extrapolation seemed inadequate for process anlaysis. After analysis of current methods of correlating data, the research took a new tack.

EQUATIONS OF STATE

Equations of state are used extensively to calculate interpolated and extrapolated values of *P-V-T* behavior and to calculate derived properties once the EOS is fitted to experimental data. Simple and complex equations have been tested for application to supercritical solubility equilibrium with only limited success. Significant errors have been encountered by even the most able investigators, particularly in predicting partial molal volumes and solubilities that agree with experimental data.

The Peng-Robinson equation was applied to the solubility of naphthalene in ethylene (*2, 3*) by fitting the binary interaction parameters to experimental data. Fractional errors were large in the pressure region in which solubility changes rapidly. Attempts to model other systems were less successful because of binary interaction parameter problems, resulting in the conclusion that a more accurate high-pressure mixture EOS appears to be necessary.

Ehrlich (*4*) compared experimental partial molar volumes for *n*-heptane in supercritical ethane with values calculated using the Redlich-Kwong EOS. Representation of the large negative values required for the increase in solute solubility as pressure increases isothermally was shown only qualitatively.

The virial expansion equations represent behavior well for low pressures (up to 60 atm for ethylene and carbon dioxide) but yield large errors for the high pressures. Jepson and Rowlinson (*5*) generalized the

Fowler-Guggenheim expansion and calculated virial coefficients using corresponding states and Lennard-Jones potentials for several kinds of supercritical solutions. With very large differences between calculated and experimental values for solubilities for high pressures and densities, they made an important conclusion relative to the authors' work. They attributed the excess solubility observed to clustering of solvent molecules around one solute molecule.

Thermodynamic analysis also provided impetus to examine solute-solvent complexing. From the partial derivative of internal energy, expression of partial molar quantities, the fact that the activity and fugacity of the pure solid solute are functions of temperature and pressure only, and use of the standard state as the pure component at the same temperature, pressure, and phase as the solution, the thermodynamic equation of state is

$$\frac{\bar{H}_2 - H_2^s}{T}\, dT + (V_2^s - \bar{V}_2)dP = RT\left(\frac{\partial \ln a_2}{\partial \ln x_2}\right)_{P,T} d \ln x_2 \tag{1}$$

From this, consider the solubility of a solid solute in a supercritical solvent at constant temperature,

$$\frac{V_2^s - \bar{V}_2}{RT\left(\dfrac{\partial \ln a_2}{\partial \ln x_2}\right)_{P,T}} = \left(\frac{\partial \ln x_2}{\partial P}\right)_T \tag{2}$$

If Raoult's or Henry's law holds,

$$\left(\frac{\partial \ln a_2}{\partial \ln x_2}\right)_{P,T} = 1 \tag{3}$$

If there is a negative deviation from Raoult's law or if $\bar{V}_2$ is less than either V_2^s or zero, the right-hand side of Eq. (2) will be positive, yielding an increase in solubility with an increase in pressure. If an aggregate or complex is formed with several solvent molecules associating with each solute molecule, the change in solution volume per mole of solute complexed, i.e., the partial molar volume of the solute, will decrease greatly, and the solubility will increase significantly with increasing pressure. Solvation-type interaction generally results in negative deviations from Raoult's law. Experiments (*4*) indicated that the partial molar volume tends to very large negative values in the supercritical solution.

From Eq. (1), solubility of a solid in a supercritical compressed solvent, at constant pressure, is

$$\frac{\bar{H}_2 - H_2^s}{RT^2\left(\frac{\partial \ln a_2}{\partial \ln x_2}\right)_{P,T}} = \left(\frac{\partial \ln x_2}{\partial T}\right)_P \tag{4}$$

The solubility depends on the partial molar enthalpy of the solid, and particularly its sign. Experimental data for the naphthalene–ethylene system show increasing naphthalene solubility with increasing temperature at constant pressure, if pressure is greater than 100 atm. This suggests that the partial molar enthalpy must be positive and must exceed the molar enthalpy of the pure solid for these conditions.

Other thermodynamic predictions also increased our interest in the idea of complex formation. One was the Gibbs' approach to predicting the change in vapor pressure of a pure solid when it is subjected to external pressure. This leads to expressions which call for a decrease in the mole fraction of the solute in solution as the pressure increases isothermally. This uses the condition that only the vapor pressure of the solid contributes to solubility; there is no association or solvation.

Selection of the Model

The generalized Lewis acid-base concept applied to complexes such as iodine in benzene, toluene, and ether (*6*), and the freezing out of a benzene–carbon tetrachloride complex showing attraction in excess of London forces (*7*), provided the basic impetus for model selection. The measured heat of sublimation of naphthalene in supercritical ethylene and CO_2 decreases as solvent density and its solubility increase, leading to the conclusion that charge-transfer interactions (*8*) were involved in the enhanced solubility. The experimental value (*8*) for entropy change suggested a rather strongly bonded complex. Kendall (*9*) suggested: 1) that for a fixed solute in a series of different solvents, increasing compound formation and solubility proceed in parallel, and (2) for a series of solutes of high melting point in a fixed solvent, the same applies.

The complex formation model has resulted from efforts to extend the basic work of Hildebrand and Scott (*10, 11*) and Prausnitz (*12*) by applying an activation energy approach to formation of a solvation complex. While the complex is, in effect, a loosely bonded chemical compound (12), it does not imply that the complex can necessarily be separated and exist by itself. In fact, such separation is usually not possible. The reaction to which the mass action law is applied is the solvation in dilute solutions of several molecules of solvent complexing with one molecule of solute. At equilibrium,

$$nA + B \underset{k_r}{\overset{k_f}{\rightleftharpoons}} (A)_nB \tag{5}$$

where $(A)_nB$ represents a solvation complex. The equilibrium constant for the reaction can be written as

$$K_c = \frac{[C_3]}{[C_1]^n[C_2]} \tag{6}$$

Also, in terms of forward and reverse reaction rates,

$$k_f = F_f \exp(-E_f^*/RT) \tag{7}$$

Thus, the equilibrium constant can be written

$$\begin{gathered} K_c = \frac{[C_3]}{[C_1]^n[C_2]} = \frac{k_f}{k_r} = F \exp(-\Delta E^*/RT) \\ \Delta E^* = E_f^* - E_r^* \end{gathered} \tag{8}$$

On substitution,

$$[C_3] = [C_1]^n[C_2]F \exp(-\Delta E^*/RT) \tag{9}$$

ΔE^* is the overall change in activation energy for the dynamic clustering in which F and ΔE^* are nearly independent of temperature for a given mechanism (*13*).

One can also examine the interaction from the statistical mechanics viewpoint in which the ratio of the number of molecules of the same kind in the activated state to those in unactivated states in a solution is

$$N_1^*/N_1 = \exp -(\varepsilon_1^* - \varepsilon_1)/kT \tag{10}$$

The molar activation energy can be expressed as

$$NA(\varepsilon_1^* - \varepsilon_1) = E_1^* \tag{11}$$

and

$$N_1^*/N_1 = [C_1]^*/[C_1] \tag{12}$$

Then

$$[C_1]^* = [C_1] \exp(-E_1^*/RT) \tag{13}$$

The same form will apply to any other component, e.g., component *B*. When these two components produce a clustering or solvation complex through their activation steps, the ratio of activated molecules as intermediates, or the solvation number, is

$$n = \frac{s_1[C_1] \exp(-E_1^*/RT)}{s_2[C_2] \exp(-E_2^*/RT)} \tag{14}$$

The steric factor should be included to consider other nonideal factors such as collision orientation, molecular configuration, etc. The solvation number will be constant at equilibrium for a fixed interaction mechanism.

At this point the relationships from the thermodynamic development and the statistical mechanical development are combined. Substituting Eq. (14) into Eq. (9) and rearranging yields

$$[C_3] = [C_1]^{n+1}\left(\frac{s_1 F}{s_2 n}\right) \exp[-(\Delta E^* + E_1^* - E_2^*)/RT] \tag{15}$$

Now, consider expressing the concentration of solute in the solution as the concentration of unsolvated solute molecules plus the concentration of solvated or clustered solute molecules:

$$[C_2]_t = [C_3] + [C_2] \tag{16}$$

where

$$[C_2]_t = (\rho_2)_t/M_2 \tag{17}$$

and

$$[C_1] = \rho_1/M_1 \tag{18}$$

in terms of the apparent densities. Substituting into Eq. (16) yields,

$$[C_2]_t = [C_1]^{n+1}\left(\frac{s_1F}{s_2n}\right) \exp\,[-(\Delta E^* + E_1^* - E_2^*)/RT] + [C_1]\,\frac{s_1}{s_2n} \exp\,[(E_2^* - E_1^*)/RT] \tag{19}$$

Now, substituting Eqs. (17) and (18) into Eq. (19) and rearranging,

$$(\rho_2)_t = (\rho_1)^{n+1}\,\frac{M_2s_1F}{(M_1)^{n+1}s_2n} \exp\,[-(\Delta E^* + E_1^* - E_2^*)/RT] + (\rho_1)\,\frac{M_2s_1}{M_1s_2n} \exp\,[(E_2^* - E_1^*)/RT] \tag{20}$$

To make it easier to work with this relationship, the following substitutions are made:

$$\alpha = -\Delta E^* + E_2^* - E_1^* \tag{21}$$

$$\gamma = E_2^* - E_1^* \tag{22}$$

Also, exponential substitutions are made as follows:

$$\exp\,(\beta_1) = \left(\frac{s_1F}{s_2n}\right)\left(\frac{M_2}{(M_1)^{n+1}}\right) \tag{23}$$

$$\exp\,(\beta_2) = \left(\frac{s_1}{s_2n}\right)\left(\frac{M_2}{M_1}\right) \tag{24}$$

Equation (20) then becomes the basic relationship for the correlation

$$(\rho_2)_t = (\rho_1)^{n+1} \exp\left(\frac{\alpha}{RT} + \beta_1\right) + (\rho_1) \exp\left(\frac{\gamma}{RT} + \beta_2\right) \tag{25}$$

The validity of the substitutions of Eqs. (21)-(24) will be shown later, i.e., the values of α, β_1, β_2, and γ are nearly constant over considerable ranges of pressure if the interaction mechanism remains the same. As a general comment, the second term on the right-hand side of Eq. (25) represents the unsolvated fraction of the solute and corresponds to the true fugacity (vapor pressure) of the solid. It will be negligible at high pressures, where the first right-hand side term will represent practically all of the solubility occurring.

Several verbal interpretations of behavior can be developed from Eq. (25). From the thermodynamic energy balance, the factors in Eqs. (21) and (25) are

$$\Delta E^* = E_f^* - E_r^* \approx \Delta H^r \tag{26}$$

$$\gamma = E_2^* - E_1^* \approx -\Delta H^v \tag{27}$$

$$\alpha = -\Delta E^* + E_2^* - E_1^* \approx -\Delta H^r - \Delta H^v \tag{28}$$

where ΔH^r is the change in enthalpy due to solvation or clustering only and ΔH^v is the enthalpy of vaporization of the pure solid; the first is negative and the second is positive. Then,

1. The interaction energy corresponding to ΔH^r becomes more negative as the pressure increase above the critical, and solubility continues to increase.
2. The greater the density of the solvent, the greater the solubility of the solute.
3. The larger the size and the greater the molecular weight of the solvent, the lower the solubility of the solute.
4. The more volatile the solute, the greater its solubility.
5. The greater the solvation number, the greater the solubility.
6. In comparing the effect of terms, the factor β_1, which includes the molecular size of the solvent, has a greater effect on solubility than the energy factor. These interpretations agree with other observations (*14*).

Analysis and Testing

The applicability of the relationship was first tested for low pressures. Here it is assumed that even if solvation or clustering occurs at low pressures, one solute molecule will be solvated with at most one solvent molecule. Thus, $n + 1$ is less than 2. From Eqs. (16) and (25),

$$\rho_2 = \rho_1 \exp\left(\frac{\gamma}{RT} + \beta_2\right) \tag{29}$$

On substitution into Eq. (25) and taking the logarithm,

$$\ln(\rho_2)_t = \ln \rho_2 + \ln[1 + \rho_1 \exp(-\Delta E^*/RT + \beta_1 - \beta_2)] \quad (30)$$

Under these conditions $(\rho_2)_t$ is very nearly equal to ρ_2. Also considering that for small values of x, $\ln(1+x) = x$,

$$\rho_1 \exp\left(-\frac{\Delta E^*}{RT} + \beta_1 - \beta_2\right) \ll 1 \quad (31)$$

Then,

$$\ln(\rho_2)_t = \rho_1 \exp(-\Delta E^*/RT + \beta_1 - \beta_2) + \ln \rho_2 \quad (32)$$

With the following substitutions, Eq. (33) is obtained:

$$\begin{aligned} b &= \ln \rho_2 \\ m &= \exp\left(-\frac{\Delta E^*}{RT} + \beta_1 - \beta_2\right) \\ \ln(\rho_2)_t &= m\rho_1 + b \end{aligned} \quad (33)$$

Constants for the relationship were obtained by regression on both low and high pressure data. These are reported for naphthalene-ethylene in Table 1 and for naphthalene-CO_2 in Table 2. The excellent fits resulting are illustrated in Tables 3 and 4 for single temperatures.

As a first approximation, at low density, b and m may be considered to be nearly independent of density, at constant temperature. When low pressure (up to 60 atm) data are used to obtain values of b and m by regression, the calculated solubility agrees very well with the experi-

TABLE 1
Constants in Eqs. (33) and (36) for Naphthalene-Ethylene

Temperature (°C)	Pressure (atm)	n	c	m	b
25	60–90	2.668	−18.933		
	90–300	5.030	−32.435		
35	0–60			0.0420	−6.482
	60–90	2.720	−18.863		
	90–300	5.202	−32.799		
45	60–90	2.346	−16.561		
	90–300	6.026	−36.896		
50	0–60			0.0414	−5.441

TABLE 2
Constants in Eq. (36) for Naphthalene–Carbon Dioxide

Temperature (°C)	Pressure (atm)	n	c
35	70–330	2.825	−22.107
45	70–100	2.808	−21.650
	100–310	3.577	−26.521
55	70–100	2.077	−16.755
	100–130	3.635	−26.377
	130–320	5.572	−38.885

TABLE 3
Solubility Data for Naphthalene in Ethylene at 35°C

Pressure (atm)	Equation
0–60	$\ln(\rho_2)_t = (0.042)(\rho_2)_t - (6.482)$
60–90	$\ln(\rho_2)_t = (3.270)\ln(\rho_1)_t - (18.863)$
90–300	$\ln(\rho_2)_t = (6.202)\ln(\rho_1)_t - (32.799)$

Pressure (atm)	Experimental *mf*	Calculated *mf*	Experimental $(\rho_1)_t$	Calculated $(\rho_2)_t$
8.0	0.0000544	0.0000533	9.2545	0.0023
13.0	0.0000409	0.0000411	15.8671	0.0030
20.0	0.0000392	0.0000383	24.8786	0.0044
30.7	0.0000427	0.0000460	41.1312	0.0087
34.0	0.0000525	0.0000512	46.7041	0.0109
40.0	0.0000728	0.0000658	57.6610	0.0174
48.2	0.0000984	0.0001041	74.7103	0.0356
55.1	0.0001570	0.0001718	91.4062	0.0719
59.1	0.0002290	0.0002430	102.3140	0.1139
62.1	0.0003720	0.0003250	111.1915	0.1655
65.0	0.0010700	0.0010089	142.2334	0.6576
70.0	0.0015200	0.0015040	164.7492	1.1360
75.0	0.0022600	0.0026441	202.8015	2.4611
80.0	0.0036900	0.0036789	229.0696	3.8719
85.0	0.0055900	0.0050916	258.2704	6.0504
90.0	0.0073800	0.0067935	281.2423	8.8059
100.0	0.0109000	0.0112131	309.6457	15.9926
113.0	0.0146000	0.0151063	327.8822	22.8064
125.0	0.0175000	0.0191620	343.2021	30.2731
145.0	0.0223000	0.0229298	355.2394	37.4892
160.0	0.0252000	0.0267998	366.0394	45.1414
190.0	0.0314000	0.0314018	377.3504	54.5189
230.0	0.0372000	0.0382733	391.9672	69.0098
270.0	0.0424000	0.0427082	400.3082	78.6369
300.0	0.0458000	0.0453337	404.9215	84.4285

TABLE 4
Solubility Data for Naphthalene in Carbon Dioxide at 45°C

Pressure (atm)	Equation
60–100	$\ln(\rho_2)_t = (3.808)\ln(\rho_1)_t - (21.651)$
100–300	$\ln(\rho_2)_t = (4.577)\ln(\rho_1)_t - (26.521)$

Pressure (atm)	Experimental *mf*	Calculated *mf*	Experimental $(\rho_1)_t$	Calculated $(\rho_2)_t$
81.0	0.0007800	0.0007686	254.1369	0.5694
84.5	0.0011000	0.0010839	287.2654	0.9080
87.0	0.0013000	0.0013354	309.4563	1.2054
91.0	0.0021000	0.0021358	365.8967	2.2813
94.5	0.0043000	0.0042300	467.0661	5.7797
96.5	0.0051000	0.0051751	502.0138	7.6073
98.0	0.0061000	0.0060856	532.0146	9.4890
100.0	0.0069000	0.0068313	554.5228	11.1108
105.0	0.0097000	0.0100188	619.8179	18.2724
108.0	0.0113000	0.0107519	632.3081	20.0195
118.0	0.0142000	0.0143620	686.3164	29.1318
125.0	0.0154000	0.0152999	698.7484	31.6264
140.0	0.0183000	0.0183535	735.8569	40.0776
153.0	0.0197000	0.0202449	756.7228	45.5492
200.0	0.0245000	0.0245153	799.2924	58.5149
275.0	0.0285000	0.0281470	831.6342	70.1631
310.0	0.0294000	0.0292247	840.5772	73.7235

mental data as shown in Table 3 for naphthalene–ethylene at 35°C. The excellent linearization obtained is shown in Figs. 1 and 4. The form of Eq. (33) is not new. If the behavior of the components in the gas phase can be represented using the virial equation limited to the second virial, the same form results. Robin and Vodar (*15*) used the virial approach and obtained the same equation which they used to predict solubilities at low pressures in several kinds of compressed gases with good agreement.

Next, and more importantly, the relationship was examined for representing high pressure data. At high pressures the solubility due to the vapor pressure of the solid is negligible relative to the total solubility:

$$\begin{gathered}\rho_1^{\,n+1} \gg \rho_1 \\ \exp(\alpha/RT + \beta_1) \gg \exp(\gamma/RT + \beta_2)\end{gathered} \tag{34}$$

The second term in Eq. (25) can be neglected, so

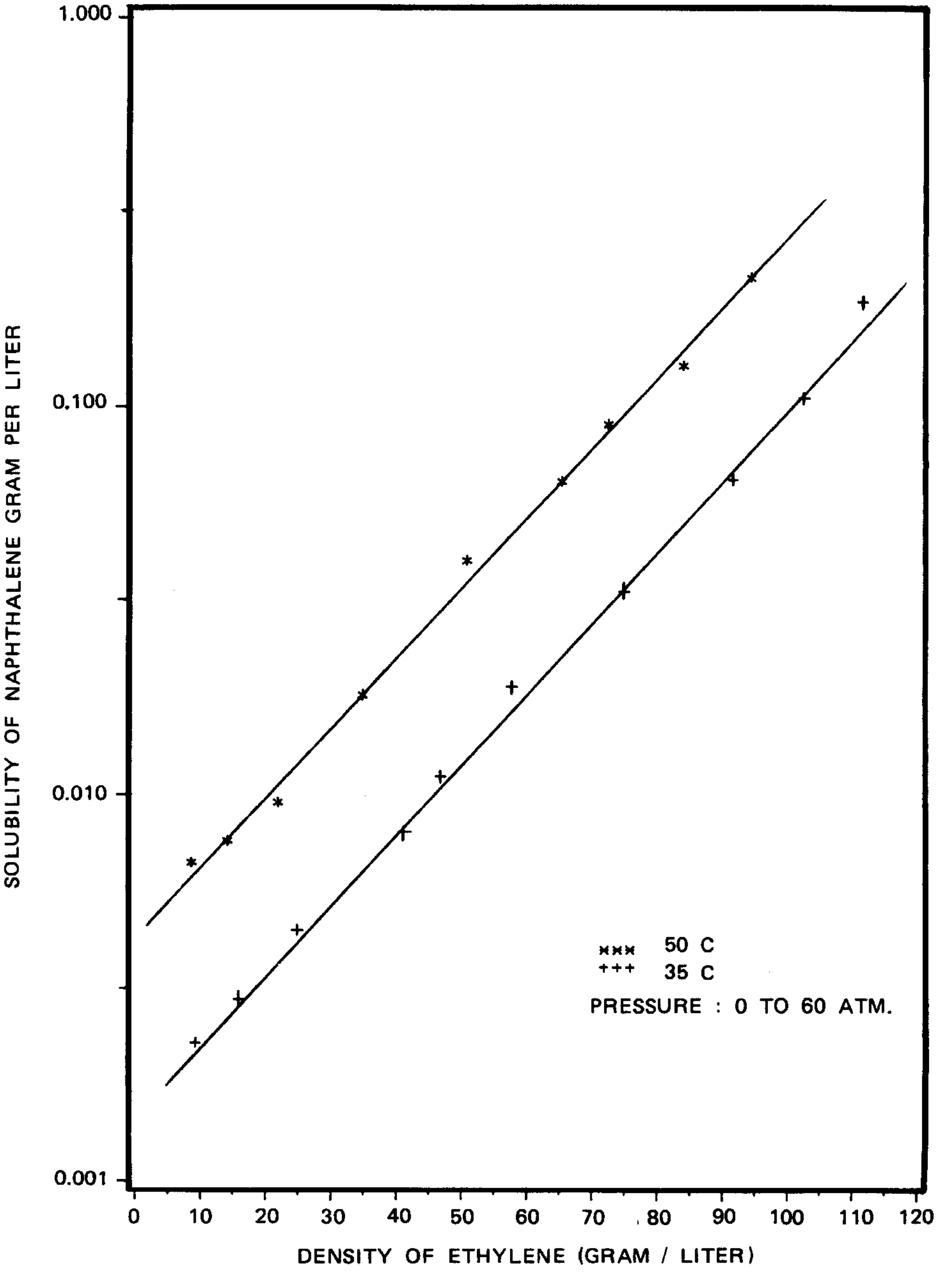

FIG. 1. Experimental solubility of naphthalene in ethylene.

$$(\rho_2)_t = (\rho_1)^{n+1} \exp\left(\frac{\alpha}{RT} + \beta_1\right) \tag{35}$$

Letting $C = (\alpha/RT) + \beta_1$, and taking the logarithm,

$$\ln(\rho_2)_t = (n + 1)\ln \rho_1 + C = (n + 1)\ln(\rho_1)_t + c \tag{36}$$

The solubilities calculated with Eq. (36) agree very well with the experimental data as shown in Tables 3 and 4 and Figs. 2 and 3. Equations (33) and (36) each have only two constants so it will be easy to fit other systems if density data are available. As with other types of behavior, Eqs. (33) and (36) show the importance of density as a correlating parameter. This was mentioned as early as 1948 (*1*) but not pursued. This form suggests that a plot of log solute density (g/L solution) versus log solvent density (g/L solution) should be linear if the average interaction mechanism does not change for the range of variables concerned. The only experimental data available which provided the necessary density values for test were those of Tsekhanskaya (*16*) for naphthalene with ethylene and carbon dioxide. These data differ by less than 2 to 4% from those of Diepen and Scheffer (*17*). The data used for pressures less than 60 atm were those of Masuoka and Yorizane (*18*).

Plots of the experimental data which verify Eq. (36) are shown in Figs. 4 and 5. For every isotherm the data plots are at least sectionwise linear, and sometimes almost completely linear. The differences in slope for different sections may represent different solvation numbers, as shown in Tables 1 and 2. It is not expected that the solvation number be an integer. As with micelles, there are probably several solvated complexes existing at one time in a dynamic equilibrium. Thus, the solvation number represents an average occurrence that is characteristic of a given solvent and solute. Once the sections are identified from a rough plot, it is easy to obtain a close fit of the data by: 1) least squares regression, 2) graphical fitting, and 3) inserting data for two points at the ends of a linear subsection. Thus, the relationship should be valuable for prediction, interpolation, and extrapolation and might reduce the data needed in experimental programs.

SYMBOLS

Roman Capitals

A	solvent
B	solute

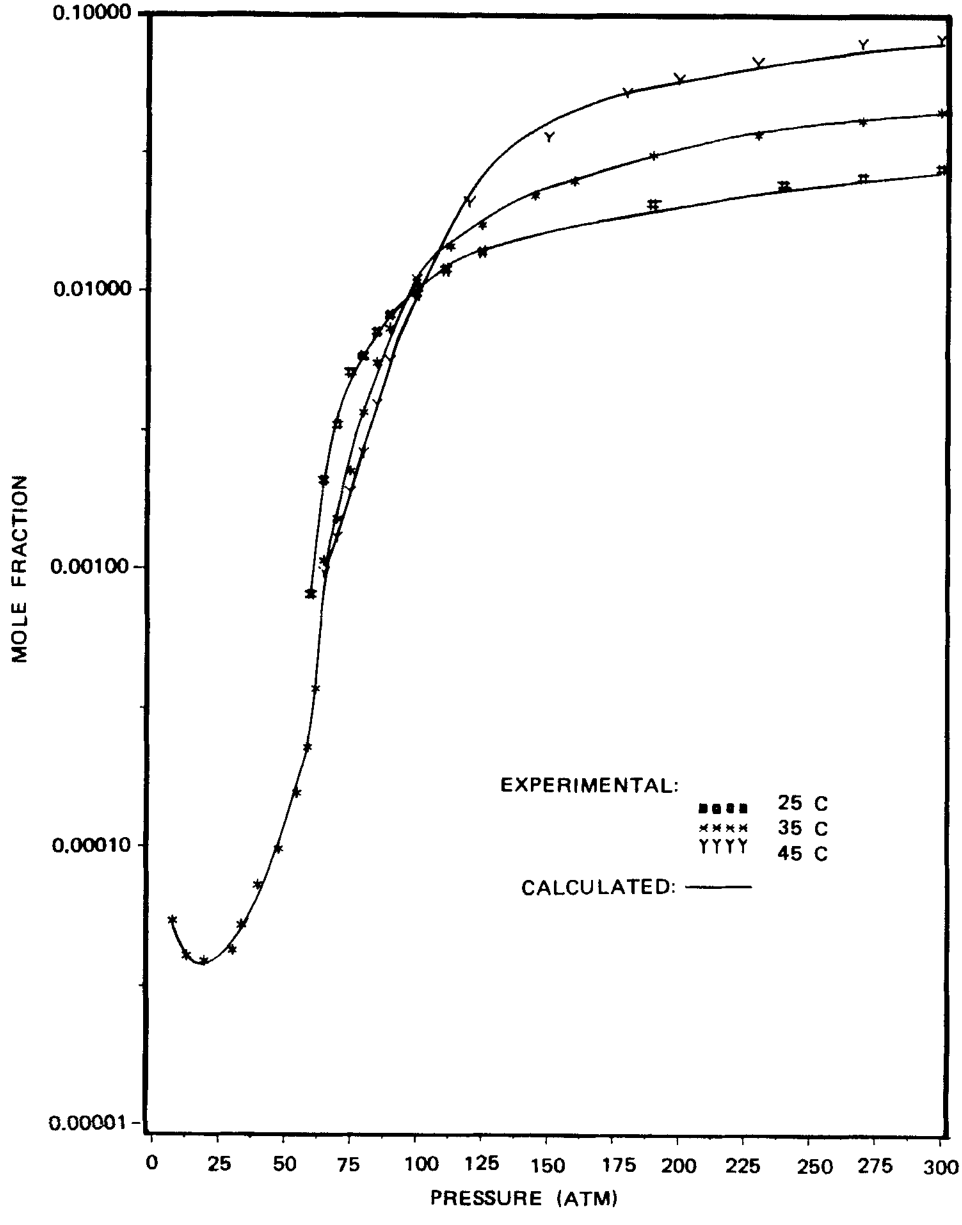

FIG. 2. Solubility of naphthalene in ethylene.

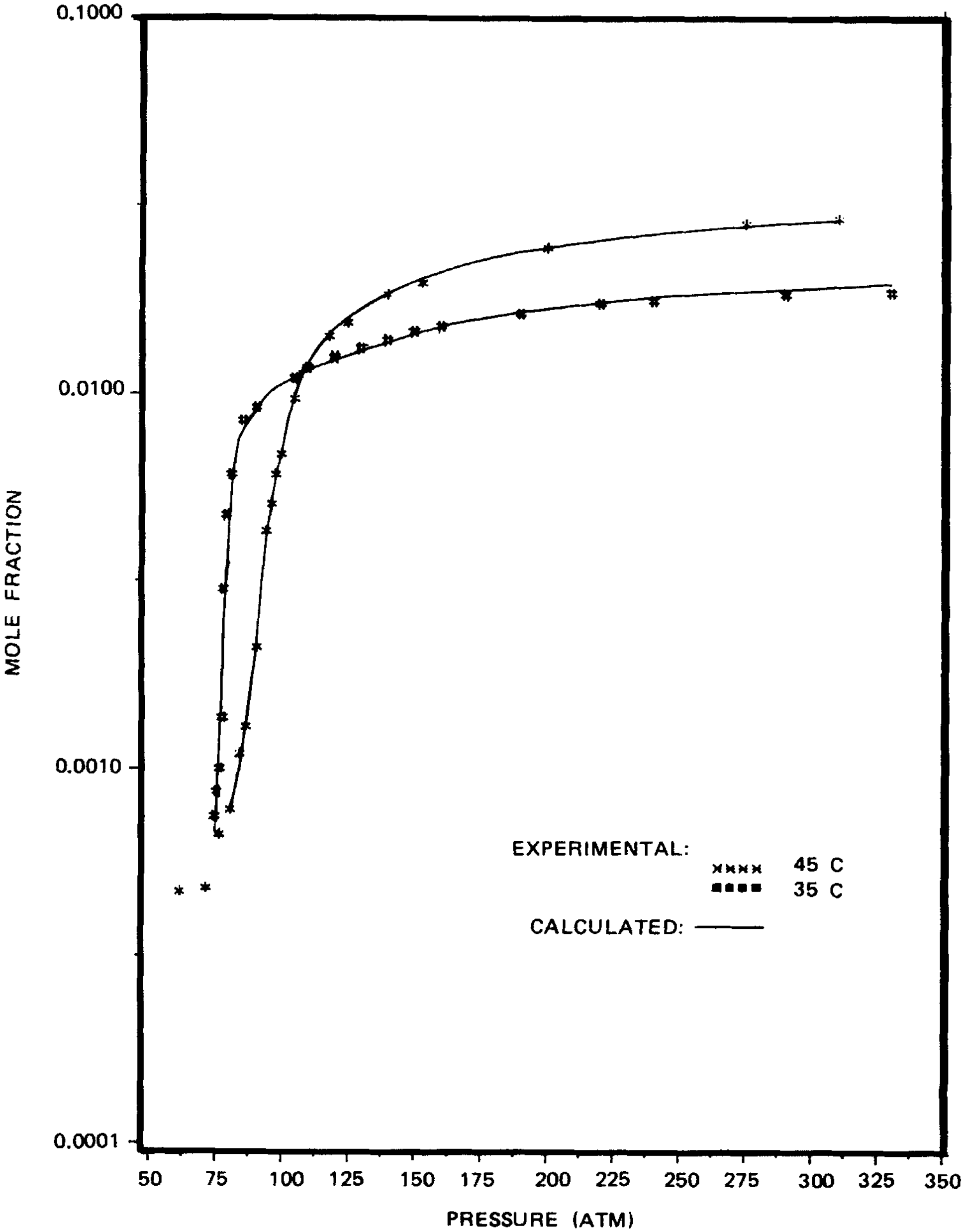

FIG. 3. Solubility of naphthalene in carbon dioxide.

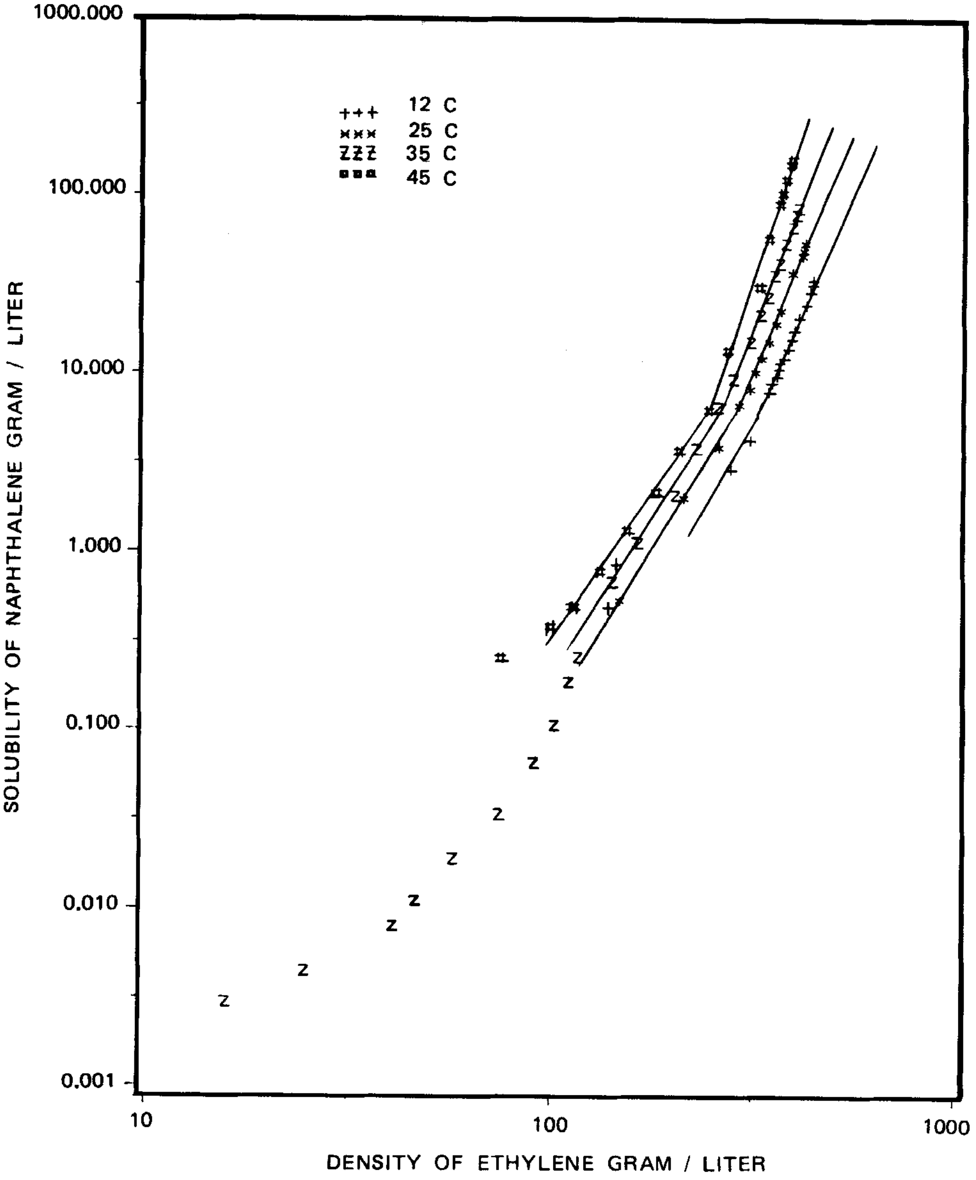

FIG. 4. Experimental solubility of naphthalene in ethylene.

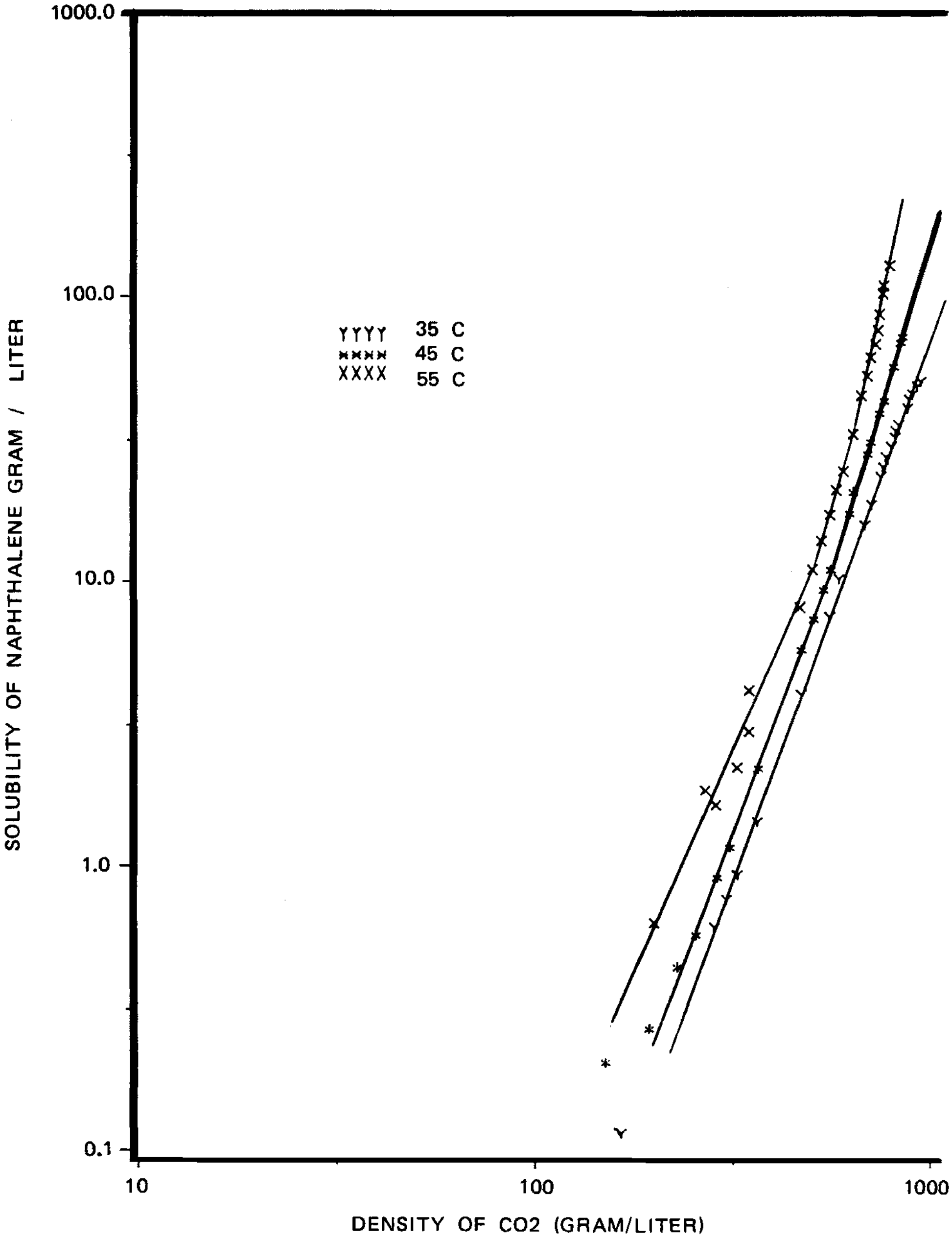

FIG. 5. Experimental solubility of naphthalene in carbon dioxide.

$[C]$	concentration, moles per liter of solution
$[C_2]$	moles of unsolvated solute per liter of solution
$[C_3]$	moles of complexes or moles of solvated solute per liter of solution
$[C_2]_t$	$[C_2]$ plus $[C_3]$, total moles of solute per liter of solution
$[C_1]$	moles of unsolvated solvent per liters of solution
$[C_1]_t$	total moles of solvent (solvated plus unsolvated) per liter of solution
C	constant
E	energy
F	frequency factor
H	enthalpy
K_c	equilibrium constant
L	liter
M	molecular weight
N	number of molecules
NA	Avagadro's number
P	pressure
R	gas constant
T	temperature
V	volume per mole

Roman Lower Case

a	activity
b	constant
c	constant
d	grams per liter of solution
g	grams
m	constant
mf	mole fraction
k	rate constant
n	solvation number
s	steric factor
x	mole fraction

Greek Capital

Δ	increment, difference

Greek Lower Case

α	constant, coefficient
β_1	constant, coefficient
β_2	constant, coefficient
γ	constant, coefficient
ρ	density, grams per liter of solution
ρ_1	density, unsolvated solvent, grams per liter of solution
ρ_2	density, unsolvated solute, grams per liter of solution
ε	energy per molecule

Subscripts

t	total apparent amount (solvated plus unsolvated)
f	Forward reaction or interaction
T	constant temperature
p	constant pressure
r	reverse reaction or interaction
1	solvent
2	solute
3	solvation complex

Superscripts

r	solvation, reaction
s	solid state
v	vaporization
—	partial molar property
*	activation

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