Effect of Entrainers and of Solute Size and Polarity in Supercritical Fluid Solutions

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New experimental data are presented for the solubility of several solid solutes and solute mixtures in entrainer-doped supercritical fluid carbon dioxide. These results, along with others from the literature, are used to demonstrate the effects of solute size (appreciable) and solute polarity (small) in pure supercritical fluids. Solvent effects appear to be far more important than solute structure, and polar and hydrogen-bonding entrainers exhibit large effects on both solute loading and selectivity. Thus, it appears that entrainers can be used to tailor supercritical fluid solvents for specific applications.

Although supercritical extraction has been widely publicized as a novel separation technique of great versatility, it now appears that its applications will be in a number of specialized situations, each characterized by a rather specific set of requirements. To develop such applications, we require a rather thorough understanding of the chemistry and physics of the supercritical fluid state at the molecular level. Only with such information can we model successfully such systems, first to tailor thermodynamic parameters and solvent composition for optimum operation, and second to do the scale-up and economic analysis necessary to prove feasibility.

Much work to date has used empirical or semiempirical equations of state with adjustable parameters to fit limited experimental data. While useful, such techniques lend themselves to neither understanding of nor extrapolation to new systems or conditions. In this work we use the solubility of a solid in a supercritical fluid as a probe to investigate the effects of solute molecular structure, especially size and polarity. Further, we use solvent additives, or entrainers, to investigate the effect of specific interactions on both solubility and selectivity. Finally, we use these results to suggest a form for a chemical–physical model of the supercritical fluid (SCF) that may be of use in tailoring entrainer–solvent mixtures for specific separations.

Pure Supercritical Solvents

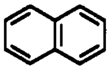
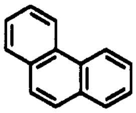
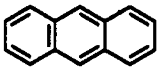
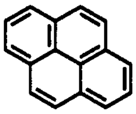
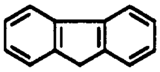
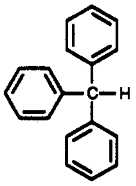
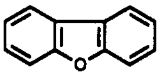
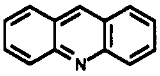
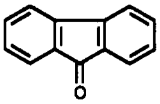
It has already been shown in a number of papers and presentations (*1–4*) that supercritical solubility data are represented in dimensionless fashion by an enhancement factor

$$E = y_2P/P^{\text{sat}} \tag{1}$$

which is the ratio of the solute supercritical partial pressure to its ideal gas partial pressure at the system temperature. This dimensionless function eliminates the effects of volatility differences and thus characterizes solely the thermodynamic nonideality of the supercritical fluid phase. Enhancement factors are therefore truer representations of the strength of solute–solvent interactions that are solubilities.

Using data from the literature (*2, 5–8*), we use enhancement factors to discern the influences of chemical structure on the solubility behavior. We first study the effect of the size of the solute species for solutes of similar type. Figure 1 shows the result for solutes with an increasing number of rings in the series naphthalene–anthracene–pyrene. The solubility enhancement increases with solute size, which suggests that the solution forces may be related in some manner to the number of solvent molecules that may group about the solute.

Table I. Model Solutes Used

structure	compound	μ (D)
	naphthalene	0
	phenanthrene	0
	anthracene	0
	pyrene	0
	fluorene	0
	triphenylmethane	0.4
	dibenzofuran	0.8
	acridine	2.1
	9-fluorenone	3.4

The next comparison concerns the influence of solute polarity or functionality on the solubility enhancement. The enhancement factors for a group of solutes of similar size (all are three-ringed compounds; pertinent structural information is given in Table I at constant solution temperature) are illustrated in Figure 2. The effect of the polar nature or the

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0021-9568/93/1738-0605$04.00/0

Table II •

P (bar)	density^b (mol/cm^3)	10^3y_2	log E	P (bar)	density^b (mol/cm^3)	10^3y_2	log E	P (bar)	density^b (mol/cm^3)	10^3y_2	log E
Phenanthrene–CO_2 (3.9% Methanol)											
104.4	0.0098	0.474	4.15	145.8	0.0156	1.28	4.72	242.3	0.0188	5.84	5.60
118.2	0.0122	0.874	4.47	173.3	0.0170	1.69	4.92	276.7	0.0194	7.94	5.79
138.9	0.0150	0.983	4.59	207.8	0.0180	4.63	5.44	345.7	0.0204	13.7	6.13
Phenanthrene–CO_2 (2.5% Methanol)											
104.4	0.0098	0.462	4.14	145.8	0.0156	1.54	4.81	345.7	0.0204	6.36	5.80
118.2	0.0122	0.948	4.51	173.3	0.0170	3.11	5.19				
132.0	0.0142	1.16	4.64	242.3	0.0188	5.49	5.58				
Phenanthrene–CO_2 (1.0% Methanol)											
104.4	0.0098	0.224	3.82	145.8	0.0156	1.28	4.72	345.7	0.0204	3.26	5.50
118.2	0.0122	0.730	4.39	173.3	0.0170	1.72	4.92				
132.0	0.0142	1.00	4.57	242.3	0.0188	2.71	5.27				
Phenanthrene–CO_2 (2.5% Acetone)											
118.2	0.0131	0.991	4.52	173.3	0.0174	2.71	5.12	173.3	0.0170	3.11	5.19
132.0	0.0142	1.77	4.82	242.3	0.0184	4.18	5.46	345.7	0.0204	5.63	5.74
Phenanthrene–CO_2 (1.0% Acetone)											
104.4	0.0098	0.142	3.62	145.8	0.0156	0.964	4.60	345.7	0.0204	2.26	5.35
118.2	0.0131	0.358	4.08	173.3	0.0174	1.98	4.99	449.0	0.0215	4.09	5.72
132.0	0.0142	0.613	4.36	242.3	0.0184	2.14	5.17				
Fluorene–CO_2 (2.5% Acetone)											
118.2	0.0125	1.33	4.11	145.8	0.0158	3.03	4.56	242.3	0.0189	8.39	5.23
132.0	0.0142	1.54	4.23	173.3	0.0174	4.89	5.47	345.7	0.0204	8.76	5.40
Fluorene–CO_2 (1.0% Acetone)											
104.4	0.0102	0.303	3.42	145.8	0.0158	3.07	4.57	345.8	0.0204	4.76	5.13
118.2	0.0125	0.714	3.84	173.3	0.0174	2.63	4.58				
132.0	0.0142	1.14	4.09	242.3	0.0189	4.94	4.99				
Dibenzofuran–CO_2 (2.5% Methanol)											
104.4	0.0102	4.02	3.65	245.8	0.0158	9.77	4.62	242.3	0.0188	17.9	5.06
118.2	0.0122	6.29	4.36	173.3	0.0174	14.0	4.73	311.2	0.0199	20.5	5.35
Dibenzofuran–CO_2 (1.0% Methanol)											
94.1	0.00764	0.258	2.87	173.3	0.0174	9.32	4.70	345.7	0.0204	30.2	5.51
118.2	0.0125	2.16	3.90	207.8	0.0180	13.5	4.94				
138.9	0.0150	3.15	4.13	276.7	0.0194	27.2	5.36				
Dibenzofuran–CO_2 (2.5% Acetone)											
118.2	0.0122	7.85	4.46	145.8	0.0156	16.6	4.87	242.3	0.0188	23.2	5.24
132.0	0.0142	11.4	4.67	173.3	0.0170	20.9	5.05	345.7	0.0204	26.5	5.45
Dibenzofuran–CO_2 (1.0% Acetone)											
104.4	0.00984	2.19	3.85	145.8	0.0156	5.61	4.40	345.7	0.0204	33.5	5.55
118.2	0.0122	3.48	4.10	173.3	0.0170	12.1	4.81				
132.0	0.0142	3.76	4.18	242.3	0.0188	16.9	5.10				
9-Fluorenone–CO_2 (2.5% Methanol)											
107.9	0.0109	1.13	4.65	152.7	0.0161	3.58	5.30	276.7	0.0194	8.44	5.93
118.2	0.0131	1.74	4.88	214.7	0.0182	6.47	5.71	345.7	0.0204	11.2	6.15
9-Fluorenone–CO_2 (1.0% Methanol)											
94.1	0.00764	0.0593	3.30	132.0	0.0142	1.67	4.89	311.2	0.0200	6.71	5.87
104.4	0.0102	0.0990	3.57	145.8	0.0158	2.19	5.06	380.1	0.0208	9.76	6.12
118.2	0.0125	0.239	4.00	242.3	0.0189	3.37	5.46				
9-Fluorenone–CO_2 (2.5% Acetone)											
107.9	0.0109	2.69	5.03	152.7	0.0161	4.46	5.40	276.7	0.0194	16.4	6.21
118.2	0.0131	2.49	5.02	187.1	0.0174	6.81	5.67				
132.0	0.0147	4.07	5.30	214.7	0.0182	7.59	5.78				
9-Fluorenone–CO_2 (1.0% Acetone)											
104.4	0.00984	0.265	3.99	132.0	0.0142	1.74	4.91	242.3	0.0188	4.90	5.63
118.2	0.0122	1.31	4.74	145.8	0.0156	2.37	5.09	345.7	0.0204	10.6	6.12
Acridine–CO_2 (3.9% Methanol)											
104.4	0.0098	0.854	4.93	132.0	0.0142	2.11	5.43	242.3	0.0188	4.31	5.99
118.2	0.0122	1.38	5.19	173.3	0.0170	3.29	5.72	345.7	0.0204	7.03	6.35
Acridine–CO_2 (2.5% Methanol)											
104.4	0.0098	0.563	3.75	145.8	0.0156	0.385	4.73	276.7	0.0194	4.15	6.04
118.2	0.0122	0.162	4.26	207.8	0.0180	1.56	5.49	345.7	0.0204	6.53	6.33
Acridine–CO_2 (1.0% Methanol)											
94.1	0.0074	0.0217	3.29	132.0	0.0142	0.498	4.80	173.3	0.0170	1.57	5.42
104.4	0.0098	0.0990	3.99	138.9	0.0150	1.10	5.16	242.3	0.0188	2.49	5.76
118.2	0.0122	0.207	4.37	145.8	0.0156	0.839	5.07	345.7	0.0204	5.17	6.23

Table II (Continued)

P (bar)	density[b] (mol/cm^3)	10^3y_2	log E	P (bar)	density[b] (mol/cm^3)	10^3y_2	log E	P (bar)	density[b] (mol/cm^3)	10^3y_2	log E
Acridine–CO_2 (2.5% Methanol) (T = 343 K)											
118.2	0.00764	0.124	3.24	207.8	0.0153	1.95	4.68	311.2	0.0197	5.98	5.34
145.8	0.0111	0.480	3.92	242.3	0.0165	2.28	4.81	414.6	0.0200	9.81	5.68
173.3	0.0135	1.13	4.36	276.7	0.0174	2.97	4.99				
Acridine–CO_2 (2.5% Acetone)											
104.4	0.0098	0.232	4.36	166.0	0.0167	1.24	5.29	345.7	0.0204	3.77	6.10
118.2	0.0122	0.649	4.86	207.8	0.0180	2.55	5.70	380.2	0.0208	4.09	6.17
145.8	0.0456	1.10	5.18	276.7	0.0194	2.43	5.81				
Acridine–CO_2 (1.0% Acetone)											
104.4	0.00984	0.0928	3.97	132.0	0.0142	0.305	4.59	242.3	0.0188	2.26	5.72
111.3	0.0110	0.185	4.29	145.8	0.0156	0.571	4.90	345.7	0.0204	4.00	6.12
118.2	0.0122	0.224	4.40	173.3	0.0170	1.36	5.35				
Phenazine–CO_2											
104.4	0.00984	0.0369	3.79	145.8	0.0156	0.225	4.72	345.7	0.0204	1.29	5.85
118.2	0.0122	0.101	4.28	173.3	0.0170	0.519	5.16				
132.0	0.0142	0.207	4.64	242.3	0.0188	1.11	5.64				
Phenazine–CO_2 (2.5% Methanol)											
104.4	0.00984	0.100	4.22	145.8	0.0156	0.601	5.15	345.7	0.0204	4.52	6.40
118.2	0.0122	0.249	4.28	173.3	0.0170	0.972	5.43				
132.0	0.0142	0.495	5.02	242.3	0.0188	2.02	5.90				
Phenazine–CO_2 (2.5% Acetone)											
104.4	0.0098	0.124	4.32	145.8	0.0156	0.541	5.10	345.7	0.0204	1.87	6.02
118.2	0.0122	0.333	4.80	173.3	0.0170	1.00	5.44				
132.0	0.0142	0.459	4.99	242.3	0.0188	1.56	5.78				

Acridine–Anthracene–CO_2 (1.0% Methanol) (T = 323 K)

P (bar)	10^3y_{acr}	10^3y_{anth}	K	P (bar)	10^3y_{acr}	10^3y_{anth}	K	P (bar)	10^3y_{acr}	10^3y_{anth}	K
104.4	0.136	0.0199	6.83	207.8	2.08	0.181	11.5	345.7	8.62	0.741	11.6
138.9	0.845	0.155	5.45	276.7	5.38	0.461	11.7				

[a] T = 323 K except in one isotherm noted. [b] Density of pure CO_2 at given temperature and pressure (*17*).

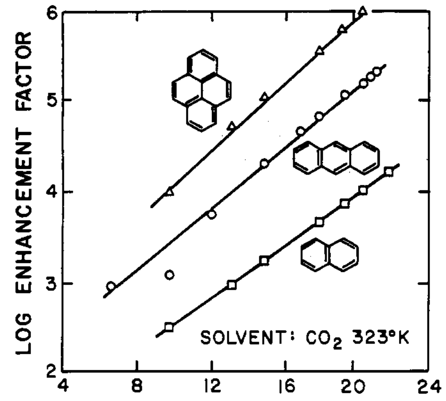

Figure 1. Effect of solute size on supercritical solubility. Solvent: CO_2 at 323 K. Data of refs 5 and 6.

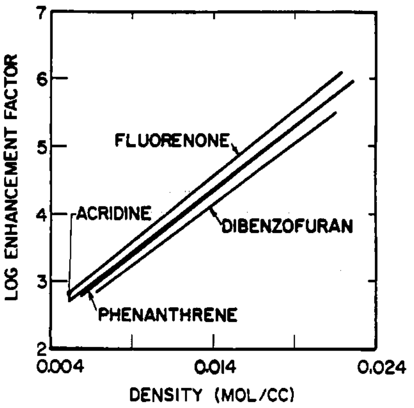

Figure 2. Enhancement factors for model solutes in supercritical CO_2. Temperature: 323 K. Data of refs 6 and 8.

functionality of the solute is minimal when dissolved within a pure SCF; the enhancement appears relatively insensitive to the structual differences in this set of solutes.

The influence of the solvent on supercritical solubility is shown by comparison of the enhancement behavior of a single solute dissolved within several SCF's. Since many fluids have quite different critical properties, the data are first scaled to a constant solvent-reduced temperature, and they are presented over the same range of reduced density, i.e., the same region of a reduced phase diagram. Figure 3 presents the results for the solute triphenylmethane in five supercritical solvents. The relatively wide splitting of the enhancement isotherms suggests that the nature of the solvent is a more important factor in supercritical solubilities.

Most often one wishes not merely to extract a solute, but to separate two or more solutes. Since the enhancement behavior of solutes is not strongly affected by the nature of the solute, pure nonpolar SCF's are probably not the best separation solvents. Such a conclusion is supported by the investigations of Kurnik and Reid (*9*) on binary solute mixture solubility. Ideally, the solvent would show all the favorable characteristics of a SCF (variability in solubility, ease of regeneration, etc.) along with relatively high loadings and selectivities. Moreover, as shown above, solvent characteristics are more important than those of the solute. Therefore, we have been conducting experiments with entrainer-doped solvents toward this goal.

Entrainer-Doped Supercritical Solvents

Though a few solubility studies using entrainers have been published (*2*, *10–12*), only very limited attention has been paid until recently to the influence of the type of system on the solubility. In most studies, it has been concluded that the type of entrainer used (whether it be methanol, methylene

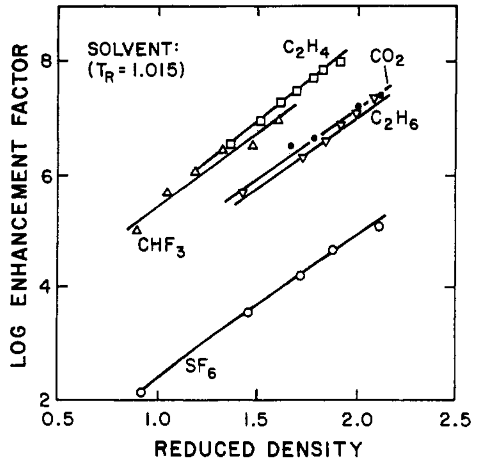

Figure 3. Solubility of triphenylmethane in various solvents at a reduced temperature of 1.15. Data of refs 6 and 8.

chloride, hexane, etc.) has little effect on the observed increase in solubility. We believe that this is not a fully accurate appraisal, as we show below.

Experimental Details. The solubility measurements were performed on the solid solutes using the dynamic technique well-described in the literature (*6, 13*). Reported temperatures (±0.02 K) and pressures (±0.3 bar) are quite accurate; the greatest uncertainty lies in the solubility measurements (±10%). The mixture of fluids used ranged from 1 to 3.9 mol % methanol in carbon dioxide and from 1 to 2.5 mol % acetone in carbon dioxide. These particular entrainers were utilized for a variety of reasons. Both are relatively polar (dipole moments: acetone, μ = 2.8 D; methanol, μ = 1.8 D) species which are good liquid solvents. Methanol is also a potential hydrogen bond donor, and might therefore interact with some of our model solutes to form complexes in solution. The high-pressure phase behavior for both the methanol- and acetone–carbon dioxide systems is available from the literature (*14–16*), and so we were confident of operating at all times in the single-phase region of the fluid. The mixed gases were obtained from the Liquid Carbonic Specialty Gases Laboratory.

Results. The solubility of six model solute compounds in three concentrations of methanol and two concentrations of acetone in carbon dioxide are presented in Table II. Since the solutes are rather dilute, and no mixture data exist, the fluid densities used are those of pure supercritical carbon dioxide, obtained from the monograph of Din (*17*). The compounds were chosen since, with the exception of phenazine, their solubilities in supercritical carbon dioxide are already available (*8*). The data have been analyzed by dividing the entrainer-doped solvent solubility by the pure solvent solubility at the same temperature (the "entrainer effect"); details of this procedure are available elsewhere (*1*).

To determine the effect of the entrainer type on solubility, the entrainer effect is plotted for a single solute species in solutions of several entrainer-doped fluids. Figure 4 illustrates such a plot for the solute 9-fluorenone (μ = 3.4 D) in four entrainer-doped solvents. Both methanol and acetone are strong entrainers for this solute, with acetone appearing significantly stronger. Figure 5 shows the entrainer effect for acridine (μ = 2.1 D) with these solvents in this case methanol is the best entrainer. These results indicate a mechanism highly dependent on the chemistry of the particular components of the system.

To isolate the effect of the solute structure on the entrainer-enhanced solubility, the entrainer effects for several solutes dissolved in a single fluid must be compared. Figure 6 shows the results from measurements of four solutes' solubilities in a 1% acetone in carbon dioxide solvent. The entrainer effect is strongly dependent on the particular solute; what is most striking is that the highly polar solutes acridine and 9-fluorenone are strongly promoted in solution while the much less polar dibenzofuran (μ = 0.8 D) and the nonpolar phenanthrene show little if any solubility increase. Furthermore, the effect cannot be ascribed entirely to the polar nature of the solutes since acridine is significantly less polar than 9-fluorenone, yet shows a stronger entrainer effect. These results suggest that with proper selection of entrainers the supercritical solvent may be made more selective to solutes than the pure solvent alone.

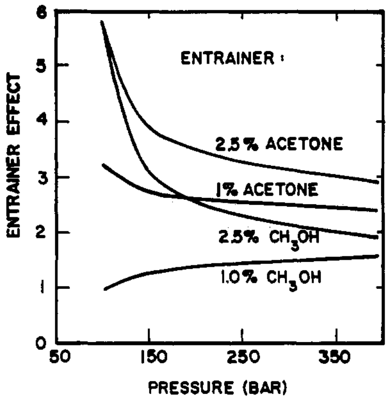

Figure 4. Effect of the entrainer on the solubility of 9-fluorenone in CO_2 at 323 K.

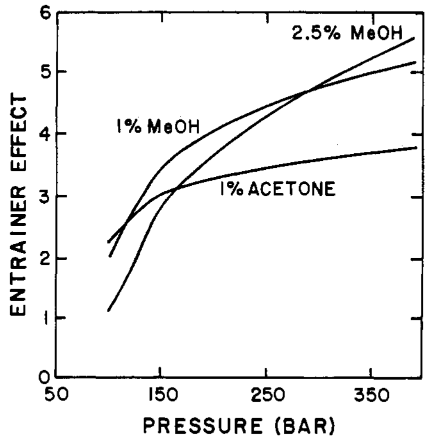

Figure 5. Effect of the entrainer on the solubility of acridine in CO_2 at 323 K.

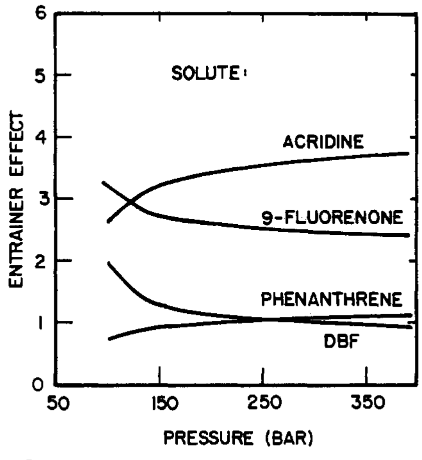

Figure 6. Comparison of entrainer effects for model solutes in a 1% acetone–CO_2 solvent at 323 K.

The concentration dependence of the entrainer effect is considered in Figure 7. This case is typical of results for

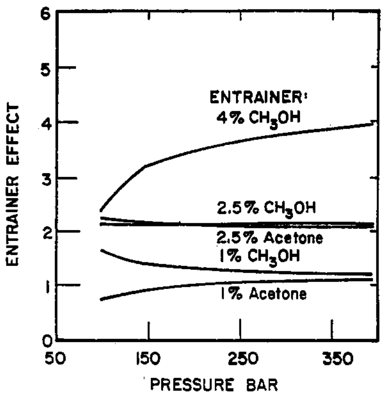

Figure 7. Solubility of phenanthrene in entrained solvents relative to pure CO_2 at 323 K.

nonpolar solutes, with the entrainer effect appearing dependent on the concentration but not the type of entrainer used. At low entrainer concentrations (ca. 1%) the entrainer effect is roughly equal to unity, meaning that there is no difference between the solubility in the doped and pure fluids. These effects are much different from those with polar solutes. In the case of polar solutes, there is a strong dependence of the entrainer effect on the entrainer type, and the effect is significant even at low entrainer concentrations.

As we have indicated, the mechanisms for entrainer-enhanced solubility are unclear. Spectroscopic studies (*18*) have indicated that coupling between dipolar species does exist in condensed phases, and this may lead to aggregation about the polar solutes by the polar entrainers. This mechanism, however, does not account for acridine showing the strongest entrainer effect, since its dipole strength is significantly less than that of 9-fluorenone. Hydrogen bonding is likely, particularly between the amine functionality of acridine and the proton of methanol; this has been observed spectroscopically for solutions of acridine and methanol in nonpolar solvents (*19*). These specific interactions would account for the increased solubility of the methanol-doped solvent over that of the acetone-doped solvent with this solute species. Acetone is a very poor hydrogen bond donor in nonpolar solvents because the formation of its enol tautomer is disfavored (the dielectric constant of carbon dioxide at these conditions is roughly 1.5 (*20*)).

The potential of entrainers lies in their ability to increase both the solubility and the selectivity of the supercritical solvent. Since low concentrations of entrainer do not appear to increase significantly the solubility of a nonpolar solute, a low concentration addition should be able to increase the selectivity of the fluid to a mixture of polar and nonpolar solutes. To test this, we have measured the solubilities of a physical solute mixture (not a solid solution) of anthracene and acridine with a 1% methanol–carbon dioxide fluid; the anthracene–acridine–carbon dioxide system has already been studied by Schmitt. We compare our results for the quaternary system to the ternary system in Figures 8 and 9; the former shows that both solutes increase in solubility, probably due to the synergistic effect first noted by Kurnik and Reid. The latter, however, compares the actual selectivity of the solvent; it is clear that the entrainer-doped solvent is far superior to the pure supercritical carbon dioxide.

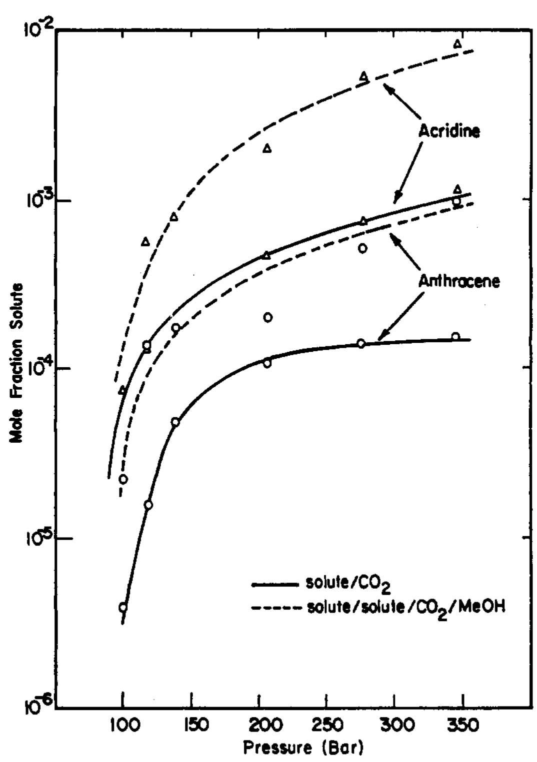

Figure 8. Change in solubility for pure acridine in pure CO_2 and pure anthracene in pure CO_2, compared with the mixed solids in CO_2–1% methanol, at 323 K.

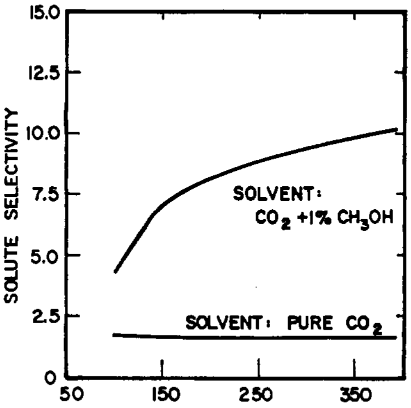

Figure 9. Increase in solvent selectivity in entrainer-doped solvent, for the acridine-anthracene mixed solute system at 323 K.

Modeling

The combination of significant physical and chemical effects in these solutions poses a significant challenge to modeling of the solubility behavior. We suggest a combined chemical–physical model to fit the data of the acridine–methanol–carbon dioxide system in which the total measured solubility is equal to the sum of the solubilities from chemical and physical effects:

$$y_2 = y_2^{\text{chem}} + y_2^{\text{phys}} \qquad (2)$$

In this model, y_2^{phys} is the solubility of the solute in the pure fluid; this system has been analyzed by Ellison (*20*). The solubility due to chemical interactions is modeled by assuming that the solute and entrainer form a 1:1 adduct (for the acridine–methanol system, this is born out by the spectroscopic data (*19*). Thus, the reaction equilibrium constant is given by

$$K = \frac{y_{23}}{y_2 y_3} \frac{\phi_{23}}{\phi_2 \phi_3} \qquad (3)$$

where the subscript 23 represents the methanol–acridine adduct (the ϕ's are the fugacity coefficients for each species in the pure SCF). Rearranging and substituting y_{23} for y_2^{chem}

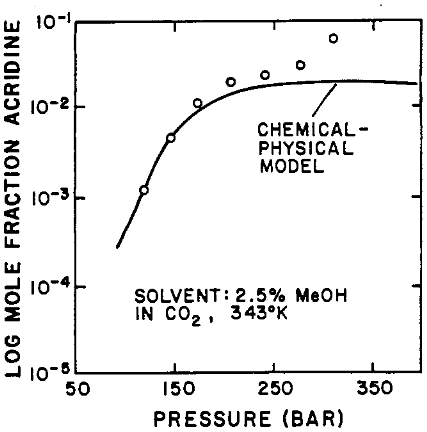

Figure 10. Results of chemical–physical model of entrainer-enhanced solubility. System: acridine in 2.5% methanol–CO_2 at 343 K.

in eq 2 gives an expression describing the measured solubility in the ternary system as a function of pure or binary information, which may be fitted to an equation of state using standard techniques. The Peng–Robinson equation was utilized in this case with a fitted adduct–carbon dioxide interaction parameter. The equilibrium constant was obtained from the infrared study of the data (*19*) and extrapolated to the system temperature using the enthalpy of formation of the methanol–pyridine hydrogen bond (*22*). Further details are available elsewhere (*1*).

Results. The fits in general were only qualitative, due to the many parameters which must be calculated and many approximations which must be made, but seem to represent well the general shape of the isotherms. An example of a fitted isotherm to experimental points is shown in Figure 10.

Conclusions

The effect of solute structure on solubilities in pure nonpolar SCF's is manifested primarily through size. Little difference due to functionality or polarity of the solute has been observed; this leads to the often poor separation characteristics of pure SCF's.

In contrast to the behavior observed with pure SCF's, entrainer-doped SCF's show an ability to differentiate between solute species on the basis of their chemical structure. The potential of these solvents for separation processes is bright, since they give increases in both loading and selectivity. The mechanisms for the entrainer effect are still unclear, although they may include phenomena such as coupling of dipoles and hydrogen bonding. Further experimental and theoretical work is continuing to isolate and model these phenomena. The goal, of course, is to develop sufficient understanding to be able to tailor solvents and thermodynamic conditions for specific applications.

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