

Solubility of Monofunctional Organic Solids in Chemically Diverse Supercritical Fluids

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Solubilities were measured for nine organic solids in four supercritical fluids over a pressure range of about 60–360 bar and from 35 to 70 °C. The solids were chosen to reflect different chemical functionalities so as to identify the role of chemical groups in solubility relationships. The four supercritical fluids, CO₂, ethane, fluoroform, and chlorotrifluoromethane, were selected as they have nearly equal critical temperatures but differ greatly in structure. It was concluded that the choice of supercritical fluid extractant should be based on the same general criteria presently used for liquid extractions. The experimental data were correlated by a modified Peng–Robinson equation of state where the solute parameters were regressed from data.

One of the principal goals of the experimental research reported herein was to measure and compare the solubilizing power of various supercritical fluids for specific solutes (or classes of solutes) based on the chemical nature of both the supercritical fluid and the solute. In liquids, temperature is often the significant parameter that influences solubility and comparisons between solvents are normally made at equivalent temperatures. In supercritical extractions, however, qualitative statements concerning *good* or *bad* solvents (for any particular solute) are difficult to defend since there is little agreement under what conditions comparisons should be made. Both temperature and pressure can affect the solubility of a solute in a supercritical fluid whereas in liquid solvents ($T < T_c$), the influence of pressure is small. Solubility comparisons in supercritical fluids require a more definitive specification of the state and behavior of the fluid.

In the past several years a number of investigators have published equilibrium solubility data for various solids in supercritical fluids. In general, two separate classes of solute molecules have been studied. At one extreme there now exist many solubility data for simple polycyclic hydrocarbons containing no chemical functionality (1–3), and, at the other extreme, solubility data for chemically complex solutes, usually natural products, containing several functional groups per molecule (4, 5). It was the purpose of this investigation to bridge the gap between the two existing sets of data by investigating systematically the solubilities of various monofunctional solid solutes closely related to simple aromatic hydrocarbons in structure.

Selection of Supercritical Fluids and Solutes

According to the law of corresponding states, different fluids behave similarly (with respect to their P – V – T properties) if they are compared at equivalent *reduced* temperatures, pressures, and volumes. However, in supercritical extraction, solubility is a strong function of the vapor pressure of the solute, and the vapor pressure is determined by the temperature of the system, not the reduced temperature of the solvent. In order to remove

the effect of vapor pressure from comparisons of a solute's solubility in a series of different solvents, the comparisons must be made at the same absolute temperature. However, in order to apply the principle of corresponding states to the dilute solvent phase, comparisons should also be made at the same reduced temperature. Only if the different solvents have essentially the same critical temperature can both conditions be simultaneously fulfilled.

Within reasonable limits, four chemically diverse supercritical solvents having nearly the same critical temperatures (29 ± 3 °C) were included in this study. These were carbon dioxide, ethane, fluoroform, and chlorotrifluoromethane. The first two have received considerable attention by previous researchers. Fluoroform was selected because of its analogous structure to chloroform, which is a known good organic solvent and is capable of hydrogen bonding. Chlorotrifluoromethane is a completely halogenated methane and is chemically inert. The properties of the supercritical fluid solvents are shown in Table I.

The solutes to be studied were selected such that each was either a simple polycyclic hydrocarbon or a monofunctional derivative of one. As noted above, we wished to examine how the addition of a specific chemical group to a hydrocarbon skeleton affected that molecule's solubility in various supercritical fluids. Most of the solutes were derivatives of naphthalene, but, for practical reasons, a few of the solutes were derivatives of either anthracene or benzene.

The principal solutes, along with several of their pertinent physical properties, are listed in Table II. Vapor pressures for all of the solutes were found in the literature with the exception of 2-aminofluorene. The sublimation vapor pressures of this compound were determined as a function of temperature with a Knudsen sublimation apparatus in our laboratory (6).

Experimental Procedure

A schematic diagram of the experimental apparatus is shown in Figure 1. It is similar to several described before (2, 12). To expedite data collection, two extraction columns (C1 and C2) were run in parallel. These could be operated at different temperatures, but the pressures in each column were identical since they were fed from a common compressor and surge tank (a 2-L autoclave). The system pressure was held to within ± 0.3 bar at pressures up to 150 bar and was maintained to within ± 1 bar at the highest pressures used (360 bar). Temperatures in the bath(s) were maintained within ± 0.1 °C and the supercritical fluid from both extraction vessels passed through lines traced with flowing water at the same temperature as in the constant temperature bath. This precaution was necessary to prevent solid precipitation in an exit line since the solubility of solutes in supercritical fluids may either increase or decrease with temperature depending upon the specific temperature and pressure employed. The precipitated solid was subsequently weighed and analyzed. The operation of the unit is similar to that described earlier (2).


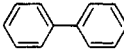
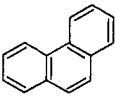
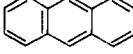
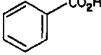
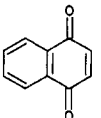
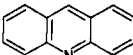
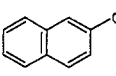
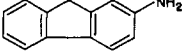
Preliminary extraction experiments were made with solid naphthalene and supercritical carbon dioxide. The results over a temperature range of 35–45 °C and a pressure range of

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Table I. Physical Properties of the Solvents

gas	formula	MW	T_c , °C	P_c , bar	ρ_c , mol/cm ³	ω
carbon dioxide	CO ₂	44.01	31.1	73.8	0.0106	0.225
ethane	C ₂ H ₆	30.07	32.2	48.8	0.0067	0.098
chlorotrifluoromethane (R-13)	CClF ₃	104.46	28.8	39.2	0.0055	0.180
fluoroform (R-23)	CHF ₃	70.01	26.1	49.5	0.0075	0.272

Table II. Physical Properties of the Solutes^a

compd	formula	structure	T_m , °C	V^* , m ³ /mol	vapor press.		supplier, purity
					A	B	
naphthalene	C ₁₀ H ₈		80.1	1.10 × 10 ⁻⁴	13.583	3733.9	Baker, >98%
biphenyl	C ₁₂ H ₁₀		69.2	1.32	14.804	4367.4	Aldrich, 98%
phenanthrene	C ₁₄ H ₁₀		100	1.51	13.545	4567.7	Aldrich, ~98%
anthracene	C ₁₄ H ₁₀		218	1.42	14.755	5313.7	Aldrich, >99.5%
benzoic acid	C ₇ H ₆ O ₂		122	0.965	14.408	4618.1	Baker, 99%
1,4-naphthoquinone	C ₁₀ H ₆ O ₂		126	1.11	14.735	4739.4	Aldrich, >97%
acridine	C ₁₃ H ₉ N		107-109	1.78	13.721	4740.1	Fluka, 98%
2-naphthol	C ₁₀ H ₈ O		122	1.18	14.815	4923.9	Aldrich, 99%
2-aminofluorene	C ₁₃ H ₁₁ N		131	1.53	14.865	5469	Aldrich, 98%

^a Vapor pressure constants in the equation $\log P^{vap}$ (Pa) = A - B/T. For use in the range 35–70 °C, except naphthalene 35–55 °C. Vapor pressure references: naphthalene (7), phenanthrene (8), 1,4-naphthoquinone (9), acridine (8), biphenyl (10), anthracene (8), benzoic acid (8), 2-naphthol (11).

Table III. Matrix of the Systems Studied^a

solvent	CO ₂	C ₂ H ₆	CHF ₃	CClF ₃	Table
naphthalene	(13)	(1), x	x	x	IV
phenanthrene	(1, 2)	x	x	x	V
anthracene	(1)	(1)	x		VI
biphenyl	(3)	x			VII
benzoic acid	(2), x	x	x	x	VIII
2-naphthol	x	x	x	x	IX
acridine	x	x	x	x	X
1,4-naphthoquinone	x	x	x	x	XI
2-aminofluorene	x	x	x	x	XII

^a x indicates new experimental data in the specified table; () indicates reference for data source.

100–300 bar agreed with those of Tsekhanskaya et al. (13) to within ± 5 mol %. Error % is here and elsewhere in this paper defined as $(y_2^{expt} - y_2^{lit}) \times 100/y_2^{lit}$. Also, as will be noted later, there were several other instances in our solvent-solute test matrix where our work overlapped those of previous investigators. In all cases except for a single reported 55 °C ethane/naphthalene datum point (14), the agreement between our solubility results and those presented in the literature was within about ± 10 mol %. Prior to these proof tests with naphthalene and carbon dioxide, we also studied the effect of flow rate variations in the extraction cell to ensure that we were

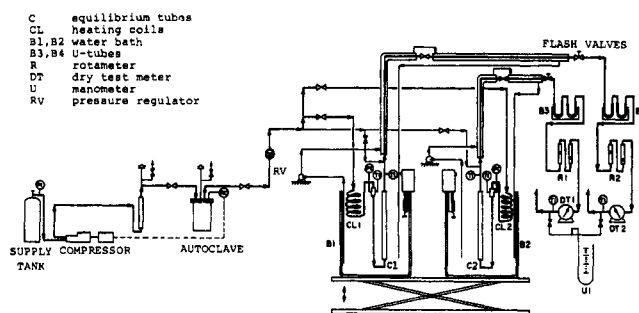


Figure 1. Supercritical extraction apparatus.

always operating in a sufficiently low flow regime that equilibrium was attained between the solid and the exit fluid (6).

Experimental Results

The matrix of systems studied is shown in Table III. With nine solutes and four supercritical fluids, there are 36 possible binaries. Three systems (biphenyl in CHF₃ and CClF₃ and anthracene in CClF₃) were not studied as the solubilities were suspected of being very small. In a few other cases, data

Table IV. Solubility of Naphthalene in Three Supercritical Solvents

temp, °C	press. (abs), bar	ρ , mol/cm ³	ρ_r	mole fraction	enhance. factor ^a	temp, °C	press. (abs), bar	ρ , mol/cm ³	ρ_r	mole fraction	enhance. factor ^a
Solubility of Naphthalene in Ethane						Solubility of Naphthalene in Fluoroform					
35.1	50.9	0.00630	0.926	0.25×10^{-2}	660	35.1	60.5	0.006809	0.9029	2.46×10^{-3}	500
35.1	55.6	0.00928	1.373	1.12	2090	35.1	73.3	0.009532	1.264	4.24	1050
35.1	60.1	0.01001	1.482	1.29	2600	34.9	96.1	0.011298	1.498	6.06	1990
35.0	65.5	0.01055	1.559	1.42	3180	35.0	141.3	0.013027	1.727	7.49	3600
35.0	69.1	0.01084	1.604	1.54	3600	35.0	221.0	0.01468	1.947	8.71	6500
34.9	91.5	0.01179	1.742	1.97	6200	35.1	351.3	0.01625	2.155	9.18	10800
35.0	99.4	0.01203	1.780	2.08	6980	45.1	60.5	0.004422	0.5864	0.857×10^{-3}	72
35.0	120.5	0.01251	1.848	2.30	9450	45.1	73.3	0.006920	0.9176	3.30	338
35.0	131.0	0.01284	1.897	2.54	11400	44.9	96.1	0.009704	1.287	7.04	962
35.0	150.8	0.01298	1.921	2.56	13100	44.9	141.3	0.011988	1.590	10.09	2000
34.9	181.0	0.01336	1.975	2.78	17200	44.9	221.0	0.01395	1.850	12.3	3870
35.1	198.7	0.01359	2.009	3.02	20000	45.0	351.3	0.01571	2.083	13.4	6620
35.1	250.0	0.01408	2.081	3.24	27600	55.0	66.0	0.004300	0.5702	1.24×10^{-3}	50
34.9	301.7	0.01451	2.144	3.19	32700	55.1	82.8	0.006547	0.8681	4.21	214
35.0	362.0	0.01486	2.196	3.48	42900	55.0	123.0	0.010043	1.332	11.1	850
45.0	51.0	0.00350	0.517	0.06×10^{-2}	43	55.0	171.0	0.011970	1.587	14.4	1530
45.0	55.5	0.00448	0.663	0.15	118	55.1	240.8	0.01359	1.802	18.4	2730
45.1	65.5	0.00763	1.127	1.36	1260	54.9	351.4	0.01517	2.012	18.5	4050
45.0	69.1	0.00862	1.276	1.40	1380	Solubility of Naphthalene in Monochlorotrifluoromethane					
45.0	91.5	0.01072	1.584	2.67	3470	35.1	50.1	0.007054	1.271	2.84×10^{-3}	478
45.0	120.5	0.01178	1.741	3.46	5940	34.9	71.5	0.009000	1.622	4.35	1070
45.1	131.0	0.01200	1.773	3.86	7130	35.0	98.2	0.01008	1.816	5.41	1800
44.9	150.7	0.01247	1.845	4.08	8750	35.0	140.9	0.01112	2.004	6.33	3000
44.9	199.0	0.01318	1.951	4.74	13400	35.1	199.8	0.01205	2.171	7.12	4800
45.0	250.0	0.01372	2.030	5.25	18600	35.1	281.3	0.01291	2.326	7.66	7200
45.1	301.7	0.01414	2.090	5.42	23000	34.9	355.3	0.01348	2.429	7.84	9500
45.0	364.0	0.01458	2.151	5.85	29900	45.1	50.1	0.004384	0.790	1.17×10^{-3}	82
55.0	56.3	0.00357	0.528	0.12×10^{-2}	41	44.9	71.5	0.007781	1.402	5.16	525
55.0	61.3	0.00425	0.625	0.19	72	45.0	98.2	0.009246	1.666	7.11	985
55.0	71.5	0.00649	0.960	1.14	503	45.1	140.9	0.010505	1.893	8.94	1760
55.1	80.2	0.00810	1.199	2.09	1020	45.1	199.8	0.01156	2.083	10.08	2800
54.9	100.8	0.00966	1.431	4.37	2750	45.0	281.3	0.01253	2.258	10.35	4100
54.9	100.8	0.01090	1.613	6.48	4920	45.1	355.3	0.01315	2.369	10.92	5500
55.1	164.0	0.01191	1.760	10.7	10900	55.0	51.6	0.003580	0.645	1.08×10^{-3}	35
55.0	175.0	0.01224	1.809	11.1	12100	54.9	61.3	0.005110	0.921	2.82	108
55.0	202.0	0.01267	1.872	13.7	17400	54.9	86.9	0.007737	1.394	7.50	407
55.0	206.0	0.01272	1.879	13.0	17000	54.7	130.3	0.009576	1.725	11.51	951
55.0	225.0	0.01298	1.918	13.6	19100	54.8	200.3	0.01108	1.996	14.71	1850
55.0	251.0	0.01326	1.959	12.9	20100	55.0	282.0	0.01214	2.187	16.2	2900
55.0	302.0	0.01373	2.029	13.6	25900	55.0	360.3	0.01284	2.314	15.8	3500
55.0	364.0	0.01420	2.098	13.4	30400						

^a Enhancement factor = $y_2 P / P_2^{vp}$.

already existed or were supplemented in this work. The new experimental data are shown in Tables IV–XII.

Over half of the results in Tables IV–XII were averages of replicate measurements and the results typically agreed within 5 mol %. Also, in the tables, the densities (and reduced densities) shown are those for the pure solvent. The solubilities were, in essentially all cases, so small that a true mixture density calculation was not warranted. The solute enhancement factors are the final entries in the data tables. The enhancement factor is defined as the actual solubility of the solute in the supercritical gas divided by the solubility of the solute in an ideal gas at the same temperature. When the logarithm of the enhancement factor is plotted against fluid density, very linear solubility isotherms are obtained over a wide range of supercritical fluid conditions (6, 12).

We show some typical solubility graphs in Figures 2 through 4. The solubilities of phenanthrene are given as a function of reduced solvent density at 55 °C in Figure 2. This plot is typical of the hydrocarbons studied (naphthalene, phenanthrene, anthracene, and biphenyl) with ethane being the most efficacious solvent for all of the simple hydrocarbons, followed by CO₂. Fluoroform and CClF₃ were poor solvents for these molecules. In Figure 3, the same type of graph is presented for benzoic acid. Here, CO₂ is distinctly a better solvent than the rest. Carboxylic acids were found difficult to dissolve in

supercritical gases, as was previously noted by Stahl et al. (15).

Finally, for 2-aminofluorene, in Figure 4, fluoroform was a very good solvent with only CO₂ exceeding it in solvent power at high reduced densities. Fluoroform was a poor solvent for hydrocarbons, but was found to be a good solvent for a few particular molecules such as 2-aminofluorene and 1,4-naphthoquinone. It appears that fluoroform is a good solvent for molecules containing functional groups capable of hydrogen-bond association with the acidic proton on fluoroform, such as carbonyl and amine. Izatt et al. (16) have also suggested that hydrogen bonding may be present in some fluorinated gases used as solvents near their critical points.

Correlation

The solubilities of solids in supercritical solvents are usually correlated with eq 1. As written, we have assumed that the

$$y_2 = (P_2^{vp} / P)(\phi_2^{-1}) \exp(V_2^s P / RT) \quad (1)$$

system pressure is much greater than the vapor pressure of the solute, that the solute is incompressible, and that no solvent dissolves in the solid solute (17). Subscript 2 refers to the solute and y_2 is the mole fraction of the solute in the fluid phase. To determine the solute solubility at a given temperature

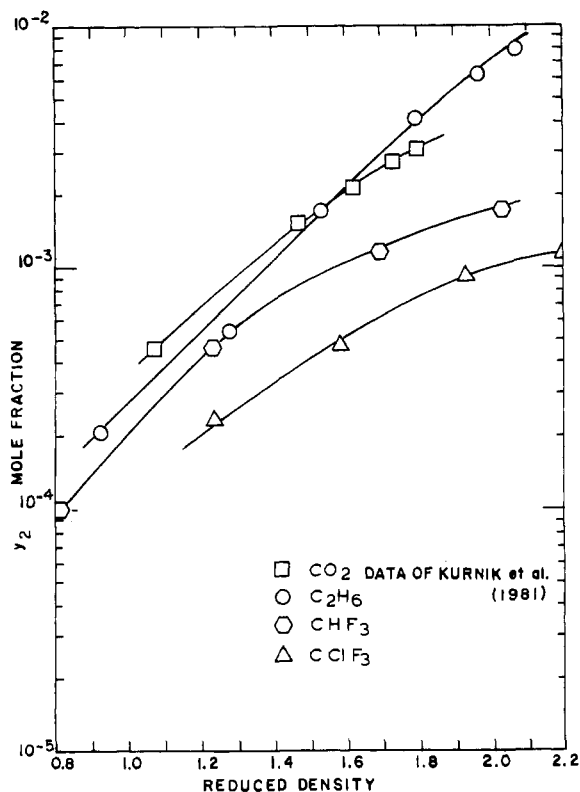


Figure 2. Solubility of phenanthrene in four supercritical solvents.

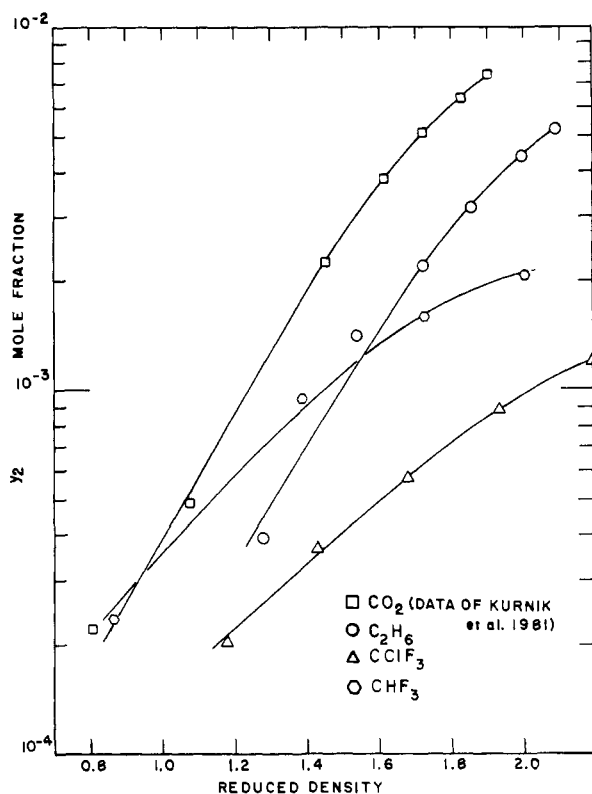


Figure 3. Solubility of benzoic acid in four supercritical solvents.

and pressure, one must know the pure solute vapor pressure (P_2^{VP}), the molar volume of the solute (V_2^S), and the fugacity coefficient of the solute in the supercritical phase (ϕ_2). It is the last that concerns us here as we assume P_2^{VP} and V_2^S are available from independent measurements or from literature data.

Table V. Solubility of Phenanthrene in Three Supercritical Solvents

temp, °C	press. (abs), bar	ρ , mol/cm ³	ρ_r	mole fraction	enhance. factor
Solubility of Phenanthrene in Ethane					
45.0	71.0	0.00893	1.313	4.00×10^{-4}	18500
45.0	85.3	0.0104	1.531	8.66	47800
45.0	109.5	0.0115	1.688	18.5	131400
45.0	171.0	0.0128	1.882	33.8	375000
44.9	264.0	0.0139	2.040	48.6	832000
45.0	355.0	0.0145	2.134	60.4	1392000
55.0	71.0	0.00631	0.928	2.02×10^{-4}	3400
55.0	85.3	0.00869	1.279	5.41	10900
55.0	109.5	0.01046	1.538	17.7	46000
55.1	171.0	0.0122	1.794	41.8	168000
54.9	264.0	0.0134	1.971	63.7	402500
55.0	355.0	0.0141	2.074	80.1	674000
Solubility of Phenanthrene in Fluoroform					
45.0	80.0	0.00803	1.064	1.48×10^{-4}	7690
45.0	111.5	0.01070	1.419	4.55	32900
45.0	202.0	0.01358	1.802	8.90	116700
45.0	364.0	0.01584	2.100	12.8	302500
55.1	80.0	0.00617	0.818	0.99×10^{-4}	1860
55.0	111.5	0.00934	1.239	4.74	12500
55.0	202.0	0.0128	1.696	11.7	55900
55.0	364.0	0.0153	2.030	17.2	148100
Solubility of Phenanthrene in Monochlorotrifluoromethane					
45.0	75.5	0.00807	1.455	2.38×10^{-4}	11650
45.0	108.0	0.00960	1.730	4.21	29500
45.0	180.0	0.01126	2.028	6.52	76200
45.0	301.0	0.0127	2.290	8.73	170300
55.0	75.5	0.00686	1.237	2.31×10^{-4}	4075
55.0	108.0	0.00880	1.587	4.78	12200
55.0	180.0	0.0107	1.933	9.02	38500
55.0	301.0	0.0124	2.221	11.0	78200

Table VI. Solubility of Anthracene in Fluoroform

temp, °C	press. (abs), bar	ρ , mol/cm ³	ρ_r	mole fraction	enhance. factor
55.1	91.8	0.00764	1.013	0.91×10^{-5}	2250
55.0	142.0	0.0109	1.452	2.98	11600
55.0	298.0	0.0145	1.923	6.65	54400
70.1	111.0	0.00748	0.992	1.2×10^{-5}	694
70.0	176.0	0.0108	1.433	7.69	7280
70.0	299.0	0.0136	1.805	12.8	20500

Table VII. Solubility of Biphenyl in Ethane

temp, °C	press. (abs), bar	ρ , mol/cm ³	ρ_r	mole fraction	enhance. factor
35.0	70.5	0.0109	1.603	1.24×10^{-2}	20600
35.2	86.0	0.0116	1.706	1.54	30200
35.2	113.0	0.0124	1.824	1.89	49000
35.2	180.0	0.0134	1.971	2.66	109800
35.2	281.0	0.0143	2.103	3.09	198900
45.0	70.5	0.00891	1.310	1.01×10^{-2}	5970
45.2	86.0	0.0106	1.559	1.77	12500
45.0	113.0	0.0116	1.700	2.66	25400
45.0	180.0	0.0129	1.903	4.81	72600
45.1	281.0	0.0136	2.051	6.22	143700

In almost all instances, ϕ_2 is determined from an equation of state applicable to the solute-solvent mixture. We employed the Peng-Robinson equation (18) although others could have been used. When used in the traditional manner, routine thermodynamics allows one to obtain ϕ_2^S in terms of the component critical properties, acentric factors, and a characteristic binary interaction parameter (2, 6, 18). For the present study, however, we did not follow this usual route for three reasons. First, in several cases, critical properties of the solutes were not available in the literature and estimation techniques were not judged to be accurate. (Note this is often the case when

Table VIII. Solubility of Benzoic Acid in Four Supercritical Solvents

temp, °C	press. (abs), bar	ρ , mol/cm ³	ρ_r	mole fraction	enhance. factor	temp, °C	press. (abs), bar	ρ , mol/cm ³	ρ_r	mole fraction	enhance. factor
Solubility of Benzoic Acid in Carbon Dioxide											
35.1	101.0	0.016 10	1.517	0.80×10^{-3}	30 600	35.0	281.5	0.014 34	2.122	18.2	192 000
35.0	113.0	0.016 86	1.589	1.03	43 500	35.0	363.6	0.014 89	2.204	19.2	261 700
35.0	120.0	0.017 24	1.625	1.38	62 800	45.1	61.6	0.006 17	0.913	0.742×10^{-4}	573
35.1	151.0	0.018 55	1.748	1.74	97 700	45.0	75.7	0.009 59	1.419	3.58	3 430
35.0	160.0	0.018 86	1.778	2.37	143 700	45.1	86.2	0.010 43	1.544	5.43	5 900
35.0	240.0	0.020 40	1.923	3.10	282 000	45.0	110.9	0.011 50	1.698	11.2	15 800
35.0	280.0	0.020 90	1.970	3.31	351 000	45.0	149.6	0.012 43	1.840	15.2	29 000
34.9	282.3	0.020 94	1.974	2.93	313 077	45.1	201.5	0.013 19	1.952	20.9	53 000
34.9	363.8	0.021 74	2.049	3.15	434 000	45.0	281.4	0.013 97	2.064	25.1	89 500
45.1	101.0	0.011 11	1.047	0.26×10^{-3}	3 400	45.0	361.9	0.014 56	2.155	26.3	120 200
45.1	105.0	0.013 00	1.225	0.493	6 550	55.0	54.8	0.005 21	0.771	0.781×10^{-1}	237
45.1	113.0	0.013 72	1.293	0.561	7 950	55.1	81.1	0.008 13	1.203	3.63	1 340
45.0	120.0	0.014 97	1.411	1.15	17 700	55.0	110.9	0.010 49	1.553	14.1	7 200
45.1	151.0	0.016 92	1.595	1.98	37 300	55.1	150.0	0.011 79	1.745	22.0	14 900
45.0	160.0	0.017 30	1.631	2.38	48 800	55.1	202.7	0.012 69	1.878	30.3	27 800
45.0	200.0	0.018 48	1.742	3.18	81 500	55.1	281.3	0.013 54	2.004	42.3	54 000
45.0	240.0	0.019 30	1.819	4.21	129 000	55.0	361.8	0.014 19	2.095	52.1	86 000
45.0	280.0	0.019 96	1.881	4.39	157 000	70.1	66.0	0.003 82	0.565	0.662×10^{-4}	48
44.9	282.3	0.020 00	1.885	4.01	145 000	70.1	81.1	0.005 75	0.851	3.00	268
45.0	302.5	0.020 24	1.908	4.444	170 000	70.1	111.2	0.008 85	1.310	16.1	1 980
45.0	363.1	0.020 93	1.973	4.87	225 000	70.1	151.0	0.010 65	1.576	33.3	5 540
55.1	101.0	0.007 75	0.730	0.140×10^{-3}	643	70.0	203.0	0.011 87	1.757	55.1	12 400
						69.9	281.2	0.012 88	1.906	75.6	23 900
						70.1	363.5	0.013 68	2.025	96.9	38 800
Solubility of Benzoic Acid in Fluoroform											
55.0	105.0	0.008 58	0.809	0.22	1 070	45.1	65.5	0.005 338	0.7078	0.704×10^{-4}	578
55.1	111.0	0.009 71	0.915	0.30	1 515	45.1	83.2	0.008 448	1.120	3.00	3 140
55.0	120	0.011 39	1.074	0.49	2 700	45.1	131.0	0.011 605	1.539	7.31	12 000
55.1	126	0.012 30	1.159	0.75	4 300	45.1	211.4	0.013 77	1.826	11.0	29 200
55.1	151.2	0.014 93	1.407	1.94	13 300	45.1	341.0	0.015 60	2.069	13.6	58 000
55.0	160	0.015 48	1.459	2.27	16 800	55.1	65.5	0.004 240	0.5622	0.384×10^{-4}	114
55.0	200.4	0.017 20	1.620	3.83	35 300	55.0	83.2	0.006 600	0.8752	2.33	886
55.0	240	0.018 25	1.720	5.16	57 300	55.1	131.0	0.010 46	1.3870	9.34	5 550
55.1	281	0.019 07	1.797	5.68	72 400	55.0	211.4	0.013 00	1.724	15.7	15 200
54.9	302.5	0.019 42	1.830	6.38	89 200	55.1	341.0	0.015 05	1.996	20.5	31 700
55.0	363.3	0.020 20	1.903	7.17	119 000	Solubility of Benzoic Acid in Monochlorotrifluoromethane					
70.1	101.0	0.005 71	0.538	0.122×10^{-3}	136	45.1	60.5	0.006 608	1.193	1.06×10^{-4}	808
70.0	111.0	0.006 87	0.648	0.222	274	45.0	72.2	0.007 836	1.414	2.03	1 850
70.1	126.0	0.088 77	0.827	0.550	763	45.1	89.9	0.008 889	1.604	3.07	3 470
70.1	151.2	0.011 63	1.096	1.54	2 575	45.0	120.8	0.009 998	1.805	3.97	6 080
69.9	200.9	0.015 05	1.418	5.00	11 150	45.1	182.5	0.011 30	2.040	5.63	12 900
70.1	281.0	0.017 53	1.652	9.02	27 900	44.9	357.9	0.013 17	2.337	8.28	38 000
69.9	364.1	0.018 97	1.788	12.8	51 800	55.0	60.5	0.004 983	0.899	0.650×10^{-4}	181
Solubility of Benzoic Acid in Ethane											
35.1	61.7	0.010 12	1.498	1.79×10^{-4}	4 100	55.0	72.2	0.006 540	1.180	2.02	667
35.1	75.7	0.011 18	1.655	3.53	9 900	55.1	89.9	0.007 922	1.430	3.69	1 500
35.1	86.7	0.011 63	1.721	5.44	17 500	55.0	120.8	0.009 278	1.675	5.74	3 200
35.1	111.0	0.012 32	1.823	9.68	39 800	55.1	182.5	0.010 78	1.946	8.81	7 300
35.1	150.2	0.012 97	1.920	12.1	67 500	55.0	281.8	0.012 13	2.189	12.00	15 500
35.1	201.5	0.013 61	2.014	14.3	106 700	49.9	357.9	0.012 83	2.316	13.57	22 500

solutes are complex organic molecules.) Second, even for those solutes where experimental critical data did exist, we found that the Peng–Robinson form did not correlate experimental solubility data particularly well over a wide range of pressures even with an optimized binary interaction parameter.

Third, when dealing with *solid* solutes, we suggest that the Peng–Robinson (or any other similar equation of state) is inappropriate since the original derivation and temperature-dependent functions are applicable only to a liquid–vapor system. The use of the Peng–Robinson equation assumes, in essence, that the solid phase is a (subcooled) liquid and the integration step used when equating fugacities proceeds from a vapor to a liquid phase.

For these reasons, an alternate correlation for binary solid–fluid equilibria was proposed. In this technique, we leave the “pure-component” parameters of the solutes as variables, use the classic Peng–Robinson relations for evaluating the component parameters of the supercritical solvent, and eliminate the

binary interaction parameter. Thus, with these assumptions, the relation for ϕ_2 becomes

$$\ln \phi_2 = (b_2/b)(Z - 1) - \ln [P(V - b)/RT] - [a/8^{1/2}RTb] \{ [2(a_{12}y_1 + a_2y_2)/a] - b_2/b \} \times \ln [(V + 2.414b)/(V - 0.414b)] \quad (2)$$

and, for the supercritical solvent (component 1)

$$a_1 = 0.4572R^2T_c^2/P_c [1 + (0.3746 + 1.5423\omega - 0.2699\omega^2)(1 - T_r^{1/2})]^2 \quad (3)$$

$$b_1 = 0.07780RT_c/P_c \quad (4)$$

while the solute parameters a_2 and b_2 are determined by nonlinear regression of the experimental data.

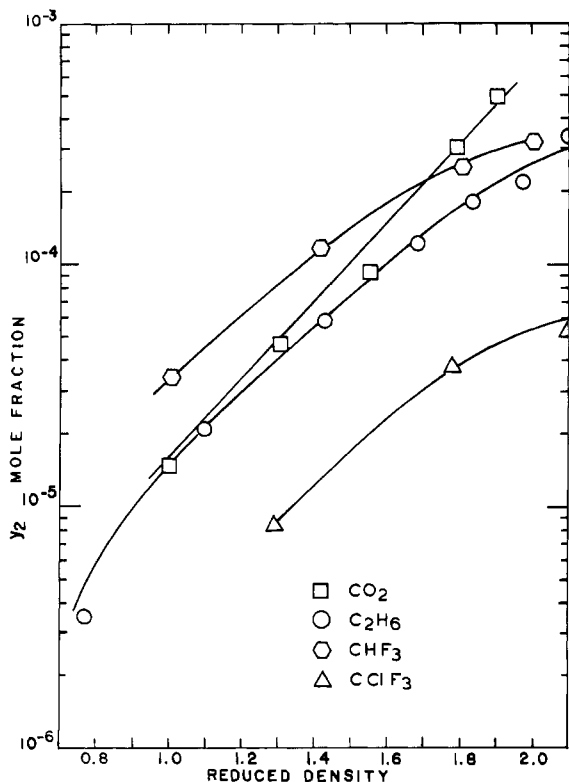


Figure 4. Solubility of 2-aminofluorene in four supercritical solvents.

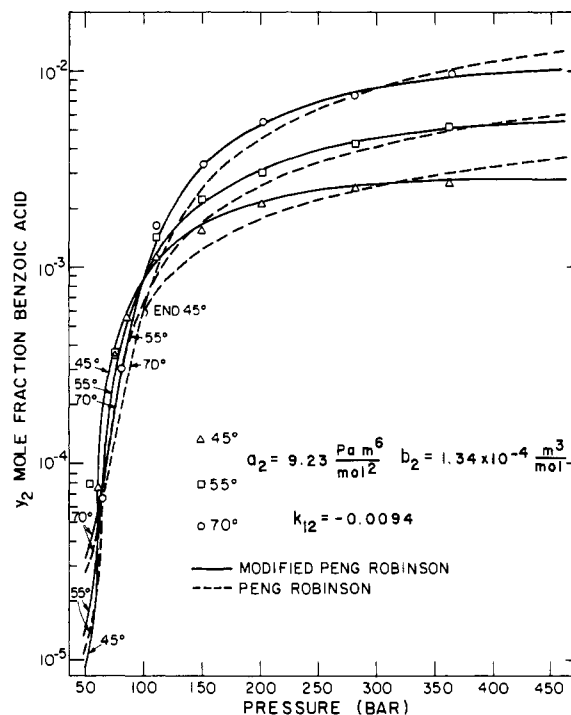


Figure 5. Correlation of the benzoic acid/ethane solubility data with two equations of state.

Table IX. Solubility of 2-Naphthol in Four Supercritical Solvents

temp, °C	press. (abs), bar	ρ , mol/cm ³	ρ_r	mole fraction	enhance. factor	temp, °C	press. (abs), bar	ρ , mol/cm ³	ρ_r	mole fraction	enhance. factor
Solubility of 2-Naphthol in Carbon Dioxide						Solubility of 2-Naphthol in Fluoroform					
35.1	102.8	0.0163	1.539	1.10×10^{-4}	16500	45.0	187	0.0130	1.924	2.86	24000
34.9	118.5	0.0172	1.624	2.02	35000	45.0	277	0.0139	2.057	3.55	44100
35.1	143.7	0.0183	1.728	4.46	93500	45.0	363	0.0146	2.161	4.61	75100
35.1	200.5	0.0197	1.860	5.28	154000	55.1	66.0	0.00529	0.783	0.26×10^{-4}	262
35.1	279.7	0.0209	1.974	6.38	260000	55.2	76.0	0.00741	1.097	0.79	896
35.1	362.0	0.0219	2.068	7.20	380000	55.1	93.0	0.00939	1.390	1.79	2500
45.1	102.8	0.0125	1.170	1.00×10^{-4}	4700	55.1	131.5	0.01125	1.665	3.15	6200
44.9	118.5	0.0149	1.404	2.35	12800	55.1	192	0.0125	1.850	4.44	12800
45.1	143.7	0.0166	1.565	4.77	31500	55.0	280	0.0135	1.998	5.49	23300
45.1	200.5	0.0185	1.744	6.81	62700	55.0	364	0.0142	2.102	6.28	34700
45.0	279.7	0.0200	1.885	7.42	95200	70.1	66.0	0.00379	0.561	0.30×10^{-4}	66
45.1	362.0	0.0211	1.989	9.50	158000	70.0	76.0	0.00508	0.752	0.63	161
54.9	105.2	0.00858	0.809	0.801×10^{-4}	1300	70.0	93.0	0.00730	1.080	1.95	608
55.1	111.5	0.00982	0.926	1.10	1900	70.0	131.5	0.00995	1.473	5.04	2200
55.1	120.0	0.0114	1.074	1.89	3500	70.0	192	0.01165	1.724	7.85	5060
55.0	145.7	0.0145	1.367	4.48	10100	70.0	280	0.01286	1.903	11.3	10600
55.1	201.0	0.0169	1.593	7.98	24800	70.0	364	0.01366	2.022	11.8	12022
55.0	281.0	0.0191	1.800	12.0	52200	Solubility of 2-Naphthol in Ethane					
55.0	363.6	0.0204	1.923	13.9	78300	35.1	61.0	0.01010	1.495	0.134×10^{-4}	2960
69.9	105.2	0.00621	0.585	0.58×10^{-4}	209	35.0	73.5	0.0111	1.643	0.80	8410
70.1	111.5	0.00692	0.652	0.965	365	35.0	92.5	0.0118	1.746	1.15	15100
70.1	120.0	0.00804	0.758	1.36	558	35.0	130.5	0.0127	1.880	1.47	27300
70.1	145.7	0.0111	1.046	4.14	2100	35.0	187	0.0134	1.983	1.77	47300
70.0	201.0	0.0149	1.404	9.60	6600	35.0	277	0.0143	2.116	2.12	83500
69.9	281.0	0.0175	1.649	16.3	15700	35.0	363	0.0149	2.205	2.34	121000
70.0	363.6	0.0192	1.810	20.0	25000	45.1	61.0	0.00606	0.897	0.28×10^{-4}	773
Solubility of 2-Naphthol in Ethane						Solubility of 2-Naphthol in Monochlorotrifluoromethane					
35.1	61.0	0.01010	1.495	0.134×10^{-4}	2960	55.0	73.0	0.00662	1.193	0.49×10^{-4}	556
35.0	73.5	0.0111	1.643	0.80	8410	55.0	101.5	0.00853	1.536	0.76	1190
35.0	92.5	0.0118	1.746	1.15	15100	55.0	151.0	0.0101	1.824	1.14	2660
35.0	130.5	0.0127	1.880	1.47	27300	54.9	259.0	0.0119	2.141	1.55	6270
35.0	187	0.0134	1.983	1.77	47300	55.0	364.0	0.0129	2.320	1.91	10800
35.0	277	0.0143	2.116	2.12	83500	70.0	73.0	0.00503	0.907	0.52×10^{-4}	130
35.0	363	0.0149	2.205	2.34	121000	70.0	101.5	0.00726	1.308	1.37	470
45.1	61.0	0.00606	0.897	0.28×10^{-4}	773	70.0	151.0	0.00922	1.661	2.52	1300
45.0	73.5	0.00855	1.265	0.84	2770	69.9	259.0	0.0113	2.023	3.52	3150
45.1	92.5	0.01080	1.598	1.51	6210	69.9	364.0	0.0124	2.230	4.31	5420
45.0	130.5	0.0120	1.776	2.22	13020						

Table X. Solubility of Acridine in Four Supercritical Solvents

temp, °C	press. (abs), bar	ρ , mol/cm ³	ρ_r	mole fraction	enhance. factor	temp, °C	press. (abs), bar	ρ , mol/cm ³	ρ_r	mole fraction	enhance. factor
Solubility of Acridine in Carbon Dioxide						44.9	209.8	0.01331	1.970	9.81	310000
35.1	102.5	0.01618	1.528	2.06×10^{-4}	101000	45.0	292.1	0.01406	2.081	11.52	501400
35.2	122.2	0.01764	1.666	3.30	191400	44.9	361.4	0.01453	21.50	12.78	696100
35.1	151.6	0.01859	1.755	6.38	431000	55.0	56.1	0.00357	0.528	0.143×10^{-4}	422
35.1	200.0	0.01968	1.858	9.07	735000	55.0	61.0	0.00426	0.630	0.292	935
35.1	270.3	0.02079	1.963	10.6	1300000	55.2	65.9	0.00529	0.783	0.540	1800
35.1	350.4	0.02165	2.044	12.5	1960000	55.1	82.3	0.00827	1.224	2.62	11100
45.0	101.8	0.01176	1.110	1.18×10^{-4}	28000	55.0	100.7	0.01002	1.482	6.41	33800
45.0	110.6	0.01393	1.315	2.47	40800	55.0	140.4	0.01153	1.705	11.55	84600
45.1	122.8	0.01524	1.439	3.26	60000	54.9	210.0	0.01279	1.893	16.8	186700
45.2	152.1	0.01701	1.606	6.81	150000	55.0	279.0	0.0135	1.997	21.1	309200
45.1	200.0	0.01847	1.744	11.3	330000	55.1	364.0	0.0142	2.101	29.4	561200
45.1	270.1	0.01976	1.866	15.1	605000	70.0	61.0	0.00328	0.485	0.299×10^{-4}	223
45.1	279.4	0.01993	1.882	15.5	640000	70.1	82.2	0.00589	0.872	1.78	1779
45.1	352.2	0.02083	1.967	17.3	897000	70.0	101.3	0.00801	1.185	5.79	7200
55.1	101.6	0.00794	0.749	0.40×10^{-4}	1600	70.0	140.5	0.01031	1.526	15.6	26800
54.9	110.6	0.00971	0.917	0.96	5600	70.0	210.0	0.01198	1.773	26.7	68900
55.1	122.5	0.01181	1.115	1.94	12300	70.1	279.0	0.01258	1.901	37.0	127900
55.1	151.0	0.01491	1.408	6.17	48100	70.1	364.0	0.0137	2.027	48.8	217900
55.1	201.1	0.01724	1.628	11.65	121300	Solubility of Acridine in Fluoroform					
55.0	279.6	0.01921	1.805	19.4	284000	45.0	65.5	0.00534	0.7063	0.36×10^{-4}	3575
55.0	355.7	0.02024	1.911	22.7	425000	45.0	75.5	0.00732	0.968	0.60	6860
70.0	111.2	0.00690	0.652	0.60×10^{-4}	930	45.0	92.5	0.00941	1.245	1.81	25200
70.0	130.1	0.00935	0.883	1.96	3100	45.0	134.5	0.01174	1.553	5.67	115000
70.0	160.7	0.01252	1.182	6.15	12100	45.0	217.0	0.01388	1.836	7.22	236100
70.0	199.7	0.01497	1.414	12.0	29400	45.0	353.0	0.01573	2.081	10.2	541100
70.0	251.4	0.01679	1.585	19.5	60500	55.0	65.5	0.00424	0.5610	0.23×10^{-4}	814
70.0	300.1	0.01791	1.691	28.5	105000	55.0	75.5	0.00555	0.7342	0.64	2580
70.0	364.1	0.01899	1.793	36.6	164500	55.0	92.5	0.00771	1.020	1.79	8750
Solubility of Acridine in Ethane						55.0	134.5	0.0106	1.405	5.39	38400
35.1	61.7	0.01012	1.498	1.22×10^{-4}	33700	55.0	217.0	0.0131	1.736	9.22	106000
35.1	76.0	0.01120	1.658	3.42	116700	55.0	353.0	0.0152	2.009	14.0	261200
35.1	100.5	0.01205	1.783	4.91	221100	Solubility of Acridine in Monochlorotrifluoromethane					
35.1	140.6	0.01251	1.851	6.03	380200	45.1	67.0	0.00738	1.330	1.05×10^{-4}	10500
35.1	209.9	0.01361	2.014	6.83	642300	45.0	81.5	0.00846	1.524	1.31	16100
35.1	283.4	0.01437	2.127	7.12	905000	45.0	115	0.00983	1.771	2.01	34900
45.1	52.8	0.00391	0.578	0.134×10^{-4}	1040	45.0	216	0.01179	2.124	3.02	98300
45.0	56.1	0.00467	0.692	0.250	2090	45.0	341	0.01304	2.350	4.07	209400
45.0	65.9	0.00775	1.147	0.593	5800	55.0	67.0	0.00593	1.068	0.93×10^{-4}	3290
45.1	75.8	0.00917	1.357	1.86	20800	55.0	81.5	0.00736	1.326	1.47	6360
45.1	82.4	0.01020	1.510	2.10	25500	55.0	115	0.009075	1.635	2.75	16760
45.0	100.4	0.01114	1.649	5.41	80900	55.0	216	0.01132	2.040	4.78	54700
44.9	140.2	0.01222	1.808	6.53	138000	55.0	341	0.01269	2.286	6.41	115800

The combining and mixing rules are

$$a_{12} = (a_1 a_2)^{1/2} \quad (5)$$

$$a = (a_1^{1/2} y_1 + a_2^{1/2} y_2)^2 \quad (6)$$

$$b = b_1 y_1 + b_2 y_2 \quad (7)$$

Finally, for most of the solutes studied, the values of y_2 were sufficiently small that eq 2, 6, and 7 could be simplified by eliminating terms with y_2 . Thus, eq 2 becomes

$$\ln \phi_2 \sim (b_2/b_1)(Z_1 - 1) - \ln [P(V_1 - b_1)/RT] - (a_1/8^{1/2} RT b_1) [2(a_2/a_1)^{1/2} - (b_2/b_1)] \ln [(V_1 + 2.414b_1)/(V_1 - 0.414b_1)] \quad (8)$$

When written in this approximate form, ϕ_2 is the infinite-dilution fugacity coefficient for the binary and could be written as ϕ_2^∞ . As shown elsewhere (19), ϕ_2^∞ and ϕ_2 are related as

$$\phi_2 = \phi_2^\infty \exp(-Ky_2) \quad (9)$$

where K is a function of temperature and pressure and the maximum range of ϕ_2/ϕ_2^∞ is from 1 to e^{-1} .

The experimental solubility data were regressed by using eq 2 to determine a_2 and b_2 for each binary studied. Over the temperature range of interest (ca. 35–70 °C), we found that a_2 and b_2 were essentially temperature-independent. An illustration of the use of these fitted parameters is shown in Figure 5 for the system benzoic acid–ethane. The fit of the predicted curve with experimental data is satisfactory over the entire pressure range. For comparison, on the same graph, the predictions of the classical Peng–Robinson equation are shown by the dashed curves. Here, a single binary interaction parameter, k_{12} (=0.0094) was used. Also, in the Peng–Robinson calculations, the a_2 and b_2 values were found by using the original relations given by Peng and Robinson with known critical properties of benzoic acid.

The temperature average a_2 and b_2 regressed parameters are given in Table XIII. The actual variation with temperature was usually only a few percent and the trends were such that a_2 and b_2 both decreased slightly with increasing temperature. Surprisingly, however, the ratio a_2/b_2 was remarkably constant for any given binary pair. It was found that the constants regressed from eq 2 (and given in Table XIII) could, in most cases, be used with the simplified fugacity-coefficient expres-

Table XI. Solubility of 1,4-Naphthoquinone in Four Supercritical Solvents

temp, °C	press. (abs), bar	ρ , mol/cm ³	ρ_r	mole fraction	enhance. factor	temp, °C	press. (abs), bar	ρ , mol/cm ³	ρ_r	mole fraction	enhance. factor
Solubility of Naphthoquinone in Carbon Dioxide						55.0	112	0.01055	1.551	6.65	3800
45.0	101.0	0.0112	1.053	0.932 × 10 ⁻³	13400	55.0	165	0.01207	1.775	10.0	8430
						55.0	275	0.01350	1.985	13.1	18500
45.0	115.8	0.0141	1.325	1.55	25600	55.0	364	0.01418	2.085	15.1	27900
45.0	145.0	0.0166	1.560	2.62	53900	70.0	63.0	0.00356	0.524	0.76 × 10 ⁻⁴	56
45.0	200.5	0.0185	1.739	4.20	119000	70.0	73.0	0.00472	0.694	1.39	121
45.0	274.5	0.0199	1.871	5.76	225000	70.0	87.0	0.00645	0.949	4.08	423
45.0	363	0.0219	1.965	6.97	359000	70.0	112	0.00889	1.307	7.30	976
55.0	100.9	0.00787	0.741	0.24 × 10 ⁻³	1250	70.0	165	0.01107	1.628	14.0	2760
55.0	116.0	0.0106	0.996	0.72	4270	70.0	271	0.01280	1.882	22.8	7360
55.0	145.0	0.0145	1.363	2.12	15700	70.0	364	0.01366	2.001	27.0	11700
55.0	200.5	0.0172	1.617	4.59	46500	Solubility of Naphthoquinone in Fluoroform					
55.0	275.0	0.0189	1.778	6.96	96500	45.0	66.0	0.00543	0.7196	0.26 × 10 ⁻³	2400
55.0	364.0	0.0202	1.899	8.88	163000	45.0	76.0	0.00740	0.9800	0.51	5580
70.1	100.8	0.00572	0.538	0.18 × 10 ⁻³	217	45.0	92.5	0.00941	1.245	0.89	12000
70.0	116.0	0.00749	0.704	0.37	508	45.0	131.0	0.01160	1.535	2.57	48900
70.0	145.0	0.0110	1.034	1.67	2880	45.0	228.0	0.01407	1.862	3.333	110200
70.0	200.5	0.0151	1.419	5.34	12800	44.9	356.0	0.1576	2.085	4.57	239000
70.0	275.0	0.0174	1.636	9.92	32500	55.0	66.0	0.00430	0.5689	0.17 × 10 ⁻³	587
70.0	364.0	0.0190	1.786	13.5	58700	55.0	76.0	0.00562	0.7433	0.37	1450
Solubility of Naphthoquinone in Ethane						55.0	92.5	0.00771	1.020	1.12	5300
35.0	63.0	0.01033	1.519	1.06 × 10 ⁻⁴	2942	55.0	131.0	0.0105	1.383	2.53	16906
35.1	74.0	0.01112	1.635	2.02	6550	55.0	228.0	0.0133	1.766	4.52	52600
35.0	91.0	0.01178	1.732	3.07	12350	55.0	356.0	0.0152	2.014	6.33	115000
35.0	141	0.01284	1.888	4.31	26850	Solubility of Naphthoquinone in Monochlorotrifluoromethane					
35.0	202	0.01361	2.001	5.03	45000	45.0	56.3	0.00589	1.061	0.90 × 10 ⁻⁴	735
35.0	283	0.01437	2.113	5.24	65500	45.0	69.2	0.00759	1.368	1.88	1890
35.1	364	0.01488	2.188	5.37	85400	45.0	91.0	0.00894	1.611	2.32	3064
45.1	63.0	0.00694	1.021	0.91 × 10 ⁻⁴	820	45.0	141	0.01051	1.894	3.22	6590
45.1	74.0	0.00942	1.385	1.86	1980	45.1	246	0.01215	2.189	3.90	13780
45.1	91.0	0.01074	1.579	3.54	4622	45.0	364	0.01321	2.380	4.31	22800
45.0	141	0.01224	1.800	5.97	12200	55.0	56.3	0.00430	0.775	0.56 × 10 ⁻⁴	160
45.0	202	0.01321	1.943	7.65	22400	55.0	69.2	0.00620	1.117	1.25	440
45.0	283	0.01397	2.054	8.99	36900	55.0	91.0	0.00799	1.440	2.99	1400
45.0	364	0.01457	2.143	9.35	49400	55.0	141.0	0.00987	1.778	4.75	3420
55.0	63.0	0.00469	0.690	0.59 × 10 ⁻⁴	190	55.0	246	0.01172	2.112	6.54	8220
55.0	73.0	0.00694	1.021	2.00	745	55.0	364	0.01288	2.321	7.56	14050
55.0	87.0	0.00885	1.301	4.14	1840						

Table XII. Solubility of 2-Aminofluorene in Four Supercritical Solvents

temp, °C	press. (abs), bar	ρ , mol/cm ³	ρ_r	mole fraction	enhance. factor	temp, °C	press. (abs), bar	ρ , mol/cm ³	ρ_r	mole fraction	enhance. factor
Solubility of 2-Aminofluorene in Carbon Dioxide						45.0	96.2	0.0108	1.599	5.98	121500
45.0	116.0	0.0141	1.330	0.17 × 10 ⁻⁴	42700	45.0	136.5	0.0121	1.797	9.19	265000
45.0	139.5	0.0163	1.538	0.40	118800	45.0	182.0	0.0128	1.908	11.1	426800
45.0	181.0	0.180	1.698	0.95	363900	45.1	262.0	0.0138	2.041	15.2	841000
45.0	270.0	0.198	1.868	1.70	973100	45.0	362.0	0.0145	2.145	18.6	1423000
45.0	364.0	0.210	1.981	2.92	2245000	55.0	66.1	0.00526	0.778	0.35 × 10 ⁻⁵	1480
55.0	116.0	0.01067	1.007	0.15 × 10 ⁻⁴	11500	55.1	76.7	0.00741	1.096	2.09	10200
55.0	139.5	0.01393	1.314	0.47	41400	55.0	95.6	0.00962	1.423	5.90	35800
55.0	181.0	0.01645	1.552	0.94	108200	55.0	136.5	0.0114	1.686	12.3	106700
55.0	270.0	0.01890	1.783	3.19	544800	55.0	182.0	0.0124	1.834	18.6	215200
55.1	364.0	0.0202	1.906	5.07	1158000	55.1	261.0	0.0133	1.967	21.8	361700
70.0	116.5	0.00755	0.712	0.12 × 10 ⁻⁴	2200	55.0	362.0	0.0142	2.101	34.5	793900
70.0	140.0	0.01044	0.985	0.40	6650	70.1	66.1	0.00383	0.567	0.37 × 10 ⁻⁵	290
70.0	181.0	0.0140	1.321	1.58	33900	70.0	76.9	0.00524	0.775	1.09	1000
70.0	272.0	0.0173	1.632	4.05	130200	70.1	95.0	0.00745	1.102	5.32	5980
70.0	364.0	0.0190	1.792	8.01	344900	70.1	138.5	0.0102	1.509	8.78	14400
Solubility of 2-Aminofluorene in Monochlorotrifluoromethane						70.0	182.0	0.0115	1.701	29.0	62400
55.0	79.5	0.00721	1.299	0.83 × 10 ⁻⁵	4150	70.1	260.0	0.0127	1.879	43.5	133800
55.0	140.0	0.00984	1.774	3.78	33500	70.1	364.0	0.0137	2.027	61.3	264000
55.0	241.0	0.0117	2.101	6.10	93000	Solubility of 2-Aminofluorene in Fluoroform					
70.0	79.5	0.00566	1.021	1.69 × 10 ⁻⁵	1590	55.1	91.3	0.00758	1.006	3.38 × 10 ⁻⁵	19600
70.0	140.0	0.00888	1.601	9.30	15400	55.0	136.0	0.0107	1.418	11.8	102000
70.0	241.0	0.0110	1.984	22.0	62700	55.0	240.0	0.0136	1.801	25.1	383000
Solubility of 2-Aminofluorene in Ethane						55.0	364.0	0.0153	2.030	31.5	729000
45.1	65.9	0.00775	1.146	1.18 × 10 ⁻⁵	16400	70.2	91.3	0.00578	0.7672	2.27 × 10 ⁻⁵	2450
45.1	76.4	0.00969	1.433	1.78	28700	70.0	136.0	0.00909	1.206	16.1	25900
						70.1	240.0	0.0125	1.662	43.1	122400
						70.0	364.0	0.0145	1.925	60.3	259700

Table XIII. Regressed Solute Parameters a_2 and b_2 in Eq 2^a

solute	solvent							
	CO ₂		C ₂ H ₆		CHF ₃		CClF ₃	
	a_2	b_2	a_2	b_2	a_2	b_2	a_2	b_2
naphthalene	6.25	123	7.18	129	7.03	145	7.00	145
phenanthrene	13.2	194	13.9	183	12.9	191	13.4	200
anthracene	11.6	174	12.8	172	12.0	190		
biphenyl	9.40	169	10.5	174				
benzoic acid	9.23	136	9.00	126	10.0	157	8.58	133
1,4-naphthoquinone	9.90	145	9.21	155	12.2	175	9.00	157
acridine	13.2	190	15.1	217	15.5	225	14.1	215
2-naphthol	9.90	155	9.00	145	10.5	169	8.0	144
2-aminofluorene	11.2	142	13.7	177	17.8	231	14.2	195

^a a_2 is expressed in Pa m⁶/mol² and b_2 is in m³/mol × 10⁶. Temperature range: 35–70 °C.

sion (eq 8) to model the solubilities with nearly the same accuracy as is achieved by using eq 2. The error introduced by using eq 8 over eq 2 was typically less than 5% for solutes of low and medium volatility, but rose to approximately 40% error when highly soluble solutes such as naphthalene were modeled. However, when the experimental solubilities of naphthalene were regressed by using the simplified form of the fugacity coefficient, a different set of a_2 and b_2 parameters were obtained which did improve the correlation considerably.

Finally, it can be seen from Table XIII that the a_2 and b_2 "solute" parameters are not actually constants for a given solute, but do vary somewhat depending on the solvent used. It is hoped that a method of correlating the constants for use in an a priori predictive method will be found.

Conclusions

The solubilities of the model solutes were found to be dependent on the choice of the supercritical solvent used to dissolve the compound. Carbon dioxide was a very encompassing solvent, performing especially well with polar compounds, while ethane was better for simple aromatic hydrocarbons. Fluoroform was a poor solvent for hydrocarbons, but a good solvent for those molecules containing potential hydrogen-bonding sites, such as C=O, NH₂, and to a lesser extent -N≡. Chlorotrifluoromethane was consistently the poorest of the four solvents. A modified Peng–Robinson equation of state, in which two parameters are required to fit experimental data, was used to correlate solubilities over a wide range of supercritical pressures. The model correlates the solubilities better than the classical Peng–Robinson equation and alleviates some of the problems associated with application of equations of state to solid-fluid equilibria.

This study has shown that chemical effects are important in determining the solubility of solutes in supercritical fluids. In the same way as one searches for appropriate liquid solvents, employing the broad concepts of polar–nonpolar, hydrogen-bonding–non-hydrogen bonding, acid–base, etc., one can apparently use the same rules in choosing appropriate supercritical fluid solvents to affect desired separations and to maximize yields.

Glossary

a	parameter in the Peng–Robinson equation of state
b	parameter in the Peng–Robinson equation of state
K	parameter in eq 9, $f(T,P)$ but not of composition
P	pressure
R	gas constant
T	temperature
y	mole fraction
Z	compressibility factor

Greek Letters

ϕ	fugacity coefficient
ω	acentric factor

Subscripts

1	component 1; the supercritical solvent
2	component 2; the solute
12	interaction parameter of 1 and 2
r	reduced property

Superscripts

s	solid solute
vp	vapor pressure
∞	infinite dilution

Registry No. CO₂, 124-38-9; CHF₃, 75-46-7; CClF₃, 75-72-9; naphthalene, 91-20-3; biphenyl, 92-52-4; phenanthrene, 85-01-8; anthracene, 120-12-7; benzoic acid, 65-85-0; 1,4-naphthoquinone, 130-15-4; acridine, 260-94-6; 2-naphthol, 135-19-3; 2-aminofluorene, 153-78-6; ethane, 74-84-0.

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