J. Chem. Eng. Data **1990**, *35*, 355-360

Measurement of Solubility in Supercritical Fluids Using Chromatographic Retention: the Solubility of Fluorene, Phenanthrene, and Pyrene in Carbon Dioxide

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The use of retention measurements in supercritical fluid chromatography to obtain solubilities in a supercritical fluid is discussed. In certain circumstances, retention measurements can be used to generate relatively rapidly a large body of solubility data at a particular temperature from a smaller number of measurements, obtained by more conventional methods, at either the same temperature or at least two similar temperatures. The basis of the method was tested with some published data for naphthalene and also the relatively small number of data published for fluorene, phenanthrene, and pyrene. A large body of data was then obtained for these last three compounds at 308.2, 318.2, 323.2, and 328.2 K with use of the two variations of the method.

Introduction

The degree of retention of a solute in supercritical fluid chromatography (SFC), as measured by the capacity factor, k', is at least qualitatively inversely related to the solvating power of the mobile phase for that solute: the more soluble it is in the mobile phase, the less it will be retained. In some situations at constant temperature solubility of solid solutes in the mobile phase can be inversely proportional to the capacity factor. When this is the case, chromatographic retention can be used to measure solubilties relatively rapidly, and this has been used for supercritical fluids. In one study, chromatographic retention has been used to obtain pressure thresholds for the solubilities of various compounds at different temperatures (*1*). In another, solubilities have been obtained at lower pressures in a supercritical fluid by using retention measurements and vapor pressure values (*2*).

The theory of the relationship has been discussed (*1*, *2*), which in its simplest form is

$$S = C/k' \qquad (1)$$

where S is the solubility (per unit volume), k' is the chromatographic capacity factor, and C is a constant for a particular column, solute, and temperature, given by

$$C = rc_{st}^{\circ} \exp[(\mu_s^{\circ} - \mu_{st}^{\circ})/RT] \qquad (2)$$

In eq 2, r is a phase ratio, which is the ratio of the amount of stationary phase to that of the mobile phase, for example the ratio of the two volumes if the concentrations in both phases are expressed in terms of per unit volume. c_{st}° is the standard (surface or volume) concentration in the stationary phase, μ_s° the chemical potential of the pure solid solute at standard pressure, and μ_{st}° the chemical potential of the solute in the stationary phase referred to infinite dilution and the standard concentration and pressure.

The validity of eqs 1 and 2 relies on the following assumptions:

1. The capacity factors are measured at essentially infinite dilution. This is the usual situation in which analytical chromatography is carried out, and if it is not the case, this is observable as a distortion of the chromatographic peak shape and a variation of the degree of retention with the amount of solute injected.

2. Capacity factors are measured with low pressure drops across the column and away from the critical point. Equations have been obtained for the average capacity factor for SFC with a pressure drop (*3*, *4*), and calculations have been carried out for a model system of the percentage difference of the true average and the value at the average of the inlet and outlet pressures (*4*). These show that differences of up to a factor of 2 are obtained for a 30-bar drop 1 K above the critical temperature and near the critical pressures. The effect decreases with a rise in temperature, with the peak effect rising to higher pressures. For the studies described here, a short column and slow flow rates were used to reduce the pressure drop to around 2 bar and the critical region was avoided.

3. The solid solutes do not absorb solvent: i.e. the method is restricted to conditions where the solid solutes remain as solids in the presence of the mobile phase, i.e. a solute-rich liquid phase does not form, and the solids are assumed not to absorb the mobile phase.

4. The partial molar volume of the solute at infinite dilution in the stationary phase is equal to the molar volume of the solid at the same temperature. As a consequence of this assumption, the difference between the chemical potentials of the solute in the solid and at infinite dilution in the stationary phase, that occurs in eq 2, will be the same at all pressures.

5. The chemical potential of the solute in the stationary phase at infinite dilution is independent of the nature and pressure of the mobile phase apart from the pressure effect described in 4. This will often not be the case, for example, with cross-linked polymer phases used in supercritical fluid chromatography, which absorb the mobile phase and swell to an extent dependent upon pressure (*5*). It is likely to be true for octadecylsilyl (ODS) bonded phases however, as it was not necessary to take into account effects of the mobile phase on the stationary phase to quantitatively account for the dependence of retention on temperature (*6*). Adsorption of carbon dioxide on an ODS phase has been observed, and this peaks in the region of the critical point (*7*). It does not follow that this affects the adsorption of solutes, however, and the effect is such that the environment of the ODS phase does not change as much with a drop in pressure as it would if this adsorption did not occur.

6. The activity (or fugacity) coefficient does not vary from its value at infinite dilution up to the solubility limit. For supercritical fluids such as carbon dioxide, where interactions are not strong or specific, the activity (or fugacity) coefficient can be calculated from equations of state with reasonable confidence, and here it is known that the assumption is a good approximation, especially as supercritical solubilities are usually low.

Of these assumptions, 1–3 and 6 are usually valid or easily achievable. Assumption 4 is a minor effect and is probably approximately true, and 5 will hold for some types of chromatographic column.

The difference in standard chemical potentials in eq 2 corresponds to the standard Gibbs function change for the precipitation of the solid solute from solution at infinite dilution in the stationary phase. In common with other types of equilibria, it may be assumed therefore that the constant C is given approximately by

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Table I. Published Solubilities, S, of Naphthalene, Fluorene, Phenanthrene, and Pyrene in Supercritical Carbon Dioxide at Various Pressures and the Chromatographic Retention Volumes, V_R, in Carbon Dioxide at the Same Pressure and with an ODS2 Column ($V_M = 1.1 \times 10^{-6}$ m^3)

T/K	P/bar	S/ (kg m^{-3})	$V_R - V_M$/ 10^{-6} m^3	$S(V_R - V_M)$/ 10^{-6} kg
		Naphthalene		
308.2	87.1	15.151[a]	2.08	31.51
	92.2	17.544[a]	1.78	31.23
	111.5	25.641[a]	1.32	33.85
	121.6	28.571[a]	1.20	34.28
	131.7	30.303[a]	0.93	28.18
	141.9	32.258[a]	0.95	30.64
	152.0	34.483[a]	0.83	28.62
	192.5	41.666[a]	0.72	30.00
	222.9	45.454[a]	0.66	30.00
	243.2	46.296[a]	0.60	27.78
				av = 30.61 ± 2.21
318.2	70.0	0.257[b]	164.59	42.30
	75.0	0.340[b]	108.76	36.98
	80.0	0.513[b]	63.70	32.68
	85.0	0.901[b]	34.83	31.38
	95.0	4.695[b]	7.54	35.40
	100.0	9.524[b]	4.36	41.52
	105.0	14.706[b]	2.89	42.50
	110.0	20.000[b]	2.37	47.40
	115.0	23.810[b]	1.90	45.24
	120.0	27.777[b]	1.72	47.78
	130.0	32.258[b]	1.44	46.45
	145.0	40.000[b]	1.06	42.40
	170.0	47.619[b]	0.92	43.81
	195.0	55.555[b]	0.73	40.55
	220.0	62.500[b]	0.63	39.37
	250.0	66.666[b]	0.55	36.67
				av = 40.80 ± 5.05
		Fluorene		
308.2	83.7	0.923[c]	7.15	6.60
	104.3	3.257[c]	2.36	7.70
	138.8	4.651[c]	1.49	6.93
	207.7	7.463[c]	0.93	6.94
				av = 7.04 ± 0.47
323.2	104.3	0.713[c]	14.05	10.19
	138.8	3.906[c]	2.54	(9.73)
	173.3	6.757[c]	1.53	10.27
	207.7	9.259[c]	1.17	10.85
				av = 10.26 ± 0.46
		Phenanthrene		
308.2	100.0	1.656[d]	4.27	6.58
	120.0	2.451[d]	2.87	6.92
	150.0	3.344[d]	2.07	7.03
	200.0	4.386[d]	1.50	7.07
				av = 6.90 ± 0.22
318.2	120.0	2.273[e]	5.05	11.48
	160.0	4.329[e]	2.49	10.78
	200.0	5.618[e]	1.75	9.83
	240.0	7.692[e]	1.41	10.85
				av = 10.73 ± 0.68
328.2	120.0	0.939[e]	12.22	(11.47)
	160.0	4.184[e]	3.25	13.60
	200.0	6.579[e]	2.06	13.55
	240.0	9.091[e]	1.52	13.82
				av = 13.66 ± 0.14
		Pyrene		
308.2	83.6	0.0816[c]	26.83	2.19
	104.3	0.2656[c]	8.47	2.25
	125.0	0.4254[c]	5.90	2.51
	138.8	0.4918[c]	4.88	2.40
	207.7	0.8430[c]	2.93	2.47
				av = 2.36 ± 0.14
323.2	104.3	0.0307[c]	98.33	3.02
	125.0	0.0189[c]	14.55	2.75
	138.8	0.3785[c]	8.19	3.10
	207.7	1.0181[c]	3.32	3.38
				av = 3.06 ± 0.26

[a] From ref 9. [b] From ref 9, by interpolation. [c] From ref 11. [d] From ref 12. [e] From ref 13.

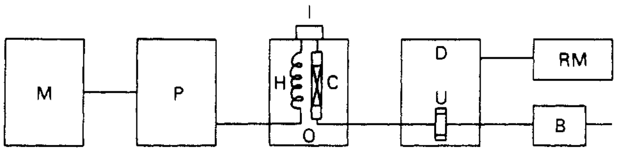

Figure 1. Schematic diagram of the experimental apparatus: M, carbon dioxide supply; P, pump; O, oven; H, preheater; I, injection valve; C, column; D, UV detector; U, cell; B, back-pressure regulator; RM, recorder and microprocessor.

$$C = A \exp(B/T) \qquad (3)$$

where A and B are constants over a limited temperature range for a particular column and solute. This equation allows the possibility of limited interpolation or extrapolation to obtain values of C, by plotting ln C versus $1/T$.

Solubilities in supercritical fluids may be determined in favorable circumstances, more rapidly than by conventional methods, by using the inverse relationship, eq 1, provided that the constant C can be determined. Five possible methods are listed for achieving this: (1) from the vapor pressure of the solute [capacity factors measured at relatively low pressures may be extrapolated to zero supercritical fluid pressure, where the corresponding "solubility" is the concentration of the vapor (*2*); at low pressures, well below the critical pressure, the extrapolation of ln k' versus pressure is linear]; (2) from at least one solubility measured by other methods at the required temperature [this would enable a small amount of data to be expanded into a larger body of data relatively easily]; (3) from solubility measurements obtained by other methods at two temperatures at least close to the required temperature, using eq 3; (4) from solubilities obtained by other techniques in another supercritical fluid [it would be necessary to be satisfied that the above assumptions were approximately valid in both fluids; the method would be a way of measuring the effect of a modifier or entrainer on solubility, for example the addition of small amounts of methanol to carbon dioxide]; (5) from solubilities in liquids, by comparing the retentions in SFC and HPLC with the same solute and column [further assumptions are necessary in this case, and experimental investigation of the validity of the method would be required].

Investigation of the first method has been reported by us earlier (*2*). In the present paper, methods 2 and 3 are used to obtain solubility data for fluorene, phenanthrene, and pyrene in carbon dioxide at four temperatures between 308.2 and 328.2 K. For these three compounds and for naphthalene, published supercritical solubility data are used to illustrate the validity of the methods.

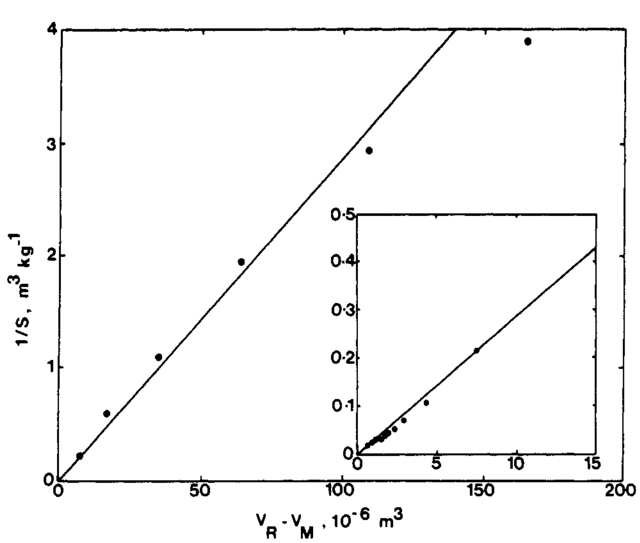

Figure 2. Plot of reciprocal solubility, $1/S$, versus retention volume, V_R, minus the mobile-phase retention volume, V_M, for naphthalene in supercritical carbon dioxide at 318.2 K.

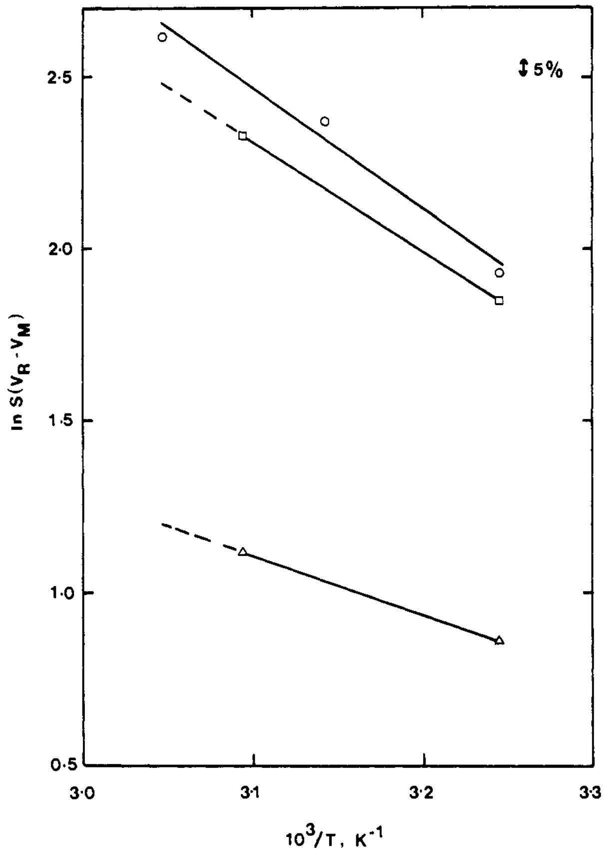

Figure 3. Plot of ln [$S(V_R - V_M)$] versus reciprocal temperature: ○, phenanthrene; □, fluorene; △, pyrene.

Table II. $S(V_R - V_M)$ for Fluorene, Phenanthrene, and Pyrene, Obtained from Figure 3

	T/K	$S(V_R - V_M)/10^6$ kg
fluorene	318.2	9.09
	328.2	11.59
phenanthrene	323.2	12.06
pyrene	318.2	2.82
	328.2	3.32

Table III. Solubility of Fluorene in Supercritical Carbon Dioxide

308.2 K		318.2 K		323.2 K		328.2 K	
P/bar	$y \times 10^3$	P/bar	$y \times 10^3$	P/bar	$y \times 10^3$	P/bar	$y \times 10^3$
78.3	0.24	85.0	0.06	89.4	0.07	85.0	0.05
79.8	0.33	90.0	0.13	92.0	0.11	90.0	0.08
80.4	0.33	95.0	0.28	95.5	0.13	95.0	0.11
80.9	0.34	100.0	0.49	100.1	0.26	100.0	0.18
82.2	0.53	105.0	0.69	102.0	0.27	105.0	0.28
82.5	0.47	110.0	0.90	105.2	0.43	110.0	0.43
83.4	0.51	115.0	1.06	105.9	0.48	115.0	0.60
84.4	0.65	120.0	1.14	106.7	0.49	120.0	0.82
85.1	0.51	124.6	1.28	108.1	0.52	125.0	1.05
85.6	0.49	130.0	1.32	108.8	0.50	130.0	1.23
86.0	0.55	134.0	1.54	110.2	0.65	134.2	1.37
89.0	0.76	145.0	1.73	114.5	0.73	137.2	1.40
89.3	0.74	156.0	1.91	118.5	0.98	145.5	1.72
91.8	0.80	169.5	1.99	121.0	0.92	157.0	2.06
95.1	0.78	184.5	2.23	125.7	1.21	166.1	2.28
96.6	0.98	198.0	2.43	129.4	1.37	174.8	2.46
97.4	0.91	216.0	2.71	130.3	1.42	186.1	2.66
99.1	1.03	224.5	2.79	135.6	1.44	194.2	2.80
100.0	0.91	232.5	2.88	137.0	1.61	205.5	3.05
100.3	0.99	244.2	2.97	140.7	1.73	209.8	3.17
109.2	1.19	254.0	3.12	145.0	1.73	214.7	3.30
109.5	1.22			146.2	1.80	225.2	3.48
110.0	1.08			151.0	1.99	237.0	3.69
111.2	1.13			156.0	2.05	245.0	3.77
116.5	1.33			156.5	2.04		
119.5	1.37			160.5	2.18		
120.7	1.34			166.0	2.36		
121.0	1.30			167.0	2.31		
121.9	1.37			168.2	2.29		
130.0	1.50			174.6	2.52		
130.5	1.50			181.0	2.36		
131.2	1.50			181.4	2.49		
140.4	1.60			193.0	2.59		
141.4	1.62			195.6	2.60		
142.0	1.61			202.0	2.74		
150.5	1.70			212.2	2.93		
151.7	1.66			219.5	2.95		
160.5	1.82			228.5	3.11		
163.0	1.82						
170.4	1.96						
171.7	1.94						
180.5	1.93						
181.0	2.00						
182.6	2.06						
191.2	2.08						
201.6	2.28						
203.5	2.23						

Experimental Section

A schematic representation of the apparatus used in this study is shown in Figure 1. CO_2 is withdrawn from a cylinder fitted with a dip tube, M, into a high-pressure syringe pump (Varian 8500), P. The pump head is cooled to about 5 °C with use of an Endocal refrigerated circulating bath (Jencons Scientific Ltd.). The liquefied gas is then pumped into the system where it is preheated in a 1-m length of stainless steel capillary, H, mounted inside a Pye 104 gas-chromatographic oven, O, before entering a Rheodyne 7125 injection valve, I, fitted with a 10-mm^3 loop. The supercritical fluid is then passed through a packed column, C, nominally of length 100 mm and 4.6-mm internal diameter, packed with 10-μm diameter porous silica particles surface-bonded with octadecylsilyl ($CH_3(CH_2)_{17}OSi-$) groups (Jones Chromatography Spherisorb ODS2). At the exit of the column a UV detector (Cecil Instruments CE2112), D, is installed, housing a purpose-built high-pressure stainless steel cell of 8-mm^3 volume and 10-mm path length, U, fitted with two quartz windows of 5-mm diameter and 3-mm thickness (York Glassware Services Ltd.). The system is pressure-controlled by a heated back-pressure regulator (Tescom 26-3220-24, Techmation Ltd.), B, and the inlet and outlet pressures of the column are measured with variable-reluctance pressure transducers (Thorn-EMI SE42). The flow rate is monitored at atmospheric pressure with a bubble flowmeter (not shown). The output of the detector is monitored by a chart recorder and

Table IV. Solubility of Phenanthrene in Supercritical Carbon Dioxide

308.2 K		318.2 K		323.2 K		328.2 K	
P/bar	$y \times 10^3$	P/bar	$y \times 10^3$	P/bar	$y \times 10^3$	P/bar	$y \times 10^3$
78.3	0.13	95.0	0.16	89.4	0.04	90.0	0.04
79.8	0.17	100.0	0.31	92.0	0.05	95.0	0.06
80.4	0.18	105.0	0.46	95.5	0.07	100.0	0.10
80.9	0.18	110.0	0.61	100.1	0.15	105.0	0.17
82.2	0.28	115.0	0.72	102.0	0.16	110.0	0.26
82.5	0.25	120.0	0.80	105.2	0.26	115.0	0.38
83.4	0.27	124.6	0.92	105.9	0.29	120.0	0.55
84.4	0.35	130.0	0.95	106.7	0.30	125.0	0.71
85.1	0.27	134.0	1.09	108.1	0.34	130.0	0.83
85.6	0.26	145.0	1.25	108.8	0.32	134.2	0.95
86.0	0.27	156.0	1.40	110.2	0.41	137.2	0.98
89.0	0.42	169.5	1.48	114.5	0.49	145.5	1.21
89.3	0.41	184.5	1.65	118.5	0.65	157.0	1.49
91.8	0.46	198.0	1.84	121.0	0.64	166.1	1.68
95.1	0.45	208.0	1.96	125.7	0.83	174.8	1.82
96.6	0.55	216.0	2.06	129.4	0.94	186.1	2.01
97.4	0.51	224.5	2.08	130.3	0.98	194.2	2.08
99.1	0.58	232.5	2.20	135.6	0.82	205.5	2.32
100.0	0.54	244.2	2.27	137.0	1.12	209.8	2.40
100.3	0.56	254.0	2.39	140.7	1.20	214.7	2.52
109.2	0.69			145.0	1.21	225.2	2.67
109.5	0.69			146.2	1.24	237.0	2.73
110.0	0.62			151.0	1.43	245.0	2.93
111.2	0.65			156.0	1.48		
116.5	0.76			156.5	1.52		
119.5	0.79			160.5	1.56		
120.7	0.78			166.0	1.69		
121.0	0.76			167.0	1.69		
121.9	0.79			168.2	1.65		
130.0	0.87			174.6	1.88		
130.5	0.87			181.0	1.74		
131.2	0.87			181.4	1.79		
140.4	0.94			193.0	1.93		
141.4	0.95			195.6	1.94		
142.0	0.95			202.0	2.09		
150.5	1.02			212.2	2.22		
151.7	1.03			219.5	2.24		
160.5	1.10			228.5	2.47		
163.0	1.09						
170.4	1.16						
171.7	1.16						
180.5	1.17						
181.0	1.21						
182.6	1.23						
191.2	1.25						
201.6	1.34						
203.5	1.33						

Table V. Solubility of Pyrene in Supercritical Carbon Dioxide

308.2 K		318.2 K		323.2 K		328.2 K	
P/bar	$y \times 10^4$	P/bar	$y \times 10^4$	P/bar	$y \times 10^4$	P/bar	$y \times 10^4$
80.4	0.25	95.0	0.15	100.1	0.12	105.0	0.13
80.9	0.23	100.0	0.29	102.0	0.14	110.0	0.22
82.2	0.35	105.0	0.45	105.2	0.23	115.0	0.33
82.5	0.32	110.0	0.62	105.9	0.26	120.0	0.50
83.4	0.36	115.0	0.77	106.7	0.26	125.0	0.67
84.4	0.44	120.0	0.86	108.1	0.31	130.0	0.82
85.1	0.34	124.6	1.00	108.8	0.30	134.2	0.94
85.6	0.33	130.0	1.06	110.2	0.38	137.2	0.97
86.0	0.35	134.0	1.21	114.5	0.48	145.5	1.23
89.0	0.55	145.0	1.41	118.5	0.64	157.0	1.54
89.3	0.53	156.0	1.60	121.0	0.64	166.1	1.76
91.8	0.58	169.5	1.72	125.7	0.84	174.8	1.95
95.1	0.62	184.5	1.96	129.4	0.98	186.1	2.19
96.6	0.74	198.0	2.18	130.3	1.00	194.2	2.31
97.4	0.68	208.0	2.35	135.6	1.08	205.5	2.55
99.1	0.78	216.0	2.45	137.0	1.17	209.8	2.69
100.0	0.77	224.5	2.54	140.7	1.27	214.7	2.82
100.3	0.76	232.5	2.64	145.0	1.30	225.2	2.97
109.2	0.95	244.2	2.76	146.2	1.38	237.0	3.17
109.5	0.95	254.0	2.87	151.0	1.52	245.0	3.29
110.0	0.87			156.0	1.60		
111.2	0.89			156.5	1.66		
116.5	1.06			160.5	1.69		
119.5	1.10			166.0	1.84		
120.7	1.09			167.0	1.84		
121.0	1.06			168.2	1.85		
121.9	1.11			174.6	2.03		
130.0	1.24			181.0	2.03		
130.5	1.21			181.4	2.10		
131.2	1.24			193.0	2.27		
140.4	1.35			195.6	2.29		
141.4	1.36			202.0	2.41		
142.0	1.37			212.2	2.62		
150.5	1.46			219.5	2.73		
151.7	1.45			228.5	2.84		
160.5	1.58						
163.0	1.59						
170.4	1.68						
171.7	1.69						
180.5	1.73						
181.0	1.78						
182.6	1.80						
191.2	1.85						
201.6	1.97						
203.5	1.96						

microcomputer, RM. The time of injection is fed to the microcomputer via a trigger switch incorporated with the injection valve, and the microcomputer displays the retention times. For a small number of experiments, where the retention was high, the peaks were too small to be detected by the computer as programmed and the retention times were measured from the recorder trace. The retention times used below were an average of 3-4 measurements.

CO_2 of 99.987% purity was supplied by BOC, and the solutes were injected as mixtures in 1% solutions in dichloromethane. The solutes were substances used for chromatographic standards and are known to be 99% pure or better. In any case, impurities are likely to be separated by chromatography during the experiment. Flow rates at pump densities of 2 mL/min were used, which gave a pressure drop across the column of 2 bar or less. Retention times were converted to retention volumes, V_R, by using atmospheric flow rates and the ratio of the CO_2 densities at atmospheric pressure and the average column pressure, the latter calculated from a published equation of state (*8*). The mobile-phase retention volume, V_M, arising from the free volume in the column and that of the connecting tubes, was taken to be 1.1 mL. This value is slightly smaller than the value obtained from solvent peaks, which were probably suffering some retention, and compares with 1.74 mL for the total internal volume of the column and connections, neglecting the effect of the porous packing. It is a value that causes all the curves of the type of Figure 2, given in the next section, which we have obtained from both SFC and HPLC, to pass through the origin and is likely therefore to be the true value. In many cases V_M is much smaller than V_R, and errors in the former are of less consequence. Probable errors in the values of $V_R - V_M$ are estimated to be 3% plus 0.2 mL.

Results and Discussion

Retention measurements from the same column and CO_2 as the mobile phase are first reported in Table I for naphthalene, fluorene, phenanthrene, and pyrene under conditions where published solubilities are available. Two or three temperatures between 308.2 and 328.2 K and pressures between 70 and 250 bar were used. For naphthalene a large number of published solubilities are available, and of these only the earliest values of Tsekhanskaya et al. (*9*) were used, as later measurements agree well with their values. At 308.2 K the lower pressures are avoided, as these are too near the critical point. Results for naphthalene at 328.2 K are not given, as they contained a high proportion of low and therefore more erroneous retention volumes.

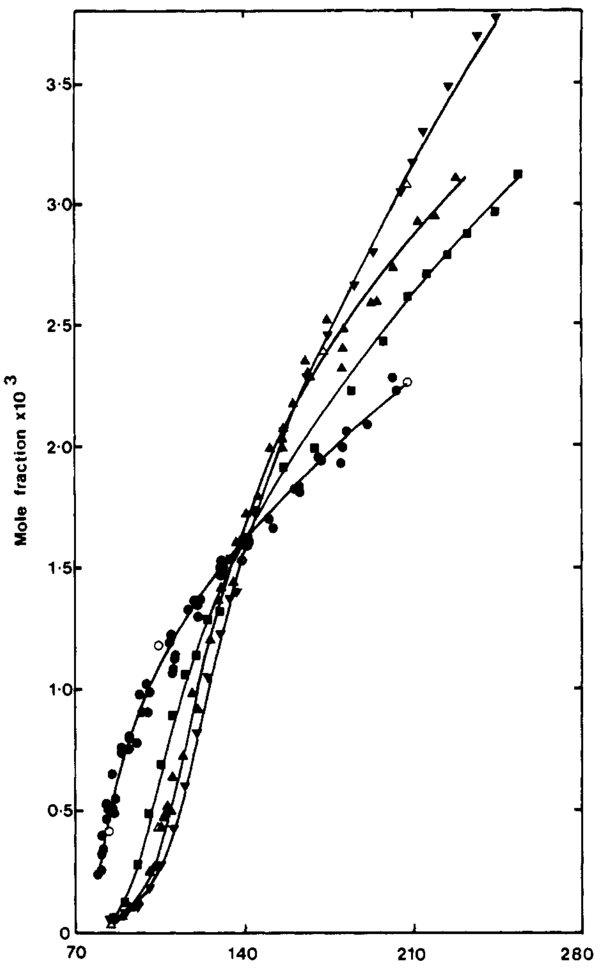

Figure 4. Solubility of fluorene in supercritical carbon dioxide. Present work: ●, 308.2 K; ■, 318.2 K; ▲, 323.2 K; ▼, 328.2 K. Johnston et al. (*11*): ○, 308.2 K; △, 323.2 K.

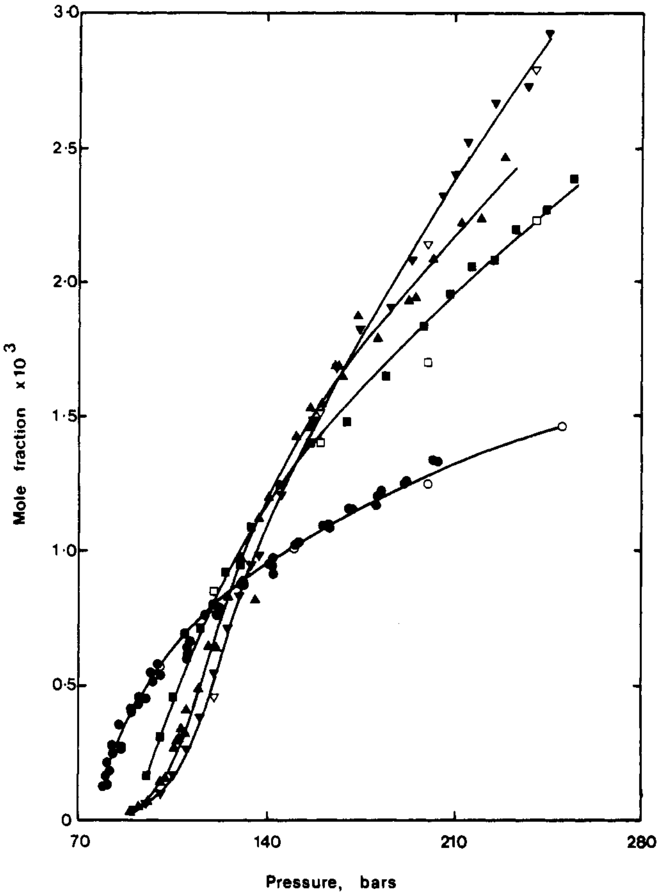

Figure 5. Solubility of phenanthrene in supercritical carbon dioxide. Present work: ●, 308.2 K; ■, 318.2 K; ▲, 323.2 K; ▼, 328.2 K. Dobbs et al. (*12*): ○, 308.2 K. Kurnik et al. (*13*): □, 318.2 K; ▽, 328.2 K.

The capacity factor, k', is related to retention volumes for the solute and mobile phase, V_R and V_M, respectively, by $k' = (V_R - V_M)/V_M$. Tests of the relationship $k' = C/S$ are therefore the constancy of the product $S(V_R - V_M)$, which is equal to CV_M if eq 1 is valid, and straight-line plots of $1/S$ against $V_R - V_M$. A test of the validity of eq 3 is a straight-line plot of $\ln [S(V_R - V_M)]$ against $1/T$.

Table I gives values of the product $S(V_R - V_M)$ for all the measurements. Also given are the average values of this product and the standard deviation of the population of values (not the standard deviation of the mean) for each solute at each temperature. Two values, one for phenanthrene and one for fluorene, shown in parentheses, are sufficiently different not to be included in the averaging. If these two values are neglected, the sets are constant to within an average of 5%, except for naphthalene at 318.2 K where there is a high proportion of low retention volumes. These worse results for naphthalene at 318.2 K are shown graphically in Figure 2. Because of the wide range of values, two plots are given with different scales to show the low and high values. (The alternative of a log–log plot is a less obvious test of linearity.) The lines drawn on both parts of the figure have the same slope and correspond to a value for $S(V_R - V_M)$ of 35 mg. In spite of some deviations, the figure is a remarkable display of linearity, in view of the fact that the data cover a range of 2.5 orders of magnitude. The major deviations from the straight line may be explained as follows. The highest point arises from a very low supercritical fluid solubility, which may be less accurate in percentage terms than the other values. The points that lie below the curve of the lower scaled plot (inset) are from low retention volumes, which will be more erroneous. Probable errors in the published solubilities are given as 3–5% and those on the retention volumes are 3% rising to around 20% for the very low values for naphthalene. Thus in general the results support the validity of eq 1 to within their combined experimental errors.

The validity of eq 3 is tested in Figure 3 for phenanthrene by plotting the natural logarithm of the mean values of the product $S(V_R - V_M)$ for each solute at each temperature against $1/T$. The values deviate from the straight line by less than 5% of $S(V_R - V_M)$. The slope of the line corresponds to a standard enthalpy of solution (absorption) into the ODS stationary phase of 23 kJ mol^{-1}. This compares with enthalpy of fusion for phenanthrene of 19 kJ mol^{-1} (*10*). Although only two points are available for each of fluorene and pyrene, these are also plotted on Figure 3 for comparison and show similar behavior.

Retention measurements were then carried out for fluorene, phenanthrene, and pyrene for a range of pressures at 308.2, 318.2, 323.2, and 328.2 K. Proportionality constants were obtained from the averages in Table I, where published solubilities were available at the same temperature, or otherwise by interpolation or extrapolation from Figure 3, in which case the values obtained of $S(V_R - V_M) = CV_M$ are given in Table II. These constants were then used to calculate solubilities in terms of per unit volume from eq 1 and then converted to mole fractions, y, assuming that the densities of these dilute solutions can be approximated by the density of pure carbon dioxide (*8*). The solubilities, in terms of mole fractions, are reported in Tables III–V and plotted in Figures 4–6, as filled points, along with the previous data, shown as open points, from which the constants were obtained. Values at the same pressure or pressures within 0.2 bar were averaged before

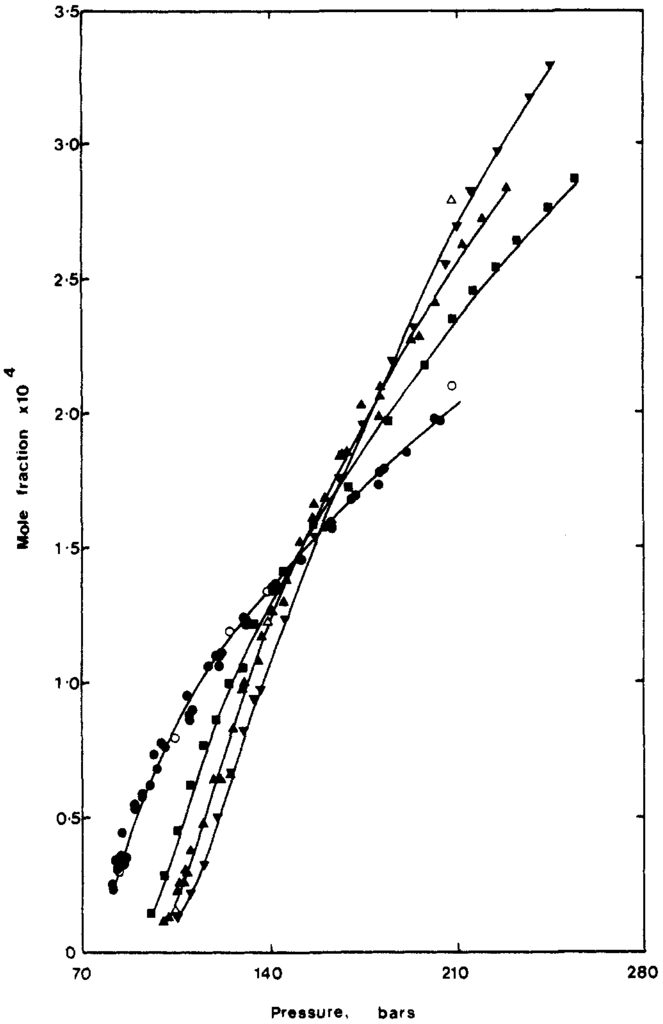

Figure 6. Solubility of pyrene in supercritical carbon dioxide. Present work: ●, 308.2 K; ■, 318.2 K; ▲, 323.2 K; ▼, 328.2 K. Johnston et al. (*11*): ○, 308.2 K; △, 323.2 K.

insertion into the tables but shown as individual points on the figures.

The two published values, one for phenanthrene and one for fluorene, which were not used in calculating the proportionality constants, are included in Figures 4 and 5 and appear as deviations from the trend of the other data. Apart from these points, all data, present and previous, lie on smooth curves with an average deviation of around 5%. On the basis of the quoted accuracy of the published data of 3-5%, the precision of the retention measurements and the variation of the proportionality constants, an estimate of 5-8% for the accuracy of the present data seems reasonable.

This study therefore demonstrates the feasibility of obtaining a large body of somewhat less accurate, but still reasonable, solubility data in supercritical fluids, using comparatively rapid chromatographic measurements and a small number of absolute measurements by, for example, a gravimetric method. Chromatographic measurements on a number of compounds can be made in the same experiment by injecting mixtures, which rapidly separate on the column. Where data is needed quickly for design purposes, this route could be a useful one.

Glossary

A,B	constants in eq 3
c	concentration
C	constant in eq 1
k'	chromatographic capacity factor
P	pressure
r	phase ratio
S	solubility (per unit volume)
T	temperature
V	retention volume
y	solubility (in terms of mole fraction)

Greek Letters

μ	chemical potential

Subscripts

M	mobile phase
R	solute
s	solid
st	stationary phase

Superscripts

^{o}	standard state (specified)

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Received for review October 31, 1989. Accepted April 3, 1990.