Solubilities of Solids and Liquids of Low Volatility in Supercritical Carbon Dioxide

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A table is given of the compounds of low volatility, whose experimental solubilities in supercritical carbon dioxide have been published up to the end of 1989, with the temperature and pressure ranges of the experimental measurements, the experimental method, and references to the source of data. The data for pure compounds, which were presented in tabular form in the original publications, are shown in a series of figures along with correlation lines for each isotherm. The method of correlation was to fit the experimental data for each isotherm, in the form of the natural logarithm of the product of mole fraction and pressure, to a linear function of density above a pressure of 100 bars. The constants obtained from the fitting procedures are given in a table. Procedures for estimating, from these constants, the solubilities of the compounds at temperatures and pressures different from those of the experimental data are suggested.

Contents

1. Introduction

1.1. Background

A supercritical fluid is a relatively modern term for a under pressure above its critical temperature. Under e conditions it does not condense to a liquid, but at high sures can achieve liquidlike densities. It has been known nore than 100 years that a supercritical fluid can dissolve bstance of low volatility and that the solubility is depen-; on pressure.[1] The ability to control solubility by means ressure as well as temperature has brought about the use percritical fluids in extraction processes, for example.

Industrial supercritical extraction processes are now established and textbooks[2-4] and published posia[4a,4b] are available on their chemical and chemical neering aspects. The technique is used on a large scale, example, for coffee decaffeination and hop extraction, on a smaller scale, for the extraction of high-value natu-products, such as perfumes.[5] More than 200 U.S. patents supercritical extraction processes have been registered,[2] rell as a large number outside the U.S., mainly in Ger-y. Research is being carried out on the feasibility of car-g out chemical reactions on an industrial scale, mainly 1 the idea of combining manufacture with separation of products.[6] Supercritical extraction is also being carried on a laboratory scale as a preliminary to chemical analy-y various techniques, such as chromatography.[7] Many esses, such as polyethylene synthesis and high-pressure oleum fractionation, which have been carried out indus-lly for decades, are in principle "supercritical."

For all these processes, knowledge of the solubility of stances in supercritical fluids is important and a large ber of experimental measurements have been made in nt years. The solubility is the concentration, or mole tion, of a substance in the supercritical phase at a partic-temperature and pressure when it is in equilibrium with pure substance. Real processes, however, usually involve tures and the solute phase may be different in character n that of the pure substance, i.e., liquid rather than solid dsorbed on a substrate. In these circumstances, the solu-ty gives only an indication of the relative extractability of stances as a function of temperature and pressure, but is important in designing operating conditions to obtain an act of the desired composition. In a separation stage, re the pressure is dropped to precipitate particular com-ents preferentially, solubility data may be more quantita-ly applicable. However, the presence of other solutes in supercritical fluid has been found to affect the solubility.[8]

1.2. Scope

This review is restricted to solubilities of substances of volatility in pure carbon dioxide. For these solutes, the rated solutions are dilute with the solute mole fraction ically below 0.1 and often much less. As explained in ail in Sec. 1.3, the solubility data covered in this paper respond only to particular solvent-rich boundaries on the se diagram of the two-component system.

The restriction to CO_2 is for reasons of size and because the principal supercritical fluid in use today. Its indus-

trial and analytical importance lies in its convenient critical temperature of 31 °C ($= 304$ K), its low cost, and its non-toxicity. The majority of the experimental solubility data published to date are in this fluid. Because the carbon dioxide molecule has no dipole, and the relative permittivity of the liquid is 1.6,[9] it is usually regarded as a nonpolar solvent. It has, however, some affinity with polar solutes because of its high quadrupole moment.[9a] To enhance this affinity, it is often used with added polar modifiers or entrainers, such as methanol. Relatively few experimental data are available in modified CO_2, however, and the data for modified solvents are not included in the present compilation.

The restriction to solutes of low volatility is first that most of the data and most of the processes of industrial importance involve this type of solute. Second, the situation in terms of the phase diagrams is relatively simple. Industrial supercritical extraction processes can involve volatile solutes, such as the proposed extraction of ethanol from water mixtures with CO_2, but in these cases more complete knowledge of a complex phase diagram is necessary. The relevant phase diagrams for involatile solutes are described in the next section.

The published data used in this review were obtained from a search of Chemical Abstracts up to December 1989. Only the data published in tabulated form are included in the correlations and the figures. The minority of papers in which the data were presented in graphical form are, however, included in the table of references.

1.3. Phase Behavior for Involatile Solutes

Solubility data, reviewed in this article, comprise a limited, though important, subset of the information necessary to construct the complete phase diagram of the solute-fluid system. It is desirable therefore at the outset to describe the appropriate phase diagrams and set the solubility data in context. The solubilities reviewed here are described as solubilities in supercritical carbon dioxide, in the sense that the pure solvent is under supercritical fluid conditions. However, the binary solute-fluid mixture may or may not be supercritical, and many would wish to describe some of the data reviewed as gas solubilities. At the same time, some solubilities, which can be legitimately described as supercritical fluid solubilities, are not included in this review. This is because they are a relatively small part of the body of data for involatile solutes and would require a separate discussion and correlation. An important part of this section, therefore, is to describe the restriction of the scope of this review to certain surfaces, or parts of surfaces, in the phase diagrams. It will be seen, however, that for a system containing a solid solute, which does not form a liquid phase under the conditions of interest, the situation is a relatively simple one.

Detailed and quantitative knowledge of phase diagrams is only available for a few of the systems covered by this review and so this description will be largely qualitative, but this is nevertheless sufficient. The phase diagrams of two component systems are classified into a number of types or classes.[10] The subject is a complex one and the purpose here is to give only the information necessary for the present purpose. For mixtures of CO_2 and solutes which have low vola-
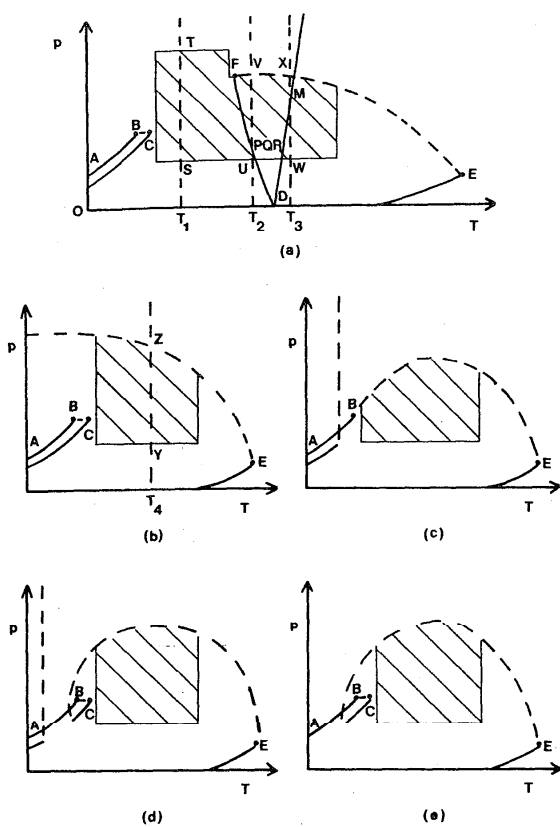
FIG. 1. p-T projections of schematic phase diagrams for mixtures of carbon
dioxide and a solute of low volatility.

tility at ambient temperature, the critical temperatures of the two components are widely separated, the vapor pressures of the solutes are low compared with pressures of interest, the two components exhibit immiscibility as liquids (subcritically), and often only fairly dilute solutions are formed under a wide range of conditions. For example, naphthalene, which is the solute for which there are many experimental solubility data, has a critical temperature of 477 °C compared with 31 °C for CO_2. Most of the substances in this review have critical temperature differences greater than that for naphthalene. Vapor pressures of the pure solutes at the temperatures of interest are typically of the order of 0.01 bar or less and solubilities are below 0.1 mole fraction under the experimental conditions that have been used.

The two-component systems described in this review are mostly classified as type III systems. This is true for water–CO_2,[10] naphthalene–CO_2, and is probably true for the majority of the systems, especially those with less volatile solutes than naphthalene. Decane–CO_2 is known to be of type II[10] and it is possible that there are other systems in this class as well as in types IV or V. Figure 1 shows p-T projections of the p-T-x phase diagrams for some of these types of system (x here being mole fraction of the solute).

Figure 1(a) is for a type III system where the solute is a solid above the solvent critical temperature and is the most typical of the systems described here. AB is the vapor pres-

sure (L-G) curve for the pure solvent ending in the cri point B. In the presence of excess solute, the vapor pres curve for pure CO_2 is shifted (slightly for a solute of volatility) and ends in the critical end point C. Here OD DE are the vapor pressure curves for the solid and li solute, respectively, ending in the solute critical point E. temperatures where the vapor pressures of the pure solv are very small these are shown coincident with the p axis. The point D is the triple point for the pure solute, the line emanating almost vertically from it is the press melting (S-L) curve for the solute. In the presence of ex CO_2, however, melting to a solute-rich liquid phase will cur at pressures and temperatures to the right of the cr DF; DF is the projection of a three-phase region in wl solid, liquid, and supercritical phases can coexist. Curve is shown with a negative slope, but in some systems it h positive slope and leans back toward the S-L line. The cr EF is a critical line above which the liquid phase and supercritical phase become identical and this ends in critical end point F.

The p-T projections of Fig. 1 give a simple view of three-dimensional p-T-x situation, but one should bea mind that there are surfaces emanating from and connect the lines in Fig. 1 which do not appear in the two-dimensi al picture. These surfaces are described to a limited exten the discussion below, associated with Fig. 2. However, s faces associated with the lines at the lower temperature of the diagrams, i.e., which connect with the curves AB not be covered, except for a comment made later about ret grade condensation. Although an understanding of the s faces at higher temperatures, which represent phase bo daries of importance to the present discussion, may obtained later from Fig. 2, a fuller description is given in next paragraph for the case of Fig. 1(a).

In Fig. 1(a) there is a three-phase (solid–liquid–g; surface perpendicular the line DF. There is also a surfa which above the temperature of C connects the solvent-r end of (close to) the diagram base, represented by OD m ing upwards in pressure and away from the solvent-r boundary. This is a supercritical fluid solubility surf; (surface 1). It connects with the three-phase surface, rep sented by DF (and in particular with the critical end po F), where it splits into two surfaces. One of these, at pr sures below F, folds over the critical line EF and conne with the liquid–gas line of the solute, DE. This surface rep sents liquid–gas equilibrium for the binary system (surf; 2). The other connects with the solute solid–liquid line, en nating from D (surface 3). This is a solid–gas or a solid–fl surface, depending on whether the pressure and temperatt are below or above the critical line EF, respectively.

Figure 1(b) is also for a type III system, but in this ca the solute is liquid over the whole temperature range show In this case the critical line which starts at E moves to high pressures. It can behave much as shown in the figure but c also behave differently. In some cases the line has a mii mum in pressure as it proceeds to lower temperatures. others it moves to higher temperatures and pressures. Fi ures 1(c), 1(d), and 1(e) are the p-T projections for sy tems of types II, IV, and V, respectively. They differ in for

:ause of the onset of immiscibility in either or both direc-
ns of temperature change in the subcritical region. The
1eral effect is that there is a critical line at higher pressures
:ending from the critical point of the pure solute to or
vard the critical point of the solvent.

The region of interest, in this review, for solubilities of
'olatile solutes in a supercritical fluid is limited in tem-
rature, pressure, and composition. The shaded areas in
;s. 1(a)–1(e) show the p-T projections of this region
1ematically for the various types of system. The lower
1perature limit is somewhat above the critical tempera-
e of the saturated solution; enough to avoid a two-phase
;ion of retrograde condensation which may be present at
;htly higher temperatures than this critical temperature.
r the solutes of low volatility the lower temperature limit
)f the order of 1 K above the critical temperature and few
ubility data are presented here at temperatures less than
} K. The upper temperature limit is a vague and pragmat-
)ne and is determined by factors such as the thermal sta-
ty of the solute and the solvating effect that can be
1ieved at reasonable pressures for industrial processes.
is temperature will be well below the critical temperature
he solute and where vapor pressure is low. For CO_2 this
1perature will usually be below 450 K. The lower pressure
it will not usually be far below the critical pressure for the
/ent (74 bars for CO_2) and so the vapor pressure curves
1g along the base of Figs. 1(a)–1(e) will not be of con-
1. At a temperature within the limits described, there
y or may not be a point on a critical line at higher pres-
:s. If there is, then the supercritical and fluid phases be-
1e identical, and solubilities in a supercritical fluid, for
purposes of this review, are no longer relevant. (See be-
for a further discussion of this statement.) The upper
;sure is therefore either a practical one or else the critical
in the temperature range, if it is present. Often data pub-
ed are well inside these schematic regions of interest. The
1position limits of the region of interest are that it is the
se boundary nearest to the pure solvent side of the p-T-x
;rams that is of concern.

Solubilities in a supercritical fluid are normally present-
s isotherms and functions of pressure. As such they form
: of the p-x cross sections of the p-T-x diagrams and are
)endicular to the projections of Fig. 1. A number of such
s sections, within the temperature range of interest, are
vn in Fig. 2. Figure 2(a) is a cross section at temperature
1n Fig. 1(a) and represents a common situation among
data presented here, where the solute is always a solid. In
ciple solids absorb the solvent, but this effect is normally
II in extent and the composition of the solid is shown
cident with the x = 1 axis. Similarly there is in principle
rve at very low pressures, representing the vapor of the
te in the presence of small amounts of the solvent, which
own coincident with the p = 0 axis. [Figures 2(b)–2(e)
1lso drawn in this way.] The only nontrivial feature of
diagram is the curve ST, which represents the supercriti-
:olubility of the solute in the region of interest. It is a
s section through what was described as surface 1 in the
1ssion of Fig. 1(a).
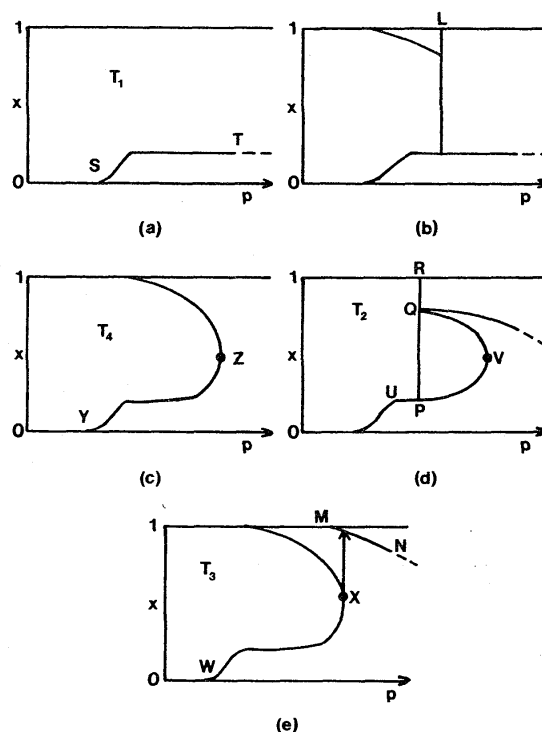
Various less common situations among the data in this

FIG. 2. x-T cross sections through schematic phase diagrams for mixtures of
carbon dioxide and a solute of low volatility.

review are shown in Figs. 2(b)–2(e). Figure 2(b) is a cross
section through a phase diagram of the type of Fig. 1(a), at a
temperature above D, but where the three-phase line DF has
a positive slope. The solute is liquid at low pressures, below
L, but becomes solid as the pressure increases. At pressures
below L, the lines are cross sections of the liquid–gas surface
(surface 2). At higher pressures, the line is a cross section of
the solid-supercritical fluid surface (surface 1), and the solu-
bility curve is similar to that in Fig. 2(a). For the purposes of
this review, the whole phase line near the solvent-rich axis,
which is similar in form to that of Fig. 2(a), is described as a
solubility in a supercritical fluid but the liquid-phase bound-
ary near the solute-rich axis is excluded.

Figure 2(c) is the simplest example of a cross section
where there is a point on the critical line at higher pressures.
It is a section at T_4 on Fig. 1(b), which is of type III with a
liquid solute. The curve YZ is described here as solubility in
a supercritical fluid, and this turns up toward the point on
the critical line, Z. At the higher pressures shown the solute
and solvent are miscible in all proportions. The curve contin-
uing on from Z gives the composition of the liquid-phase
boundary, formed by solution of CO_2 in the higher boiling
liquid and is excluded from the review. At very high pres-
sures, the liquid solute is likely to be solidified, and this
would result in a line, not shown, emanating from the solute-
rich axis, which would be a solid-supercritical fluid-phase
boundary. This type of supercritical fluid solubility is also
excluded from this review. Figure 2(c) is also the form of
cross sections of the phase diagrams represented in Figs.

1(c)–1(e), taken at any point in the temperature range of interest.

Other examples of cross sections intersecting with a critical line are given in Figs. 2(d) and 2(e). These correspond to temperatures T_2 and T_3, respectively, on Fig. 1(a) and involve solid phases. In Fig. 2(d), the solute is a solid at low pressures and then melts to a liquid phase at pressures corresponding to PQR of composition given by the line RV. The line UP is a cross section of the solid-supercritical fluid surface (surface 1). The line PV is the gas-phase boundary of cross section of the liquid-gas surface (surface 2). The full curve of solubility in a supercritical fluid covered by this review is the line UPV. The liquid-phase boundary QV and the line emanating from Q, which is a cross section of what was described earlier as surface 3, are not included in this discussion.

Figure 2(e) is a cross section at temperature T_3 on Fig. 1(a), which shows a situation similar to that for a liquid solute given in Fig. 2(c), except that the components are not miscible in all proportions above the critical line. Solid solute can be present above that of point M and will precipitate from liquids with solute compositions greater than those given by the line MN. Hence the supercritical phase composition will move with increasing pressure from W to the critical point X, when it will shift onto the curve MN as shown by the arrow. The curve MN is a cross section of what was described in the discussion of Fig. 1(a) as surface 3, which is not covered by this review, and so the curve of interest here is WX.

To summarize, the discussion above serves to define the boundaries of interest in this review. In particular some solid-supercritical fluid boundaries, such as MN in Fig. 2(e) and the line emanating from Q in Fig. 2(d), and also the liquid boundaries, such as QV in Fig. 2(d), are not included here. Some experimental measurements in the literature are concerned with these boundaries, however. One example is the body of measurements of the solubility of CO_2 in some hydrocarbons,[11] which corresponds to the solute-rich boundary curving upwards from point Z in Fig. 2(c). Another involves the part of the study of the critical end point [point F in Fig. 1(a)] in the CO_2–naphthalene system.[12] At 64.9 °C and above the pressure where a liquid phase is formed, the results obtained refer to the liquid phase, and are shown in brackets in the table of solubilities.

Finally, Fig. 3 shows the general features that may be exhibited by a curve of solubility in a supercritical fluid, given in terms of mole fraction, versus pressure at constant temperature. There is an initial fall at low pressures, AB, which starts at $x = 1$ and the solute vapor pressure, when no solvent is present. As the solvent is added and the solute is diluted without being much solvated, x falls toward B. This initial fall is at rather low pressures for solutes of low volatility, is shown coincident with the $p = 0$ axis in Fig. 2, and is not exhibited by the data covered in this review at the pressures at which they were obtained. The second feature is a rise in solubility BC, which is a feature of all the data presented. The rise is due to solvation arising from attractive forces between the solvent and solute molecules. It has a steep portion near the critical pressure of the solvent, where its den-
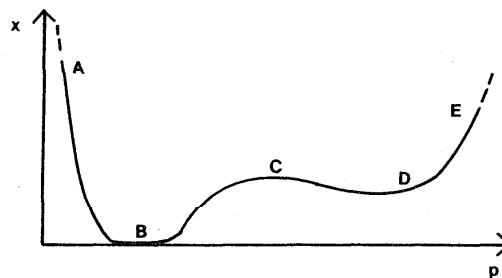

FIG. 3. Features which can occur in solubility isotherms.

sity is rising most rapidly. Thereafter the solubility may e hibit a fall, represented by CD. If this occurs, it is because higher pressures, where the solvent is becoming compress and repulsive solute–solvent interactions are becoming ir portant, and the solute chemical potential is raised to greater extent than is occurring in the liquid or solid pha: Finally a rise DE may occur if there is a critical line prese at high pressures at the temperature of the isotherm and t] solubility will rise toward it as shown in Figs. 2(c)–2(e Most solutes reviewed do not show this rise, but some d The most extreme example given here is decane, which known to have a type II phase diagram with CO_2.[10] T] squalene–CO_2 system has a type III phase diagram [Fi 2(b)], with a minimum in the critical line emanating from at 370 K and 370 bars.[10] Its higher temperature isotherr rise dramatically from around 300 bars, whereas at 323 a 328 K the isotherms do not show this rise and, in fact, fall pressure rises above 500 bars. It should also be noted th when the solute or solute-rich phase undergoes a pha change, as in Figs. 2(b), 2(d), and 2(e), there is no disco tinuity in the solubility-versus-pressure curve, as can be su ported by thermodynamic arguments.

1.4. Method Used for Correlation of Solubilities

Correlation of data exhibiting the features described the last paragraph is not straightforward. All the featur and those of the rest of the relevant phase diagrams can I reproduced qualitatively by an equation of state, and inde the forms of the phase diagrams were first studied using tl van der Waals equation.[13] For quantitative fitting more r fined equations of state are more useful in certain regior and of these the Peng–Robinson equation has been the mo widely used. However, even this equation is not successful fitting all the data presented here at all pressures and ter peratures and, moreover, the necessary parameters are n always available. This problem has been discussed in a rece paper by Johnston et al.[14] They come to the conclusion thal correlation of the so-called enhancement factor with densi is the best available route. The enhancement factor, E, is tl ratio of the partial vapor pressure of the solute in the supe critical phase to the vapor pressure of the pure solute at tl same temperature, p_v,

$$E = xp/p_v,$$

where x is the mole fraction of solute at saturation and p

ressure. It is thus a measure of the solvating effect and at pressures can be related to second virial coefficients.[4]

A correlation much used previously, an early example g in the analysis of experimental data by Tsekhans-ı,[15] is a linear relationship between the logarithm of the bility in concentration terms and density, ρ, i.e.,

$$\ln(x\rho) = a' + b'\rho, \qquad (2)$$

re a' and b' are constants at constant temperature. Equa-(2) was found not to fit the wide range of data presented well. The enhancement factor can be fitted to a similar tion of density, i.e.,

$$\ln(E) = a + b\rho, \qquad (3)$$

re a and b are also constants at constant temperature. ever, vapor pressures, needed to calculate E, are not vn or well known for many of the solutes, particularly olids. Substituting Eq. (1) into Eq. (3) gives

$$\ln(xp/p_{ref}) = A + B\rho; \qquad (4)$$

$$A = a + \ln(p_v/p_{ref}), \quad B = b, \qquad (5)$$

gain constants at constant temperature and p_{ref} is a refce pressure, for which 1 bar is used in all the calculations w.

The published solubility data were fitted to both Eqs. and (4) at each temperature, i.e., allowing the constants functions of temperature. The isotherms for each publi-

cation were treated separately. The density was assumed to be that of pure carbon dioxide, as the solubilities are low, and was obtained from the Ely equation of state.[16] Equation (4) was found to fit all the data reasonably well, except at lower pressures and gave a better fit, in general, than Eq. (2). It was therefore used to correlate the data presented in this review. However, to achieve the best fit possible, the minority of data for pressures below 100 bars were not included in the correlations. The values of A and B obtained from the fits

E 1. Constants a, b, and a'' for naphthalene and phenanthrene for rms published by various authors.

|	T (K)	a (bars)	$b \times 10^3$ $(m^3\ kg^{-1})$	a'' (bars)	Reference
thalene	308.0	2.392	8.00	7.992	15
		2.545	7.82	8.019	39
		2.030	8.50	7.980	12
		1.663	8.86	7.865	68
		2.046	8.45	7.961	84
	318.0	3.559	6.50	8.109	15
		3.873	6.07	8.122	57
	323.0	3.373	6.70	8.063	20
	328.0	2.903	7.50	8.153	12
		2.624	7.84	8.112	57
		2.762	7.59	8.075	20
		2.609	7.91	8.146	68
		2.957	7.41	8.144	15
	331.5	2.350	8.02	7.964	20
	333.4	2.391	8.50	8.341	12
	337.9	2.036	8.77	8.175	12
anthrene	308.0	4.237	9.95	11.202	39
	313.0	2.236	12.36	10.888	65
	313.1	6.933	6.39	11.406	27
	318.0	5.253	8.50	11.203	23
	323.0	4.651	8.89	10.874	56
	328.0	4.977	8.48	10.913	23
	338.0	4.835	8.18	10.561	23
	343.0	3.066	9.84	9.954	56
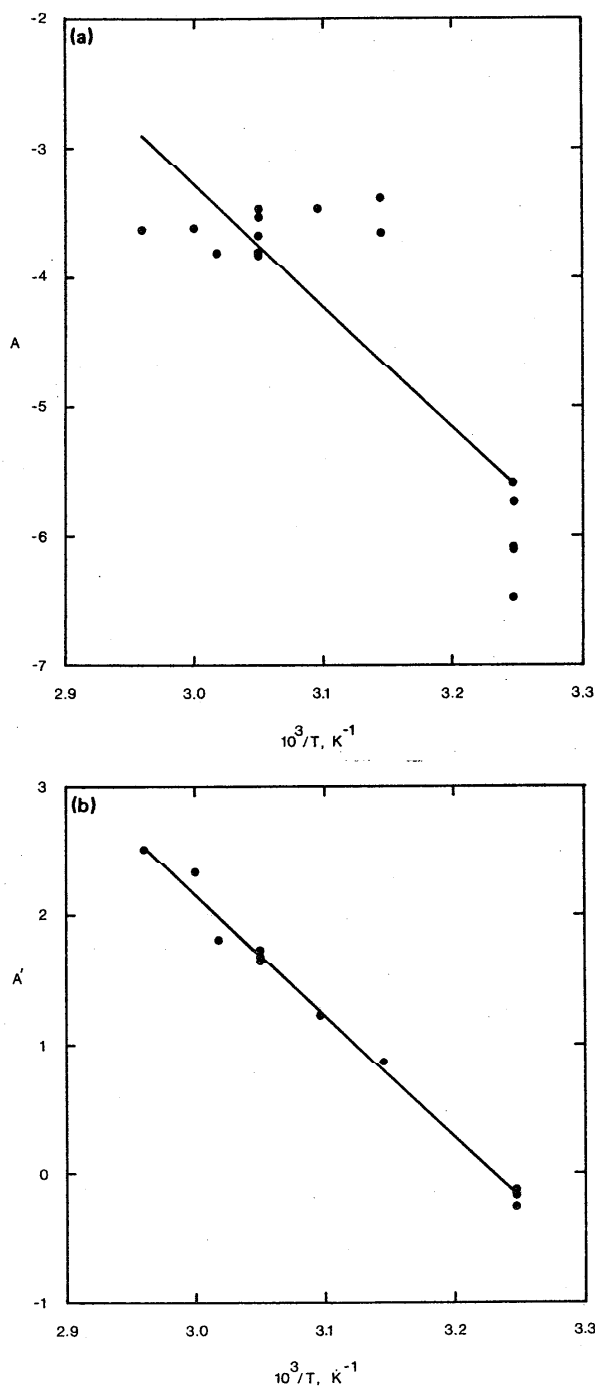
FIG. 4. Plots of the constants A and A' vs $1/T$ for naphthalene.

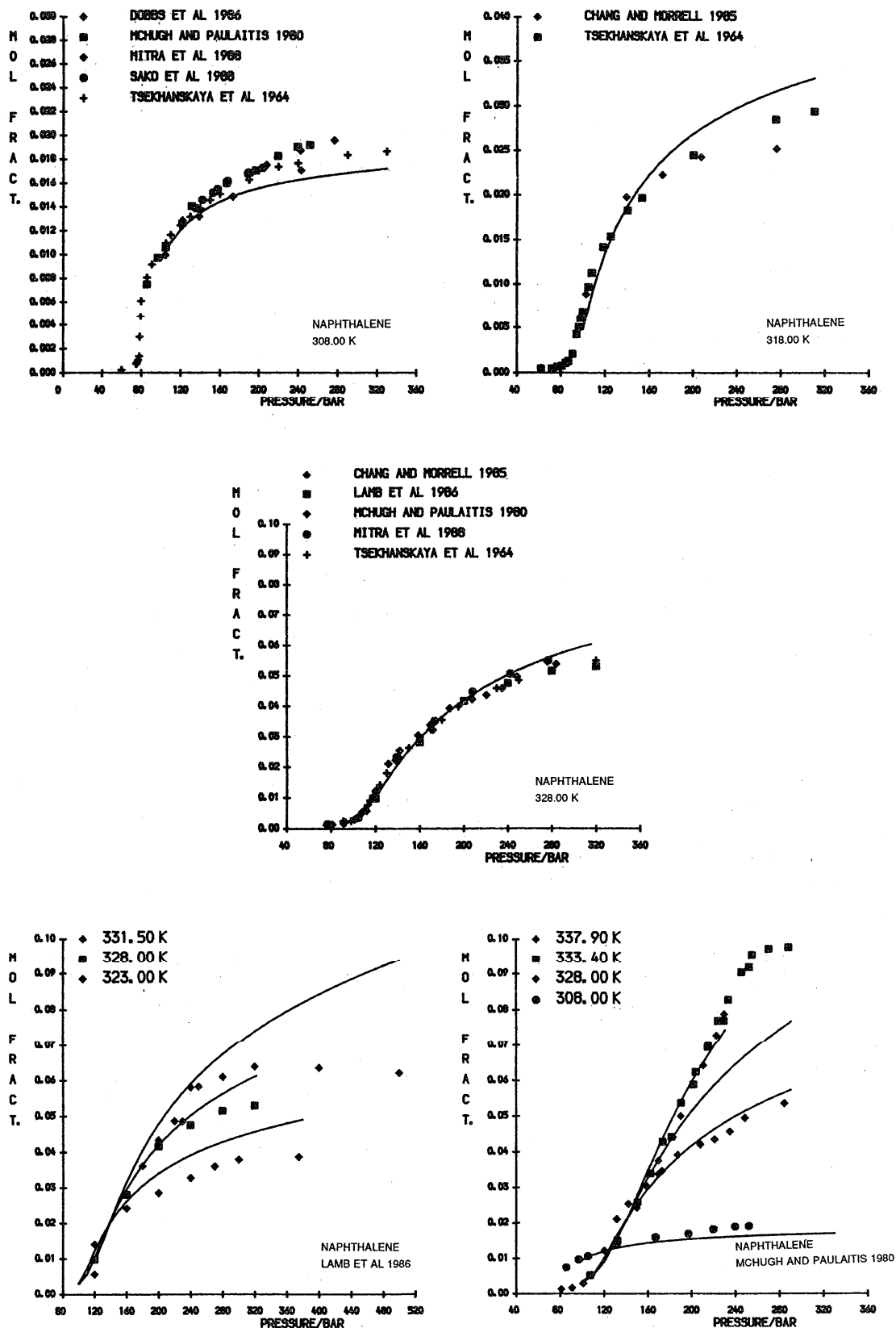# SOLUBILITIES OF COMPOUNDS IN SUPERCRITICAL CARBON DIOXIDE

FIG. 5. Comparison of the experimental results for naphthalene and the predictions, shown as curves, of an approximate estimation

are given in Table 4 below and calculated curves obtained from these values are shown on Fig. 7, the main plots of the data reviewed.

The separation of volatility and solvation effects implicit in the definition of the enhancement factor, gives rise to the hope that the constants a and b will not be very dependent on temperature. The variations obtained for $b = B$ can be observed for all the compounds reviewed by reference to Table 4. For naphthalene and phenanthrene, for which good vapor pressure data are available,[17,18] values of a and b, calculated from Eq. (5) for sets of data at different temperatures and published by different authors, are shown in Table 1. This table shows values of b going through a shallow minimum for both compounds and a variation of about $\pm 18\%$ for both compounds, although most values are well inside this range. The values of $b = B$ given in Table 4 show similar variation. Values of a, given in Table 1, show even wider variation. The reason for these variations is that the data above 100 bars cover a small density range above 700 kg m^{-3} at the lowest temperature and above 500 kg m^{-3} at the highest. In particular, a, which is the intercept at zero density, is vulnerable to error. It can be seen from Table 1 that high values of a correspond to low values of b and vice versa. Hence, rather than use an intercept at zero density, it is preferable to use a value at a reference density ρ_{ref}. In the calculations below a value of $\rho_{ref} = 700$ kg m^{-3} is used as this density is usually within the experimental data at all temperatures. In terms of the reference density,

$$\ln(E) = a'' + b(\rho - \rho_{ref}), \qquad (6)$$

where

$$a'' = a + b\rho_{ref}. \qquad (7)$$

Values of a'' are given in Table 1 and are seen to show a much smaller variation than the values of a and a small trend with temperature, upwards with temperature in the case of naphthalene and downwards for phenanthrene.

For most solutes good vapor pressure data are not available and a method of using the constants A and B is required for solubility estimations. From Eq. (5) and the presence of the term $\ln(p_v/p_{ref})$ in A, a plot of A vs $1/T$ might be expected to be a straight line. Figure 4(a) shows such a plot for naphthalene, for which there is the largest amount of experimental solubility data. It can be seen that the variation in the intercepts, as discussed for the constant a above, causes the plot to be unusably scattered. A quantity

$$A' = A + B\rho_{ref} \qquad (8)$$

is therefore defined so that

$$\ln(xp/p_{ref}) = A' + B(\rho - \rho_{ref}). \qquad (9)$$

A plot of A' vs $1/T$ is shown in Fig. 4(b) and is seen to be a satisfactory straight line for correlation purposes. The slope of this line corresponds to an enthalpy change of 77 mol^{-1}, compared with a value for the enthalpy of vaporization of solid naphthalene, ΔH_v^ϕ, of 70 kJ mol^{-1}.[19] The difference in the two values arises from the small temperature dependence of a, as described earlier.

A number of methods of predicting approximate values of solubilities from the constants A and B are suggested in the

next section. One of the cruder methods is now tested for naphthalene, again because of the amount of published data, although the particular method would not be the most suitable for naphthalene in practice. The same average value for B of 7.78 is used for all temperatures and values for A' are taken from the straight line on Fig. 4(b). The predicted curves are shown in Fig. 5 and compared with published data. The large majority of the data are within 10% of the predicted values, but differences of up to 30% are observed in some cases. The latter is true of the data of Lamb et al.,[20] especially at pressures above 300 bars, and also the data of McHugh and Paulaitis[12] at 333.4 K, which gave an a'' value in Table 1 out of the range of the other values and seems to follow the experimental data and predictions for 337.9 K, rather than the prediction for 333.4 K. The crude method shown therefore appears capable of giving estimates of solubility of sufficient quality for some industrial design purposes.

1.5. Estimation of Solubility Using the Correlations

For a solute for which a large amount of solubility data has been published, and for which critical parameters, vapor pressure data, and hence an acentric factor is available, the best method for prediction of solubility at any pressure and temperature would be to correlate the data using an equation of state with adjustable parameter(s) in the temperature–pressure region of interest. Failing the necessary information, or the will to carry out the correlation, less accurate estimates of the solubility of the compounds covered in this review may be made using the A and B values given in Table 4. The pressure and temperature ranges in which this would generally be appropriate are 100–350 bars and 308–373 K.

The procedures suggested for calculating the solubility in carbon dioxide of one of the solutes listed in Table 4 at a particular temperature and pressure are as follows.

(1) The density of carbon dioxide is calculated from one of the established equations of state, preferably that of Ely,[16] although outside the critical region, predictions from different good equations are close.

(2) If the temperature of interest is within 2 K of that of a pair of values of A and B given in Table 4, then those A and B values are used, with the density at the required temperature and pressure, in Eq. (4) to obtain the solubility. If not, procedures (3)–(5) are followed.

(3) A value of B appropriate for the temperature of interest is obtained from the data in Table 4. In some cases, if there are a number of values, this is done by plotting B against temperature followed by interpolation or limited extrapolation to obtain B at the desired temperature. In other cases, it is assumed that B is constant with temperature and a single or average value used.

(4) A value of A' is obtained from the data in Table 4 by one of two methods.

(a) If reliable vapor pressures are available, calculation of the constants a from Eq. (5) is carried out. Then, using Eq. (7) and the fact that $b = B$, values of a'' are calculated. Again, if there are a number of values, plotting against temperature and interpolation or limited extrapolation is carried out to obtain a'' at the desired temperature. In

other cases a single or average value of a'' would be used. An A' value would then be obtained from $A' = a''$ $+ \ln (p_v/p_{ref})$.

(b) If vapor pressure data are not available, the available (one or more) A values are converted to A' values using Eq. (8). These are then plotted against $1/T$. If there are sufficient points of good quality a straight line is fitted to them and a value of A' read off at the desired temperature. If not, a straight line of slope $-\Delta H_v^{\phi}/R$ is drawn through the point or points, and a value of A' read off at the desired temperature.

(5) Finally, Eq. (9) would be used to obtain the solubility.

Since the errors in A and B are correlated, it is essential that both values of a pair should be used in the procedure chosen.

The reliability of the procedures outlined above obviously depends on how much information on A and B is available for the solute, how close the temperature and pressure of interest is to the experimental solubilities used to obtain the A and B values, and which procedure it is necessary to use. If very close, predictions will be similar in quality to the correlation curves given in Fig. 7. If not, the reliability of the predicted values will depend on the temperature difference and the procedure that has to be used, and in the worst cases will only be a guide to the true solubility. An estimate of the probable error would need to be made and based on the procedure and data in each case. It may need to be repeated that predictions would not be very reliable below 100 bars and in the critical region.

2. Experimental Methods

The various experimental methods used to obtain supercritical fluid solubilities can be classified in two different ways. The first relates to the way in which the saturated solution is obtained, which can be static or dynamic, i.e., in a closed cell or in a flow system. The second classification describes how this solution is analyzed and the methods used can be grouped into four categories: gravimetric, spectrometric, chromatographic, and miscellaneous. There is some correspondence between these two classifications. To produce enough material for accurate gravimetric analysis, a flow system is normally used. The two other techniques can use either, but a static system is typically used with spectroscopic analysis. The classification used in the description of experimental methods below is primarily in terms of the analytical method. A review of experimental methods for supercritical solubilities has appeared in a recent textbook.[2]

Of the techniques described, the gravimetric method is most widely used, with a few research groups, having established a particular procedure and given data in one publication, following this up with subsequent publications using essentially the same apparatus. Chromatographic analysis is the second most popular technique. Other methods tend to be limited to a single paper, describing the development of the experimental procedure and giving a body of data so obtained. A fair assessment of the present situation is there-

to a lesser extent chromatographic analysis are the prese established and reliable procedures. The other methods a attempts to find alternatives, but none of these have yet be generally accepted as being superior. Spectroscopic tec niques offer more convenience, with *in situ* analysis, but he the effect of the supercritical fluid on the absorption prope ties complicates the procedures.

2.1. Gravimetric Methods

Most of the gravimetric methods used have the sar basic structure. The main motivation has been the need 1 solubility data for extraction processes and the philosophy the methods reflect this interest. Briefly, these methods : volve the production of a saturated solution by passing t supercritical fluid over the solute in an extraction cell, dr ping the pressure to precipitate the solute, and weighing The experimental procedures were developed by Ecke Paulaitis, Reid, and their co-workers in the late 1970s.[21-

A schematic diagram of the basic system is shown Fig. 6. The CO_2 is pumped, as a gas by a compressor or a liquid by a pump with a cooled head into a thermostat, wh it first passes through a preheating coil. It then passes into extraction or equilibrium cell where a saturated solutior formed. The solute is usually dispersed in the cells, e.g., coating it onto sand particles, and filters are positioned at t ends of the cells to prevent the entrainment of undissolv solute. The solution is then dropped to atmospheric pressi via a restrictor or valve, such as a back-regulator, whicl heated to prevent the solute being lost in the valve and cl ging it. The gas containing finely divided solute precipita passes to a trapping system, which can vary in type (e.g., tubes are often used), or complexity (e.g., switching circt between traps are sometimes described). More than one t in series is often used and methods for ensuring compl trapping, such as cooling and/or packing with absorbe are typically employed. Finally The CO_2 passes throt some kind of flow meter. The pressure in the system, i.e., t of the experiment and the flow rate are controlled by pump and the valve. In the most straightforward systen back-pressure regulator would control the pressure and pump the flow rate. Various systems are used, however, a are described in the many original papers, which are refer to in Table 2.

A typical experiment is to set the flow and allow system to reach a steady state and then switch in a weigl
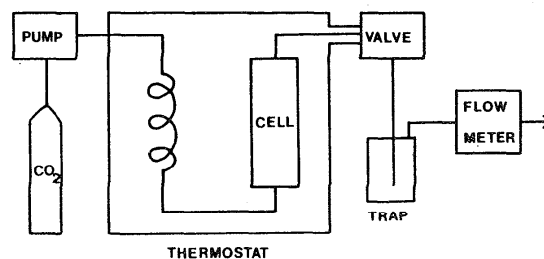
hod	Compound	T(K)	P(Atm)	Reference
vimetric	acridine	308	118–345	63
vimetric	acridine	308–343	101–359	59
ɔtrometric	adamantane	340–400	99–987	50
vimetric	alachlor	323–393	88–272	81
vimetric	2-aminobenzoic acid	308	118–345	63
vimetric	2-aminofluorene	318–343	114–359	59
vimetric	5-aminoindole	308	82–185	41
vimetric	anthracene	313	99–197	27
vimetric	anthracene	303–343	91–414	56
vimetric	anthracene	293–368	68–1141	49
vimetric	anthracene	308–318	103–273	31
omatographic	anthracene	308	118–345	62
ɔtrometric	anthracene	294–473	51–888	85
omatographic	artabsin	313	69–188	36
ɔtrometric	behenic acid	313–333	80–250	43
ɔtrometric	behenyl behenate	313–333	100–250	43
omatographic	benzo(e) pyrene	318–398	83–124	46
omatographic	benzoic acid	313	79–395	35
vimetric	benzoic acid	318–338	118–276	23
vimetric	benzoic acid	318–343	100–359	59
vimetric	benzoic acid	308	118–276	63
vimetric	biphenyl	309–330	104–484	12
vimetric	biphenyl	328	503–531	71
vimetric	brassylic acid	328–343	148–359	67
ɔtrometric	cafestol	313–353	80–250	43
ɔtrometric	caffeine	328–433	50–250	60
vimetric	canola oil	298–363	100–360	70
vimetric	carbazole	313	99–197	27
ɔmatographic	carbowax 1000	313	270–1900	53
ɔmatographic	carbowax 4000	313	270–1900	53
vimetric	p-chlorophenol	309	80–237	22
ɔtrometric	cholesterol	313–353	80–200	43
vimetric	codeine	291–313	59–197	64
vimetric	corn germ oil	353	265	77
vimetric	cottonseed oil	313–353	476–1020	77
ɔtrometric	decane	340–400	99–197	50
vimetric	1,10-decanediol	318–328	131–303	58
ɔmatographic	dexynivalenol	365–398	165–194	46
ɔmatographic	diacetoxyscirpenol	335–365	121–123	46
vimetric	dibenzothiophene	309–338	76–273	68
vimetric	3,4-dichloroaniline	313	197	40
vimetric	2,4-dichlorophenol	309	79–203	22
vimetric	(2,4-dichlorophenoxy acetic acid)	313	197	40
vimetric	2- (4- (2,4-dichlorophenoxy) -phenoxy) propanoic acid	313	197	40
vimetric	2- (4- (2,4-dichlorophenoxy) -phenoxy) propanoic acid methyl ether	313	197	40
vimetric	di-n-dodecylamine	310–320	108–202	67
vimetric	didodecylphosphine	320	125–149	67
vimetric	didodecylthioether	310–320	108–198	67
vimetric	m-dihydroxybenzene	328	306	72
vimetric	o-dihydroxybenzene	328	306	72
vimetric	p-dihydroxybenzene	328	306	72
vimetric	2,3-dimethylnaphthalene	308–328	98–276	23
vimetric	2,3-dimethylnaphthalene	308	98–276	26
vimetric	2,6-dimethylnaphthalene	308–328	95–276	23
vimetric	dioctyl ether	320	106–131	67
vimetric	diphenylamine	305–310	40–206	55
vimetric	docosane	310–320	117–186	67
vimetric	n-dotriacontane	308	91–159	82
vimetric	eicosane	310–320	110–276	67
ɔmatographic	ergosterol	313	79–198	74
ɔmatographic	estradiol	313	79–198	74
ɔmatographic	ethinylestradiol	313	79–198	74
ɔmatographic	eugenol	280–333	20–79	36
vimetric	fluorene	313	99–197	27
vimetric	glycerol trioleate	298–333	69–197	83
vimetric	hexachloroethane	308–328	96–276	23

TABLE 2. Published solubility data in carbon dioxide—Continued

Method	Compound	$T(K)$	$P(Atm)$	Reference
Gravimetric	1-hexadecanol	318–338	142–416	69
Gravimetric	hexamethylbenzene	303–343	70–483	56
Chromatographic	hexamethylbenzene	308	148–345	39
Gravimetric	m-hydroxybenzoic acid	373	204–409	72
Gravimetric	o-hydroxybenzoic acid	373	204–409	72
Gravimetric	p-hydroxybenzoic acid	373	204–409	72
Gravimetric	5-hydroxyindole	308	88–185	41
Gravimetric	indole-3-aldehyde	308	79–159	41
Chromatographic	jojoba oil	293–353	99–2568	75
Gravimetric	indole-3-carboxylic acid	308	91–194	41
Gravimetric	lauric acid	313	77–248	34
Chromatographic	limonene	280–323	25–60	36
Gravimetric	linuron	313	197	40
Gravimetric	methoxychlor	313	197	40
Gravimetric	5-methoxyindole	308	79–184	42
Gravimetric	methoxy-1-tetralone	308	82–273	57
Chromatographic	1-methylnaphthalene	308	30–80	47
Gravimetric	methyl nitrobenzoate	308	82–274	57
Gravimetric	monocrotaline	308–328	89–274	33
Gravimetric	mono-olein	308–333	102–187	82
Gravimetric	morphine	291–313	59–197	64
Gravimetric	myristic acid	313	82–249	34
Gravimetric	myristic acid	313–323	200	73
Gravimetric	naphthalene	307–318	40–206	55
Gravimetric	naphthalene	308–328	60–330	15
Gravimetric	naphthalene	308–338	81–288	12
Gravimetric	naphthalene	328	123–250	23
Gravimetric	naphthalene	308	99–173	27
Gravimetric	naphthalene	318–328	82–272	57
Gravimetric	naphthalene	309–328	74–273	68
Gravimetric	naphthalene	308	80–124	82
Gravimetric	naphthalene	308	120–201	84
Spectrometric	naphthalene	297–346	1–130	61
Spectrometric	naphthalene	323–328	118–493	20
Chromatographic	naphthalene	308	30–80	47
Chromatographic	naphthalene	313	69–395	35
Chromatographic	naphthalene	308	120–240	39
Gravimetric	α-naphthol	308–328	91–170	32
Gravimetric	β-naphthol	308–328	91–170	32
Gravimetric	β-naphthol	308–343	102–359	59
Gravimetric	β-naphthol	308	118–345	63
Chromatographic	β-naphthol	313	89–395	35
Gravimetric	naphthoquinone	318–343	100–359	59
Gravimetric	nonadecane	310–320	109–201	67
Gravimetric	nonadecanenitrile	320	109–200	67
Gravimetric	2-nonadecanone	320	109–141	67
Gravimetric	noscapine	291–313	59–197	64
Spectrometric	octacosane	320–360	99–987	50
Gravimetric	octacosane	308–325	81–322	30
Gravimetric	octadecane	310–320	118–198	67
Gravimetric	1-octadecanol	310–320	109–275	67
Chromatographic	1-octadecanol	313	270–1900	53
Gravimetric	octadecylmercaptan	310–320	109–201	67
Gravimetric	oleic acid	313–333	200–300	73
Gravimetric	oleic acid	308–333	84–189	82
Spectrometric	oleic acid	313–333	100–250	43
Gravimetric	oxindole	308	85–189	41
Gravimetric	palmitic acid	318–338	142–575	69
Gravimetric	palmitic acid	313	80–248	34
Gravimetric	palmitic acid	298–313	80–187	24
Gravimetric	palmitic acid	308–323	200–300	73
Spectrometric	palmityl behenate	313–333	100–250	43
Gravimetric	papaverine	291–313	59–197	64
Gravimetric	phenanthrene	318–338	118–276	23
Gravimetric	phenanthrene	313	99–197	27
Gravimetric	phenanthrene	303–343	81–414	56
Gravimetric	phenanthrene	313	136–544	65
Chromatographic	phenanthrene	308	99–345	39
Chromatographic	phenanthrene	313	79–395	35
Chromatographic	phenol	313	69–395	35

Method	Compound	T(K)	P(Atm)	Reference
ravimetric	phenol	309–333	78–246	22
hromatographic	phenol blue	308	101–300	66
ravimetric	phthalic anhydride	308	118–345	63
ravimetric	polychlorinated biphenyl	373	117–265	81
ravimetric	pyrene	308–343	84–483	56
hromatographic	pyrene	318–398	8–70	46
hromatographic	pyrene	313	89–395	35
ravimetric	rapeseed oil	313–353	100–850	79
ravimetric	silicone oil	373	156–245	81
hromatographic	sitosterol	313	79–198	74
hromatographic	sitosterol	293–353	99–988	75
ravimetric	skatole	308	75–190	42
hromatographic	solasodin	313	79–198	74
hromatographic	soybean oil	298–353	99–2568	36
hromatographic	soybean oil	293–313	148–346	76
ravimetric	soybean oil	313–343	207–689	77
ravimetric	soybean oil	323–333	136–681	78
ravimetric	stearic acid	310–320	112–359	67
ravimetric	stearic acid	313–333	200–300	73
pectrometric	stearic acid	313–333	100–250	43
hromatographic	stearic acid	313	270–1900	53
pectrometric	squalane	320–385	99–987	50
ravimetric	squalane	310–320	109–229	67
hromatographic	sunflower seed oil	313	178–691	76
ravimetric	tetracosane	310–320	108–257	67
ravimetric	thebaine	291–313	59–197	64
hromatographic	thujone	313	49–89	36
ravimetric	titanium tetrachloride	298–388	0–136	25
ravimetric	α-tocopherol	298–313	100–183	24
pectrometric	α-tocopherol	313–353	100–250	43
hromatographic	t-2 toxin	335–365	118–155	46
pectrometric	tributyrin	313–333	100–250	43
ravimetric	trihexylamine	310–320	110–153	67
ravimetric	trilaurin	313	91–253	34
pectrometric	trilinolein	313–333	80–250	43
ravimetric	trimyristin	313	95–304	34
ravimetric	trioctylamine	320	109–232	67
ravimetric	trioctylphosphine	320	109–251	67
ravimetric	trioctylphosphine oxide	310–320	109–200	67
ravimetric	triolein	313–333	200–300	73
pectrometric	triolein	313–353	80–250	43
pectrometric	tripalmitin	313–353	80–250	43
ravimetric	tripalmitin	313	122–297	34
ravimetric	tripalmitin	298–313	86–182	24
ravimetric	triphenylamine	310–320	108–201	67
ravimetric	triphenylmethane	303–323	70–414	56
ravimetric	triphenylphosphate	310–320	112–281	67
ravimetric	triphenylphosphine	310–320	109–277	67
ravimetric	tristearin	313–333	200–300	73
pectrometric	tristearin	313–333	80–250	43
ravimetric	vegetable oil	293–328	160–480	81
pectrometric	water	313–353	100–250	43
hromatographic	water	323–348	50–500	45
ravimetric	water	298–348	1–700	80

rap or traps for a measured period, during which the rate of ow of CO_2 is monitored. After reweighing the trap(s) and alculating the total mass of CO_2 passing in the period, the olubility is obtained directly in terms of mole fraction. Jsually the errors in the experiment are quoted as 3%–5% or all the solubilities. It is likely, however, that the lower olubilities for any isotherm will be less accurate than the igher ones, because of less efficient trapping and perhaps the smaller solute weights. Sometimes errors are quoted as being an absolute mole fraction.

An important consideration in the use of this method is that equilibrium has been reached in the extraction cell and different ways are used to ensure and check this, including the following: varying the flow rate;[22,23] using more than one extraction cell;[22] varying the distribution of the solute in the extraction cell;[23] recycling;[24] and saturating at a lower tem-

perature, where the solubility is higher, before equilibrating at the required temperature.[25] The other important test is that all the precipitated solute has been collected after depressurizing. This can be done by using two or more successive traps and weighing both to show that the great majority of solute is collected in the first trap.[23] Problems can arise with precipitation inside the pressure-reducing valve, which can be overcome by washing out the valve after an experiment.[26]

The amount of solute can also be determined in a flow system by observing its loss of weight in the extraction cell.[27] To ensure equilibrium, the extraction cell is in sections, and the experiment is conducted so that the latter sections do not lose weight. Although flow systems are most often used with the gravimetric method, there are some cases of static systems being used. Tsekhanskaya[15] in one of the earliest studies of supercritical solubility, measured the loss in weight of a pellet of naphthalene after it had been equilibrated with a supercritical fluid in a static cell. It is also possible to use a traditional phase-equilibrium view cell to measure supercritical solubilities. A weighed amount of solute is put into the cell, the solvent added in known amounts and the pressure varied at constant temperature to find the point at which solution and precipitation occurs.[28-30] Some solubility data have been obtained by this method, but it is mainly used for a more comprehensive study of the solute–solvent phase diagram.

2.2. Chromatographic Methods

Most chromatographic methods used are modifications of the gravimetric method shown in Fig. 6. In one type of modification, the solute is precipitated as before in a trap, perhaps containing a solvent. The solute is then washed out of the trap, made up to volume, and analyzed by any suitable chromatographic method. In some cases the solute is precipitated directly onto a chromatographic plate. Gas chromatography (GC),[31-34] thin layer chromatography (TLC),[35,36] and high performance liquid chromatography (HPLC),[37] including size exclusion chromatography (SEC sometimes called GPC)[38] are used. After calibration and analysis, followed by calculation of the mass of CO_2 passing during the sampling period as before, the method gives solubilities in terms of mole fraction directly. Accuracy comparable with the gravimetric method has been obtained, but some variants of the method, e.g., using direct precipitation onto a TLC plate, are intended only to give a rough indication of solubilities.

A second type of modification of the apparatus of Fig. 6 for chromatographic analysis, consists of removing the trap and flow meter and inserting a sampling valve between the extraction cell and the valve or back-pressure regulator. This is commonly a multiport chromatographic sampling valve, with a sample loop. Using this device a fixed volume of the saturated solution is sampled and injected directly into a chromatograph (or, alternatively, let down to atmospheric pressure, the solute dissolved in a solvent, and then injected into a chromatograph) and analysis carried out by GC,[30,12,39] an HPLC,[40] or supercritical fluid chromatography (SFC).[41,42] Because only small samples are needed, the

extraction section of the apparatus can be small scale and commercially available supercritical fluid extraction (Sl systems designed for analytical applications,[39] or eve small static system,[43] can be used. The apparatus is calil ted by loading a liquid solution of the same solute of knc concentration into the same sample loop. The solubility sults are obtained directly in terms of concentration rat than mole fraction. Careful use of this method can also ﹛ results of accuracy comparable with the gravimetric m﹛ od.

A third and very different type of chromatograp method arises from the fact that it can be shown experim tally that under some circumstances chromatographic ret tion in SFC is inversely proportional to solubility.[44] A nt ber of methods are available for obtaining proportionality coefficient and the method could be a ra way of obtaining data of less, but still acceptable accura Some data of a qualitative and untabulated type had b﹛ published by the end of 1989.[45-47]

2.3. Spectrometric Methods

Spectroscopic analysis can also be used following a fl system and precipitation by dissolving the solute in a suita solvent and making photometric measurements on the so tion after calibration with standard solutions.[48] This meth would seem to be a reliable one, although no tabulated d﹛ on pure compounds have been published.

A more convenient technique is to make absorpti measurements in the UV or infrared directly in a high-pr﹛ sure static equilibrium cell, but in this case a number of prc lems arise. These include (a) the variation in band sha with the supercritical fluid pressure, (b) variation of in grated absorption intensity of an absorption band with t nature and pressure of the solvent, and (c) adsorption solute on the cell windows from the saturated solution These problems can be addressed, respectively, by (a) me suring the integrated absorption intensity of a band,[50] (1 measuring the integrated intensities of nonsaturated sol tions of known composition in the supercritical fluid,[50] a (c) varying the optical path length.[49] Not all these probler are properly treated in all publications, and in several cas extinction coefficients measured in liquids have been us﹛ incorrectly to obtain concentrations from absorption coef cients in a supercritical fluid. Pulsed NMR measuremen have been made on naphthalene/CO_2 solutions as part of wider study of the phase diagram, and solubility results co﹛ sistent with previous measurements were obtained.[20]

2.4. Miscellaneous Methods

The following four methods, which do not fit into tl above categories, have been described. Naphthalene h﹛ been precipitated as the picrate from solution after trappin and the latter determined gravimetrically.[51] The remainin three methods give solubilities reported graphically rathe than numerically. A radioactive tracer technique has bee used in a static system.[52] Fatty acids have been analyzed b titration after extraction and trapping in a flow system,[48] an the effluent gas and precipitated solute from a flow system

roduced after dropping the pressure, has been analyzed us-
ng a flame ionization detector.[53]

1. Review and Correlation of Published Experimental Results

References to solubilities of single involatile substances
n carbon dioxide published up to the end of 1989 are listed in
Table 2. The temperature and pressure ranges and the cate-
ory of the experimental method are given. Data given for
ure substances in a tabulated form in the original publica-
ions are plotted in the many graphs of Fig. 7. An alphabeti-
al index to the graphs is given in Table 3. Data are plotted in
erms of the mole fraction at saturation. Most published data
re in this form. Where data have been published as concen-
rations (per unit volume) the data have been converted to
nole fractions using the Ely equation of state for pure carbon
ioxide.[16] Table 5 contains some densities for CO_2 in moles
m^{-3}, calculated from the Ely equation, for convenient ap-
roximate conversion of data from the graphs into concen-
ration units.

The data have been correlated by fitting the data to Eq.
4) at each temperature, and from each publication, using
nweighted least-squares, using the Ely equation of state for
ure carbon dioxide to obtain the density. However, data
elow 100 bars were not included in the fitting procedure.
'he constants A and B thus obtained are listed in Table 4. In
ne minority of cases where there is more than one source of
ata, a decision was made that one A–B pair is superior and
nis is indicated by an asterisk on the A value. This decision
vas made on the basis of the experimental method or, failing
nat, on the goodness of fit of the correlation. These con-
ants may be used to obtain solubilities for the compounds
t other pressures and temperatures using the procedures
utlined in Sec. 1.5. The curves calculated from these con-
ants and Eq. (4) are shown on the graphs in Fig. 7, using
ne values marked by an asterisk where there is more than
ne A–B pair.

The majority of published tabulated data were obtained
either by a gravimetric method or by using a flow system
followed by gas chromatography. Estimates of errors made
by the authors for these data are in the 3%–5% range.
Agreement between different workers and study of the scat-
ter of the data using Eqs. (2) and (4), the Peng–Robinson
equation of state,[54] and the relationship to chromatographic
retention,[44] indicates that this claim is justified in general.
These studies do, however, expose the fact that occasional
data points lie outside this error band, and are up to 10%–
15% in error, and this can be observed in Fig. 7 for particular
cases. In addition, some of the lower (i.e., low-pressure)
solubilities in a set of data are likely to be subject to larger
errors in percentage terms than those quoted, because the
trapping and analysis of smaller quantities in a gas stream is
more difficult. This is sometimes, but not always, stated by
the authors. The extent of this problem is difficult to assess
from the original papers, when it is not discussed. It can only
be said that the low values in a data set should be treated at
first with more caution.

In general, data from other methods are less reliable
and this is especially the case for spectroscopic methods us-
ing a high-pressure cell, where unreliable extinction coeffi-
cients are used to obtain concentrations. The effect of this
can be seen in the plots of the reviewed data in Fig. 7, where
some values obtained by spectroscopic techniques differ
markedly from those obtained gravimetrically, for example.
Before spectroscopic values are used therefore, the precise
method should be studied in the original paper and a com-
parison of the data made with those obtained by other meth-
ods, if available, in Fig. 7. Also, in general, data obtained
spectroscopically or by one of the miscellaneous methods,
are presentated graphically and no estimates of error given.
Exceptions, where the data are more reliable and have prob-
able errors approaching those of the gravimetric methods,
are the precipitation of naphthalene as a picrate,[51] infrared
studies on hydrocarbons,[50] pulsed NMR studies on naph-
thalene,[20] and some HPLC and SFC studies.[40-42]

TABLE 3. Alphabetical index to the compounds in Fig. 7.

Compound	Figure(s)	Compound	Figure(s)
Acridine	7.15–7.18	Monocrotaline	7.107
Adamantane	7.61	Mono-olein	7.125
2-Aminobenzoic acid	7.95	Myristic acid	7.98
2-Aminofluorene	7.31	Naphthalene	7.4–7.8
5-Aminoindole	7.85	α-Naphthol	7.34
Anthracene	7.9–7.14	β-Naphthol	7.35–7.38
	7.127–7.130		
Behenic acid	7.96	Naphthoquinone	7.33
Benzoic acid	7.117–7.121	Nonadecane	7.75
Biphenyl	7.116	Nonadecanenitrile	7.68
Brassylic acid	7.78	2-Nonadecanone	7.77
Carbazole	7.19	Octacosane	7.59,7.111
p-Chlorophenol	7.49	Octadecane	7.66
Cholesterol	7.108	1-Octadecanol	7.63
Decane	7.60	Octadecylmercaptan	7.67
1,10-Decanediol	7.52	Oleic acid	7.99,7.122
			7.123
Dibenzothiophene	7.20	Oxindole	7.86
2,4-Dichlorophenol	7.50	Palmitic acid	7.100–7.102
Di-N-Dodecylamine	7.53	Phenanthrene	7.23–7.27
Didodecylphosphine	7.71	Phenol	7.47
Didodecylthioether	7.70	Phenol blue	7.48
2,3-Dimethylnaphthalene	7.30,7.32	Phthalic anhydride	7.55
2,6-Dimethylnaphthalene	7.29	Pyrene	7.28
Dioctylether	7.73	Skatole	7.109
Diphenylamine	7.51	Squalane	7.58,7.62
Docosane	7.64	Stearic acid	7.103–7.104
n-Dotriacontane	7.124	Tetracosane	7.65
Eicosane	7.76	Titanium tetrachloride	7.126
Fluorene	7.21–7.22	α-Tocopherol	7.105–7.106
Hexachloroethane	7.112	Tributyrin	7.87
1-Hexadecanol	7.54	Trihexylamine	7.57
Hexamethylbenzene	7.45–7.46	Trilaurin	7.88
5-Hydroxyindole	7.81	Trimyristin	7.89
m-Hydroxybenzoic acid	7.114	Trioctylamine	7.72
o-Hydroxybenzoic acid	7.113	Trioctylphosphine	7.74
p-Hydroxybenzoic acid	7.115	Trioctylphosphine oxide	7.110
Indole-3-aldehyde	7.82	Triolein	7.94
Indole-3-carboxylic acid	7.83	Tripalmitin	7.90–7.92
Lauric acid	7.97	Triphenylamine	7.79
5-Methoxyindole	7.84	Triphenylmethane	7.56
5-Methoxy-1-tetralone	7.44	Triphenylphosphate	7.80
6-Methoxy-1-tetralone	7.43	Triphenylphosphine	7.69
7-Methoxy-1-tetralone	7.42	Tristearin	7.93
Methyl-m-nitrobenzoate	7.40	Water	7.1–7.3
Methyl-o-nitrobenzoate	7.39		
Methyl-p-nitrobenzoate	7.41		

7.1
WATER
WIEBE AND GADDY 1941

◆ 348.00 K
■ 323.00 K
◆ 304.00 K

MOLE FRACT.

PRESSURE/BAR

7.2
WATER
CHRASTIL 1982

◆ 353.00 K
■ 323.00 K

MOLE FRACT.

PRESSURE/BAR

7.3
WATER
323.00 K

◆ WIEBE AND GADDY 1941
■ CHRASTIL 1982

MOLE FRACT.

PRESSURE/BAR
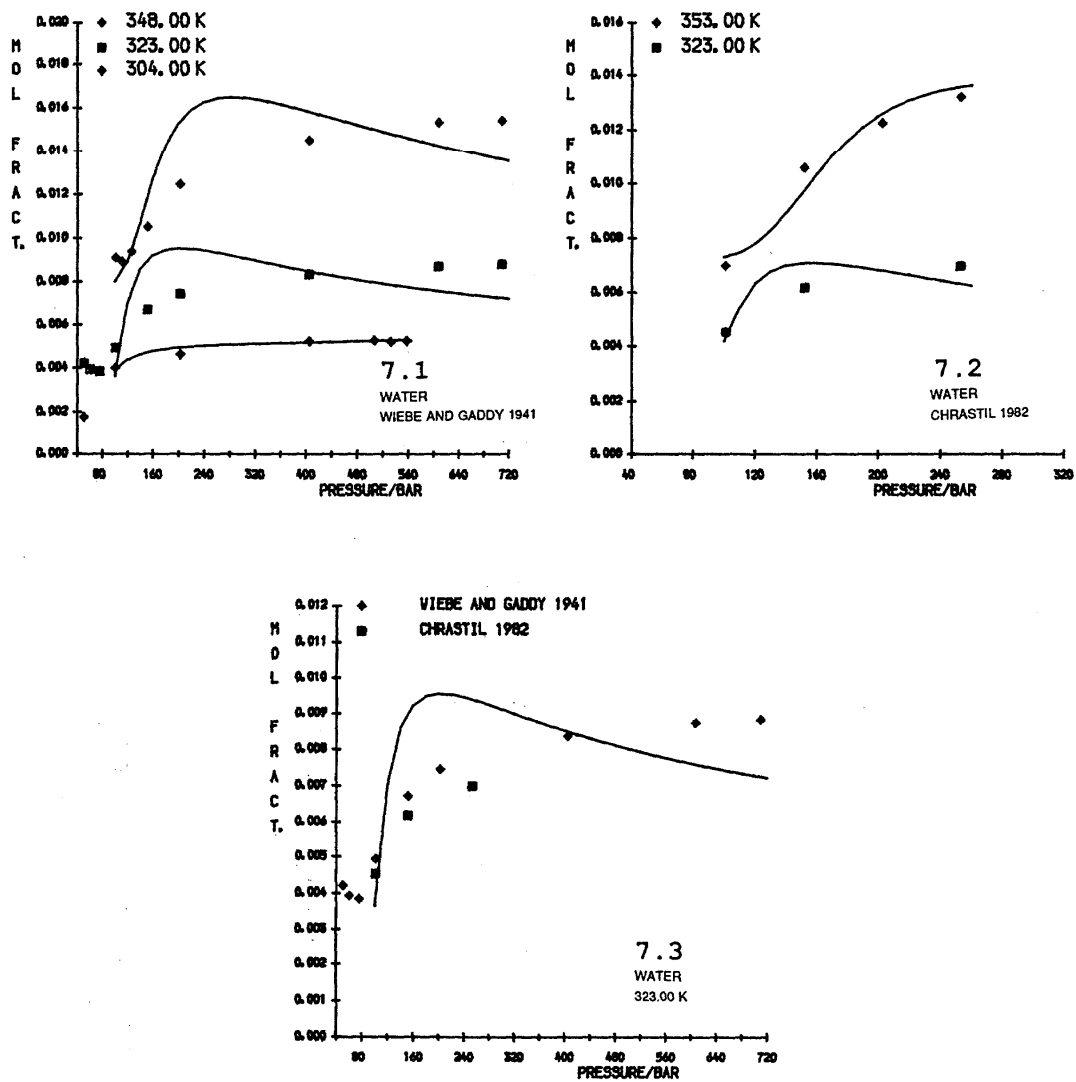
FIG. 7. Published tabulated data for solubilities in carbon dioxide, shown as points, and curves obtained by fitting an isotherm to Eq. (4). The constants used for the correlation curves shown are given in Table 5. An alphabetical index to the compounds in the figure is given in Table 3.

FIG. 7. Continued

0.00010 ♦ 303.00 K

M
O
L
F
R
A
C
T.

0.00009
0.00008
0.00007
0.00006
0.00005
0.00004
0.00003
0.00002
0.00001
0.00000

80 120 160 200 240 280 320 360 400 440
PRESSURE/BAR

7.9
ANTHRACENE
JOHNSTON ET AL 1982

0.00012 ♦ KOSAL AND HOLDER 1987
■ DOBBS AND JOHNSTON 1987
♦ ZERDA ET AL 1986

M
O
L
F
R
A
C
T.

0.00011
0.00010
0.00009
0.00008
0.00007
0.00006
0.00005
0.00004
0.00003
0.00002
0.00001
0.00000

80 120 160 200 240 280 320 360 400 440 480
PRESSURE/BAR

7.10
ANTHRACENE
308.00 K

0.00010 ♦ ZERDA ET AL 1986
■ KWIATKOWSKI ET AL 1984
♦ ROSLING AND FRANCK 1983

M
O
L
F
R
A
C
T.

0.00009
0.00008
0.00007
0.00006
0.00005
0.00004
0.00003
0.00002
0.00001
0.00000

80 160 240 320 400 480 560 640 720
PRESSURE/BAR

7.11
ANTHRACENE
313.00 K

0.00015 ♦ KOSAL AND HOLDER 1987
■ ZERDA ET AL 1986

M
O
L
F
R
A
C
T.

0.00014
0.00013
0.00012
0.00011
0.00010
0.00009
0.00008
0.00007
0.00006
0.00005
0.00004
0.00003
0.00002
0.00001
0.00000

80 120 160 200 240 280 320
PRESSURE/BAR

7.12
ANTHRACENE
318.00 K

♦ ZERDA ET AL 1986
■ JOHNSTON ET AL 1982
♦ ROSLING AND FRANCK 1983

M
O
L
F
R
A
C
T.

0.00020
0.00018
0.00016
0.00014
0.00012
0.00010
0.00008
0.00006
0.00004
0.00002
0.00000

80 160 240 320 400 480 560 640 720 800
PRESSURE/BAR

7.13
ANTHRACENE
323.00 K

0.00050 ♦ JOHNSTON ET AL 1982
■ ZERDA ET AL 1986

M
O
L
F
R
A
C
T.

0.00045
0.00040
0.00035
0.00030
0.00025
0.00020
0.00015
0.00010
0.00005
0.00000

80 160 240 320 400 480 560 640 720 800 880 960 1040
PRESSURE/BAR

7.14
ANTHRACENE
343.00 K

FIG. 7. Continued

SOLUBILITIES OF COMPOUNDS IN SUPERCRITICAL CARBON DIOXIDE

7.15
ACRIDINE
308.00 K

7.16
ACRIDINE
318.00 K

7.17
ACRIDINE
328.00 K

7.18
ACRIDINE
343.00 K

7.19
CARBAZOLE
KWIATKOWSKI ET AL 1984

7.20
DIBENZOTHIOPHENE
MITRA ET AL 1988

FIG. 7. Continued

7.21
FLUORENE
JOHNSTON ET AL 1982

7.22
FLUORENE
KWIATKOWSKI ET AL 1984

7.23
PHENANTHRENE
JOHNSTON ET AL 1982

7.24
PHENANTHRENE
KURNIK ET AL 1981

7.25
PHENANTHRENE
DOBBS ET AL 1986
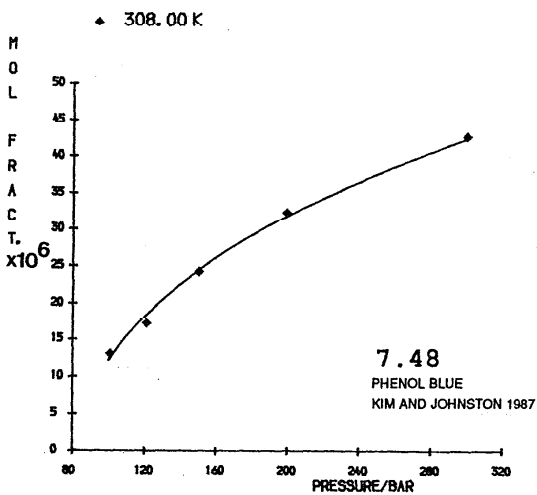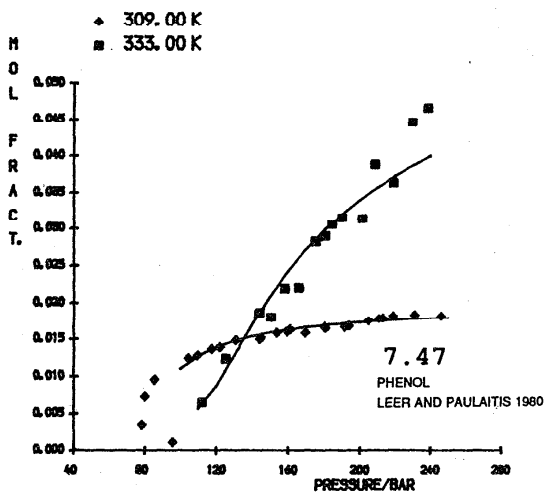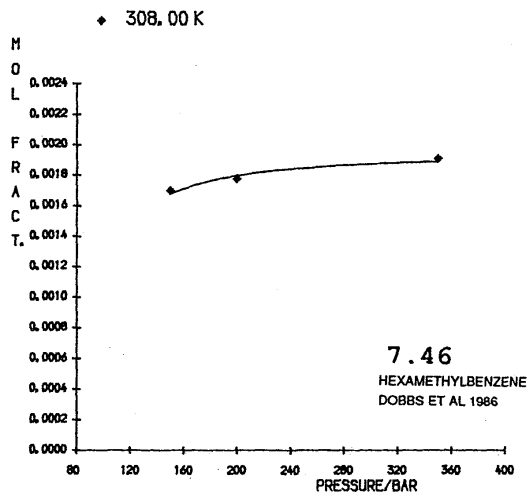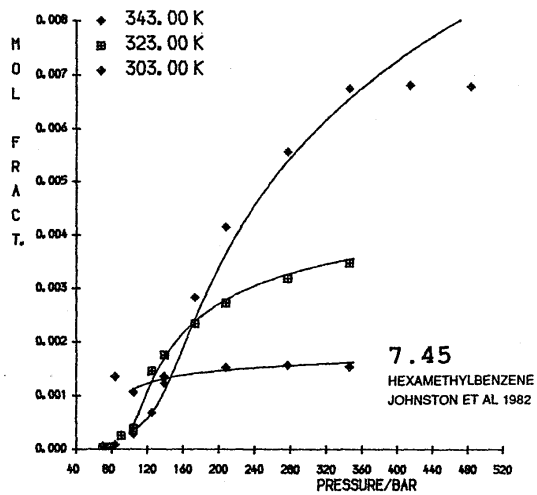
7.26
PHENANTHRENE
KWIATKOWSKI ET AL 1984

FIG. 7. Continued

SOLUBILITIES OF COMPOUNDS IN SUPERCRITICAL CARBON DIOXIDE

EISENBEISS 1964
KWIATKOWSKI ET AL 1984

MOL FRACT.

7.27
PHENANTHRENE
313.00 K

PRESSURE/BAR

308.00 K
323.00 K
343.00 K

MOL FRACT.

7.28
PYRENE
JOHNSTON ET AL 1982

PRESSURE/BAR

308.00 K
318.00 K
328.00 K

MOL FRACT.

7.29
2,6-DIMETHYLNAPHTHALENE
KURNIK ET AL 1981

PRESSURE/BAR

308.00 K
318.00 K
328.00 K

MOL FRACT.

7.30
2,3-DIMETHYLNAPHTHALENE
KURNIK ET AL 1981

PRESSURE/BAR

318.00 K
328.00 K
343.00 K

MOL FRACT.

7.31
2-AMINOFLUORENE
SCHMITT AND REID 1986

PRESSURE/BAR

KURNIK ET AL 1981
MORADINIA AND TEJA 1986

MOL FRACT.

7.32
2,3-DIMETHYLNAPHTHALENE
308.00 K

PRESSURE/BAR

FIG. 7. Continued

7.33
NAPHTHOQUINONE
SCHMITT AND REID 1986

318.00 K
328.00 K
343.00 K

MOL FRACT.

PRESSURE/BAR

7.34
ALPHA-NAPHTHOL
TAN AND WENG 1987

328.00 K
318.00 K
308.00 K

MOL FRACT.

PRESSURE/BAR

SCHMITT AND REID 1986
DOBBS ET AL 1987
TAN AND WENG 1987

7.35
BETA-NAPHTHOL
308.00 K

MOL FRACT.

PRESSURE/BAR

SCHMITT AND REID 1986
TAN AND WENG 1987

7.36
BETA-NAPHTHOL
318.00 K

MOL FRACT.

PRESSURE/BAR

SCHMITT AND REID 1986
TAN AND WENG 1987

7.37
BETA-NAPHTHOL
328.00 K

MOL FRACT.

PRESSURE/BAR

SCHMITT AND REID 1986

7.38
BETA-NAPHTHOL
343.00 K

MOL FRACT.

PRESSURE/BAR

FIG. 7. Continued

7.39
METHYL-O-NITROBENZOATE
CHANG AND MORRELL 1985

7.40
METHYL-M-NITROBENZOATE
CHANG AND MORRELL 1985

7.41
METHYL-P-NITROBENZOATE
CHANG AND MORRELL 1985

7.42
7-METHYL-1-TETRALONE
CHANG AND MORRELL 1985

7.43
6-METHOXY-1-TETRALONE
CHANG AND MORRELL 1985

7.44
5-METHOXY-1-TETRALONE
CHANG AND MORRELL 1985

FIG. 7. Continued

7.45
HEXAMETHYLBENZENE
JOHNSTON ET AL 1982

7.46
HEXAMETHYLBENZENE
DOBBS ET AL 1986

7.47
PHENOL
LEER AND PAULAITIS 1980

7.48
PHENOL BLUE
KIM AND JOHNSTON 1987

7.49
P-CHLOROPHENOL
LEER AND PAULAITIS 1980

7.50
2,4-DICHLOROPHENOL
LEER AND PAULAITIS 1980

FIG. 7. Continued

7.51

DIPHENYLAMINE
TSEKHANSKAYA ET AL 1962

- ◆ 305. 40 K
- ⊞ 310. 20 K

MOL FRACT. (y-axis)
PRESSURE/BAR (x-axis)

7.52

1.10-DECANEDIOL
PENNISI AND CHIMOWITZ 1986

- ◆ 318. 00 K
- ⊞ 323. 00 K
- ◆ 328. 00 K

MOL FRACT. (y-axis)
PRESSURE/BAR (x-axis)

7.53

DI-N-DODECYLAMINE
SCHMITT AND REID 1988

- ◆ 310. 00 K
- ⊞ 320. 00 K

MOL FRACT. (y-axis)
PRESSURE/BAR (x-axis)

7.54

1-HEXADECANOL
KRAMER AND THODOS 1988

- ◆ 318. 00 K
- ⊞ 328. 00 K
- ◆ 338. 00 K

MOL FRACT. (y-axis)
PRESSURE/BAR (x-axis)

7.55

PHTHALIC ANHYDRIDE
DOBBS ET AL 1987

- ◆ 308. 00 K

MOL FRACT. (y-axis)
PRESSURE/BAR (x-axis)

7.56

TRIPHENYLMETHANE
JOHNSTON ET AL 1982

- ◆ 323. 00 K
- ⊞ 313. 00 K
- ◆ 303. 00 K

MOL FRACT. (y-axis)
PRESSURE/BAR (x-axis)

FIG. 7. Continued

0.08 ◆ 310.00 K
M   ⊞ 320.00 K
O 0.07
L
  0.06
F
R 0.05
A
C 0.04
T.
  0.03
  0.02
  0.01
  0.00
      80   120   160
              PRESSURE/BAR

7.57
TRIHEXYLAMINE
SCHMITT AND REID 1988

0.0050 ◆ 320.00 K
M   ⊞ 310.00 K
O 0.0045
L
  0.0040
F
R 0.0035
A 0.0030
C
T. 0.0025
  0.0020
  0.0015
  0.0010
  0.0005
  0.0000
      80   120   160   200   240
                  PRESSURE/BAR

7.58
SQUALANE
SCHMITT AND REID 1988

0.020 ◆ 362.50 K
M   ⊞ 343.20 K
O 0.018 ◆ 323.70 K
L
  0.016
F
R 0.014
A 0.012
C
T. 0.010
  0.008
  0.006
  0.004
  0.002
  0.000
    240 320 400 480 560 640 720 800
              PRESSURE/BAR

7.59
OCTACOSANE
SWAID ET AL 1985

0.09 ◆ 402.00 K
M   ⊞ 382.00 K
O 0.08 ◆ 362.50 K
L   ● 343.00 K
  0.07
F
R 0.06
A
C 0.05
T.
  0.04
  0.03
  0.02
  0.01
  0.00
    80   120   160   200
              PRESSURE/BAR

7.60
DECANE
SWAID ET AL 1985

0.040 ◆ 402.00 K
M   ⊞ 382.00 K
O 0.035 ◆ 362.50 K
L   ● 343.00 K
  0.030
F
R
A 0.025
C
T. 0.020
  0.015
  0.010
  0.005
  0.000
    160 240 320 400 480 560 640 720
              PRESSURE/BAR

7.61
ADAMANTANE
SWAID ET AL 1985

       ◆ 323.60 K
M   ⊞ 328.50 K
O   ◆ 343.20 K
L 0.030 ● 362.80 K●
  0.028 + 382.30 K●
  0.026
F 0.024
R 0.022
A 0.020
C 0.018
T. 0.016
  0.014
  0.012
  0.010
  0.008
  0.006
  0.004
  0.002
  0.000
   160 240 320 400 480 560 640 720 800 800
              PRESSURE/BAR

7.62
SQUALANE
SWAID ET AL 1985

FIG. 7. Continued

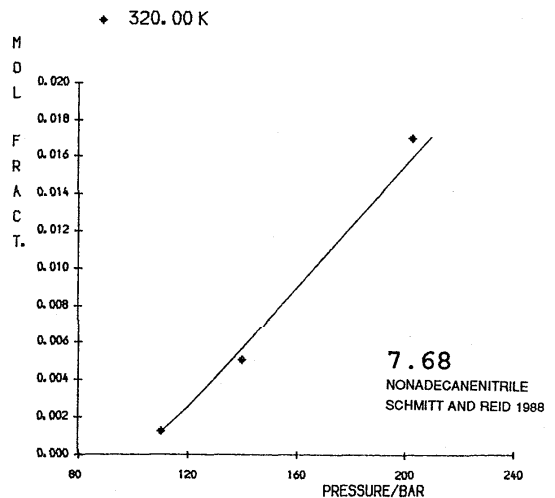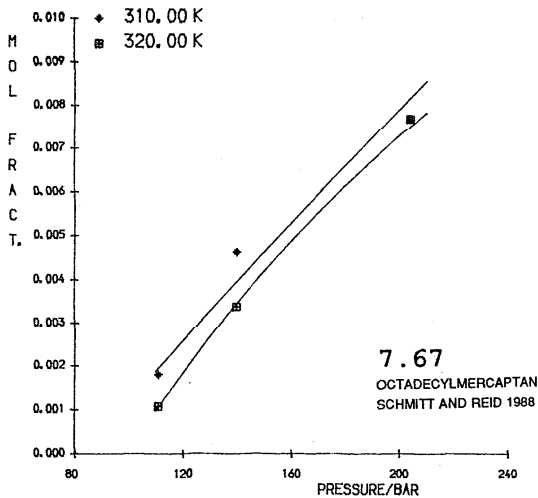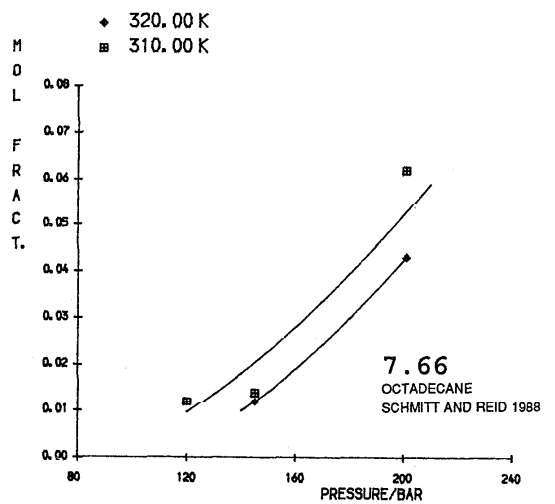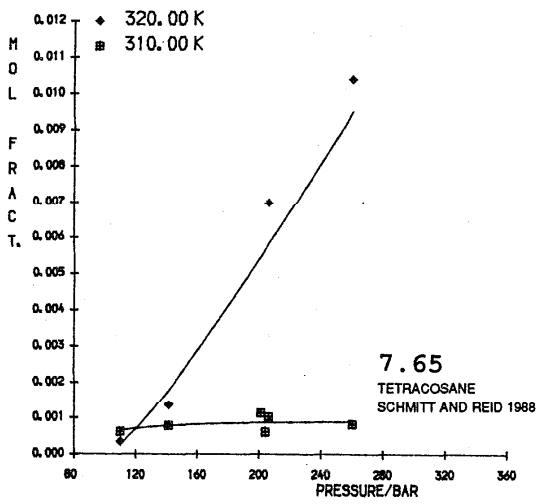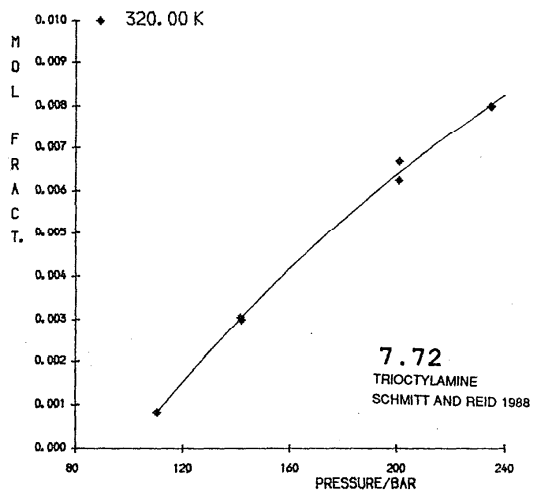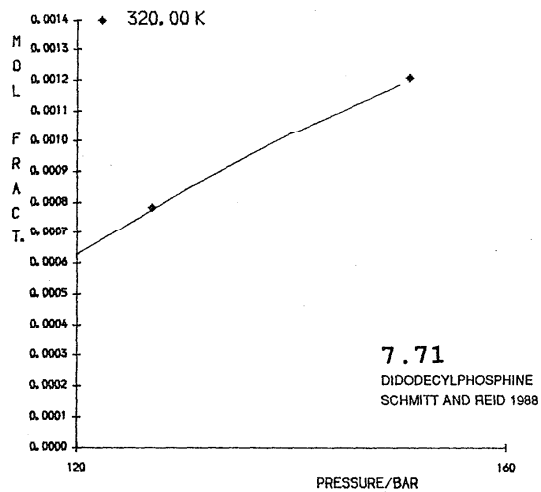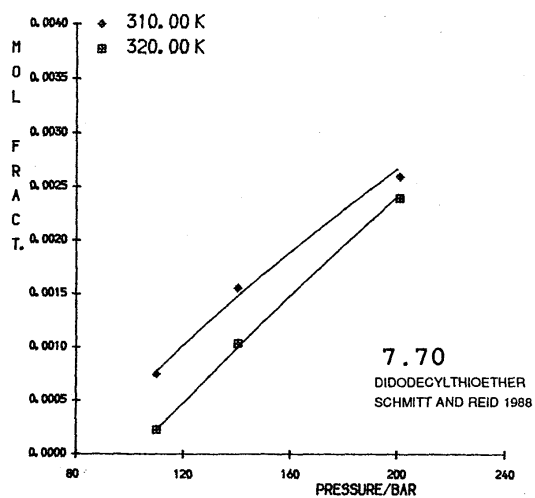# SOLUBILITIES OF COMPOUNDS IN SUPERCRITICAL CARBON DIOXIDE

7.63
1-OCTADECANOL
SCHMITT AND REID 1988

320.00 K
310.00 K

MOL FRACT. / PRESSURE/BAR

7.64
DOCOSANE
SCHMITT AND REID 1988

320.00 K
310.00 K

MOL FRACT. / PRESSURE/BAR

7.65
TETRACOSANE
SCHMITT AND REID 1988

320.00 K
310.00 K

MOL FRACT. / PRESSURE/BAR

7.66
OCTADECANE
SCHMITT AND REID 1988

320.00 K
310.00 K

MOL FRACT. / PRESSURE/BAR

7.67
OCTADECYLMERCAPTAN
SCHMITT AND REID 1988

310.00 K
320.00 K

MOL FRACT. / PRESSURE/BAR

7.68
NONADECANENITRILE
SCHMITT AND REID 1988

320.00 K

MOL FRACT. / PRESSURE/BAR

FIG. 7. Continued

7.69
TRIPHENYLPHOSPHINE
SCHMITT AND REID 1988

7.70
DIDODECYLTHIOETHER
SCHMITT AND REID 1988

7.71
DIDODECYLPHOSPHINE
SCHMITT AND REID 1988

7.72
TRIOCTYLAMINE
SCHMITT AND REID 1988

7.73
DIOCTYL ETHER
SCHMITT AND REID 1988
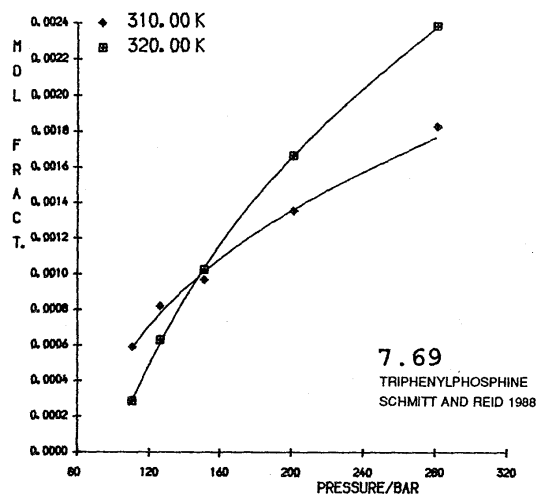
7.74
TRIOCTYLPHOSPHINE
SCHMITT AND REID 1988

FIG. 7. Continued

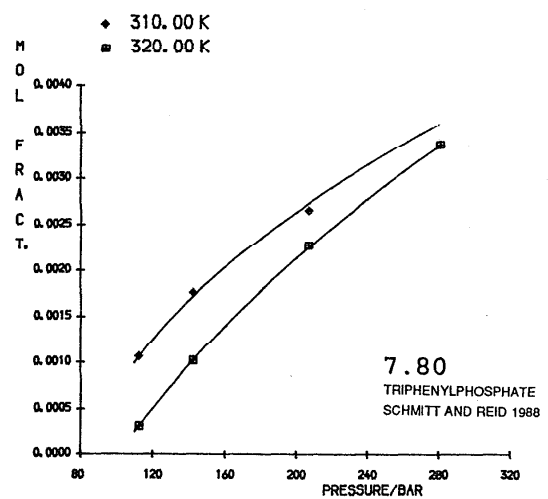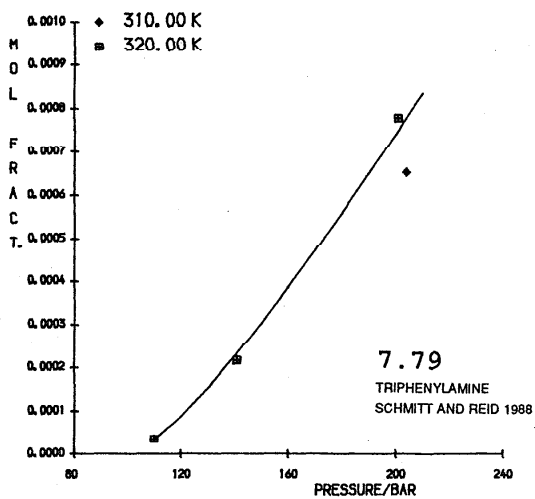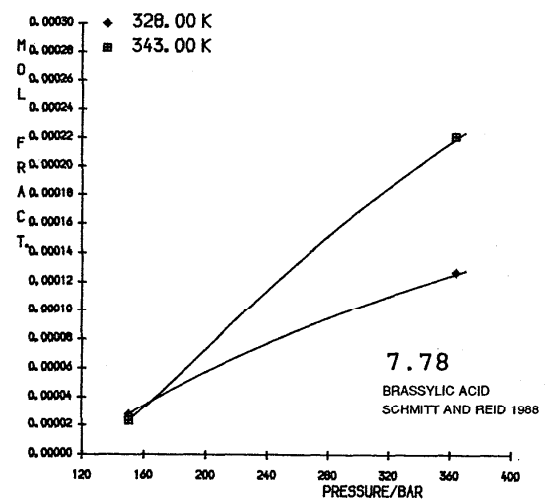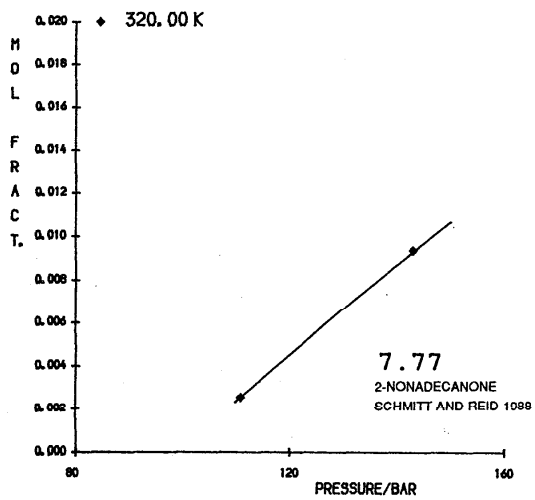# SOLUBILITIES OF COMPOUNDS IN SUPERCRITICAL CARBON DIOXIDE

7.75
NONADECANE
SCHMITT AND REID 1988

7.76
EICOSANE
SCHMITT AND REID 1988

7.77
2-NONADECANONE
SCHMITT AND REID 1988

7.78
BRASSYLIC ACID
SCHMITT AND REID 1988

7.79
TRIPHENYLAMINE
SCHMITT AND REID 1988

7.80
TRIPHENYLPHOSPHATE
SCHMITT AND REID 1988

FIG. 7. Continued

308. 15 K

M
O
L

F
R
A
C
T.

0.00020
0.00018
0.00016
0.00014
0.00012
0.00010
0.00008
0.00006
0.00004
0.00002
0.00000

7.81
5-HYDROXINDOLE
NAKATANI ET AL 1989

80   120   160   200
PRESSURE/BAR

308. 15 K

M
O
L

F
R
A
C
T.
$\times 10^6$

20
18
16
14
12
10
8
6
4
2
0

7.82
INDOLE-3-ALDEHYDE
NAKATANI ET AL 1989

40   80   120   160   200
PRESSURE/BAR

308. 15 K

M
O
L

F
R
A
C
T.
$\times 10^6$

20
18
16
14
12
10
8
6
4
2
0

7.83
INDOLE-3-CARBOXYLIC ACID
NAKATANI ET AL 1989

80   120   160   200
PRESSURE/BAR

308. 15 K

M
O
L

F
R
A
C
T.

0.0020
0.0018
0.0016
0.0014
0.0012
0.0010
0.0008
0.0006
0.0004
0.0002
0.0000

7.84
5-METHOXYINDOLE
SAKO ET AL 1989

40   80   120   160   200
PRESSURE/BAR

308. 15 K

M
O
L

F
R
A
C
T.

0.00010
0.00009
0.00008
0.00007
0.00006
0.00005
0.00004
0.00003
0.00002
0.00001
0.00000

7.85
5-AMINOINDOLE
NAKATANI ET AL 1989

80   120   140   200
PRESSURE/BAR

308. 15 K

M
O
L

F
R
A
C
T.

0.00050
0.00045
0.00040
0.00035
0.00030
0.00025
0.00020
0.00015
0.00010
0.00005
0.00000

7.86
OXINDOLE
NAKATANI ET AL 1989

80   120   140   200
PRESSURE/BAR

FIG. 7. Continued

7.81
5-HYDROXINDOLE
NAKATANI ET AL 1989

7.82
INDOLE-3-ALDEHYDE
NAKATANI ET AL 1989

7.83
INDOLE-3-CARBOXYLIC ACID
NAKATANI ET AL 1989

7.84
5-METHOXYINDOLE
SAKO ET AL 1989

7.85
5-AMINOINDOLE
NAKATANI ET AL 1989

7.86
OXINDOLE
NAKATANI ET AL 1989

FIG. 7. Continued

SOLUBILITIES OF COMPOUNDS IN SUPERCRITICAL CARBON DIOXIDE

7.87
TRIBUTYRIN
CHRASTIL 1982

7.88
TRILAURIN
BAMBERGER ET AL 1988

7.89
TRIMYRISTIN
BAMBERGER ET AL 1988

7.90
TRIPALMITIN
CHRASTIL 1982

7.91
TRIPALMITIN
OHGAKI ET AL 1987

7.92
TRIPALMITIN
313.00 K

FIG. 7. Continued

7.93
TRISTEARIN
CHRASTIL 1982

7.94
TRIOLEIN
CHRASTIL 1982

7.95
2-AMINOBENZOIC ACID
DOBBS ET AL 1987

7.96
BEHENIC ACID
CHRASTIL 1982

7.97
LAURIC ACID
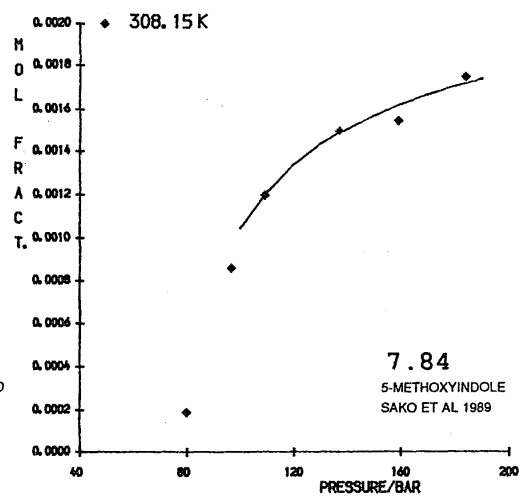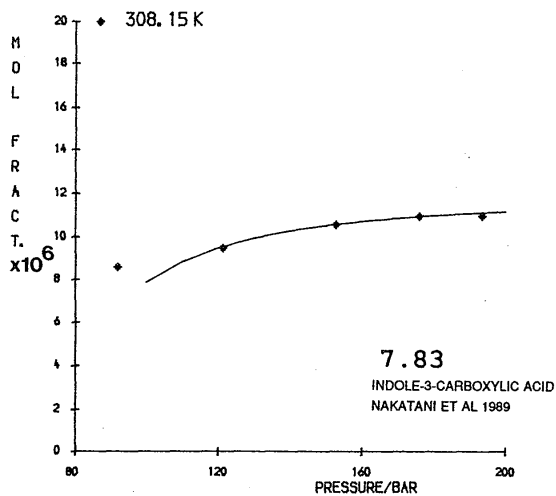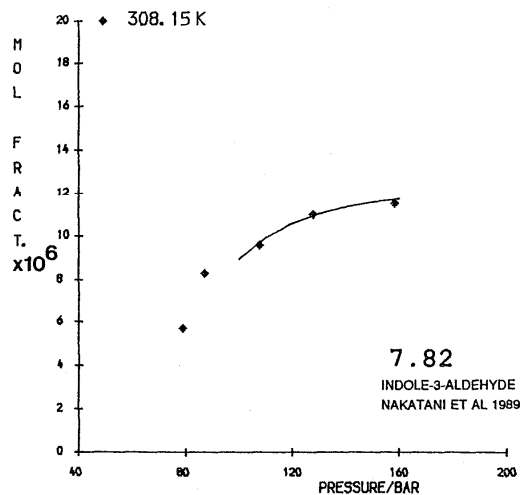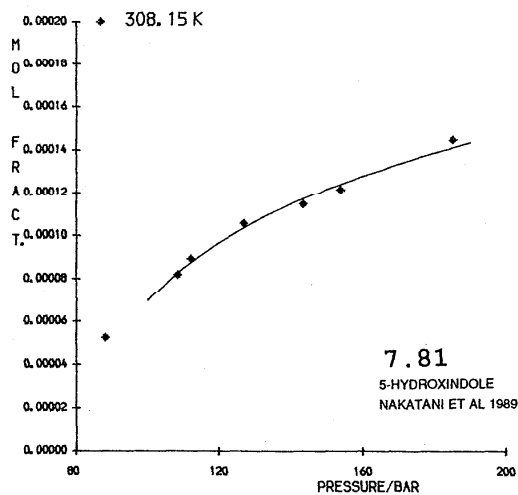BAMBERGER ET AL 1988

7.98
MYRISTIC ACID
BAMBERGER ET AL 1988

FIG. 7. Continued

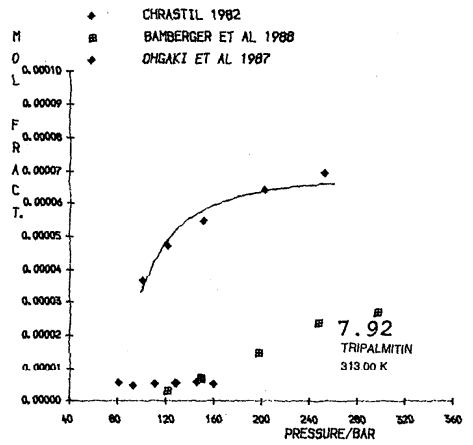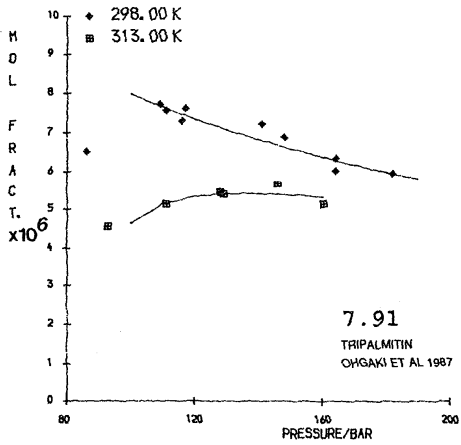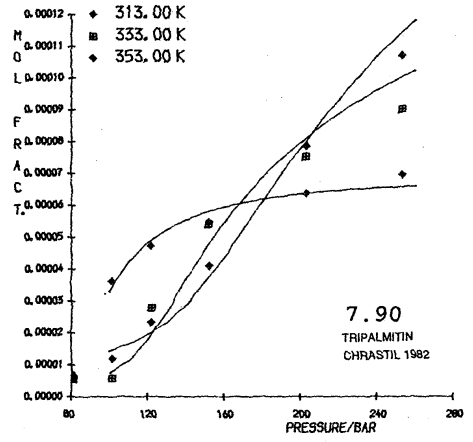## SOLUBILITIES OF COMPOUNDS IN SUPERCRITICAL CARBON DIOXIDE

7.99
OLEIC ACID
CHRASTIL 1982

7.100
PALMITIC ACID
OHGAKI ET AL 1987

7.101
PALMITIC ACID
KRAMER AND THODOS 1988

7.102
PALMITIC ACID
313.00 K

7.103
STEARIC ACID
CHRASTIL 1982

7.104
STEARIC ACID
SCHMITT AND REID 1988

FIG. 7. Continued

7.105

353.00 K
333.00 K
313.00 K

MOL FRACT.

PRESSURE/BAR

ALPHA-TOCOPHEROL
CHRASTIL 1982

7.106

CHRASTIL 1982
OHGAKI ET AL 1987

MOL FRACT.

PRESSURE/BAR

ALPHA-TOCOPHEROL
313.00 K

7.107

308.15 K
318.15 K
328.15 K

MOL FRACT. x10^6

PRESSURE/BAR

MONOCROTALINE
SCHAEFFER ET AL 1988

7.108

353.00 K
333.00 K
313.00 K

MOL FRACT.

PRESSURE/BAR

CHOLESTEROL
CHRASTIL 1982

7.109

308.15 K

MOL FRACT.

PRESSURE/BAR

SKATOLE
SAKO ET AL 1989

7.110

310.00 K
320.00 K

MOL FRACT.

PRESSURE/BAR

TRIOCTYLPHOSPHINE OXIDE
SCHMITT AND REID 1988

FIG. 7. Continued

7.111
OCTACOSANE
MCHUGH ET AL 1984

7.112
HEXACHLOROETHANE
KURNIK ET AL 1981

7.113
O-HYDROXYBENZOIC ACID
KRUKONIS AND KURNIK 1985

7.114
M-HYDROXYBENZOIC ACID
KRUKONIS AND KURNIK 1985

7.115
P-HYDROXYBENZOIC ACID
KRUKONIS AND KURNIK 1985

7.116
BIPHENYL
MCHUGH AND PAULAITIS 198

FIG. 7. Continued

7.117
BENZOIC ACID
308.00 K

7.118
BENZOIC ACID
318.00 K

7.119
BENZOIC ACID
328.00 K

7.120
BENZOIC ACID
338.00 K

7.121
BENZOIC ACID
SCHMITT AND REID 1986

FIG. 7. Continued
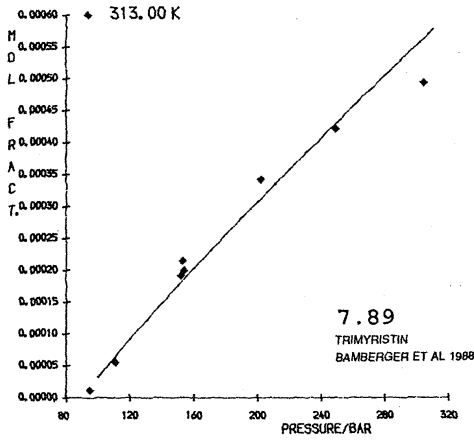
SOLUBILITIES OF COMPOUNDS IN SUPERCRITICAL CARBON DIOXIDE

7.122
OLEIC ACID
333.00 K

7.123
OLEIC ACID
KING ET AL 1983

7.124
N-DOTRIACONTANE
KING ET AL 1983

7.125
MONO-OLEIN
KING ET AL 1983

7.126
TITANIUM TETRACHLORIDE
TOLLEY AND TESTER 1989

FIG. 7. Continued

7.127
ANTHRACENE
ROSSLING AND FRANCK 1983

373.00 K
353.00 K
348.00 K
324.00 K
323.00 K
313.00 K

PRESSURE/BAR

7.128
ANTHRACENE
ROSSLING AND FRANCK 1983

393.00 K
403.00 K
423.00 K
453.00 K
473.00 K

PRESSURE/BAR

7.129
ANTHRACENE
348.00 K

ZERDA ET AL 1986
ROSSLING AND FRANCK 1983

PRESSURE/BAR

7.130
ANTHRACENE
353.00 K

ZERDA ET AL 1986
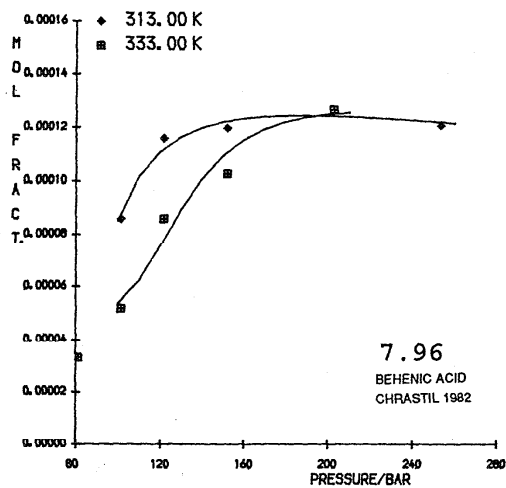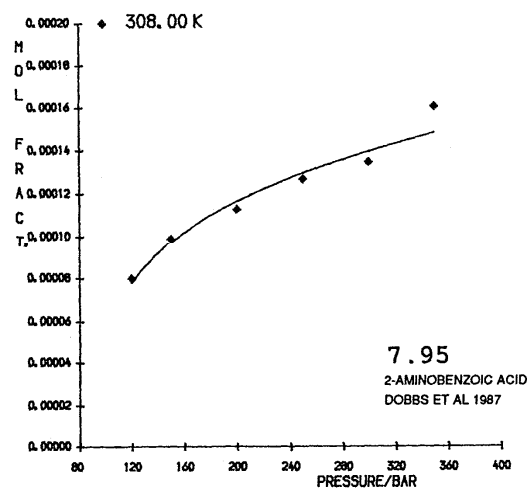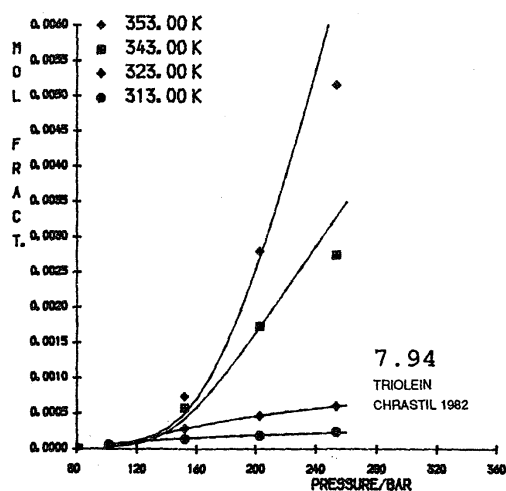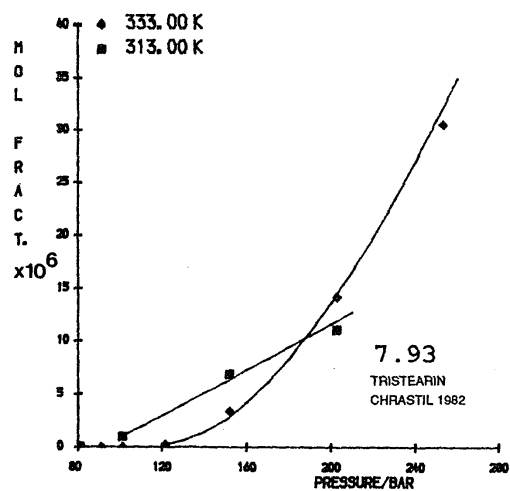ROSSLING AND FRANCK 1983

PRESSURE/BAR

FIG. 7. Continued

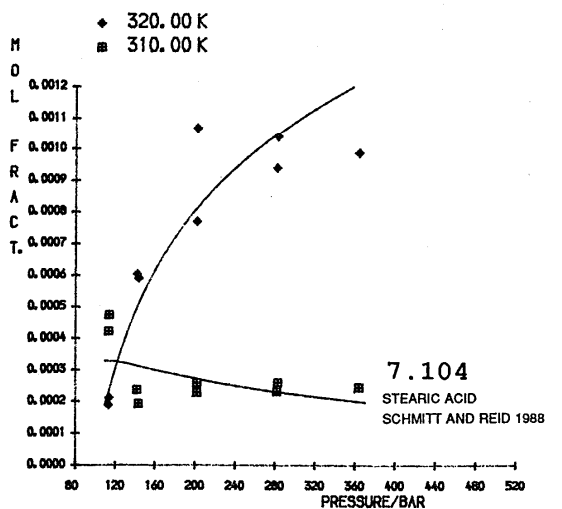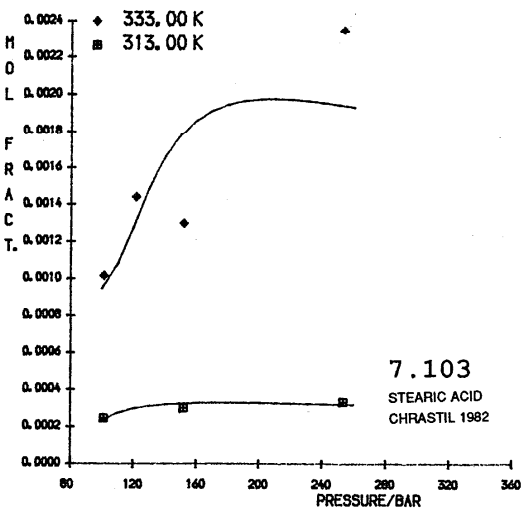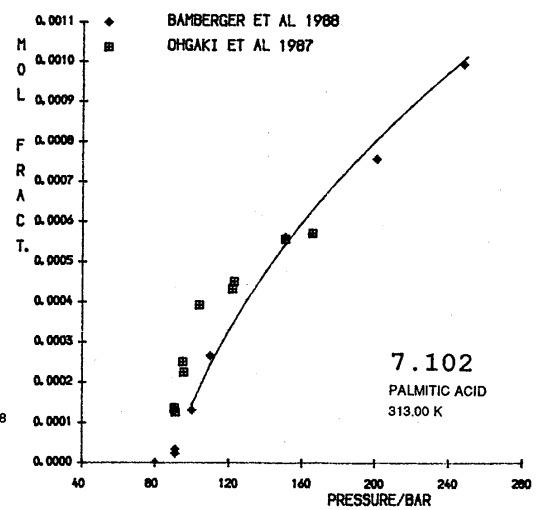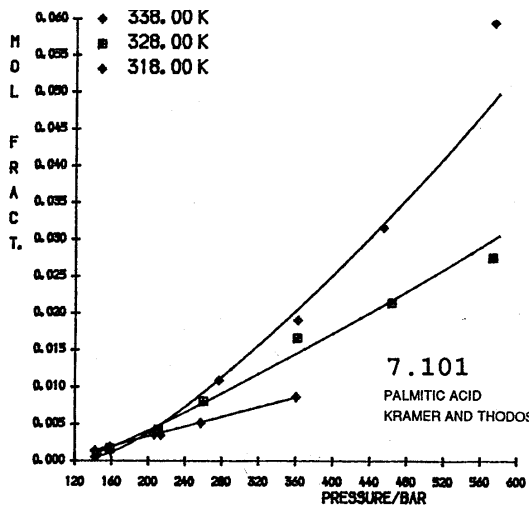# SOLUBILITIES OF COMPOUNDS IN SUPERCRITICAL CARBON DIOXIDE

TABLE 4. Correlation constants A and B in Eq. (4) calculated from literature solubility data.

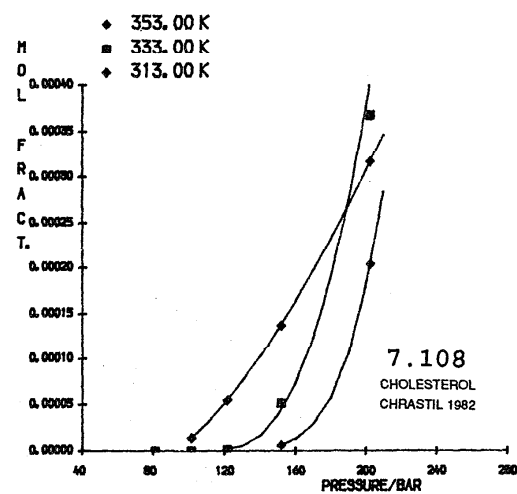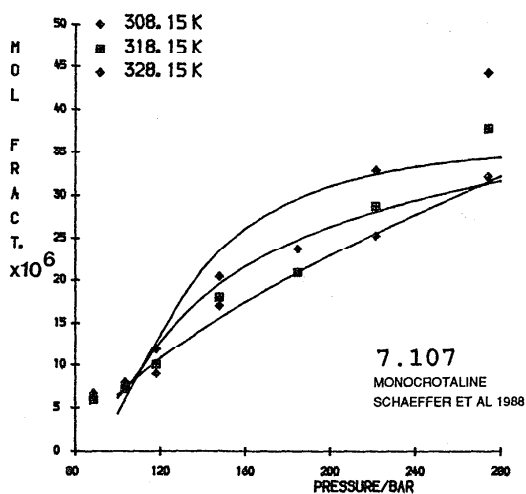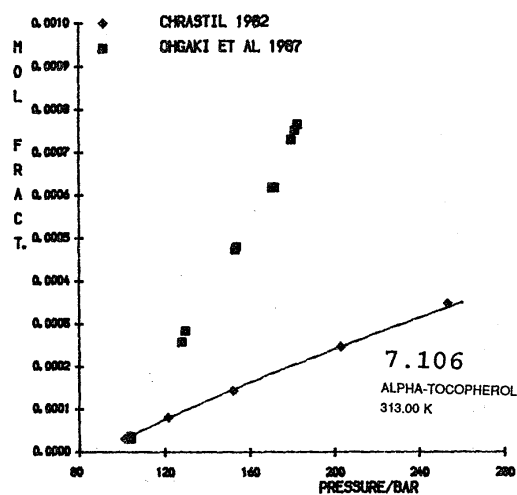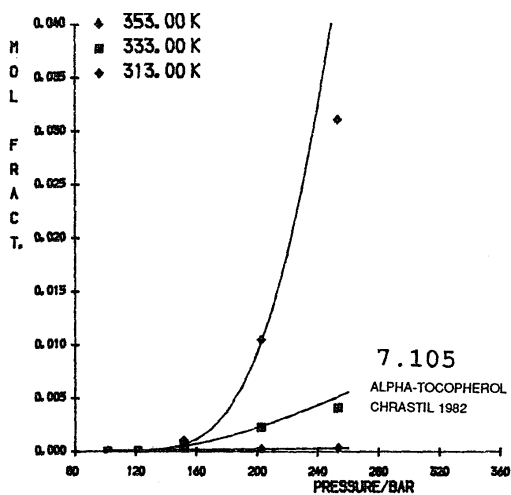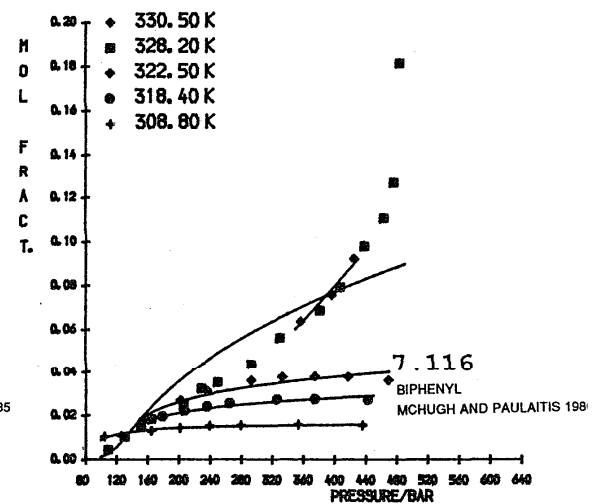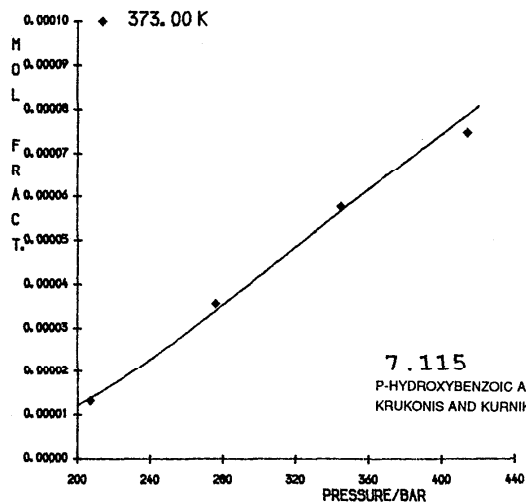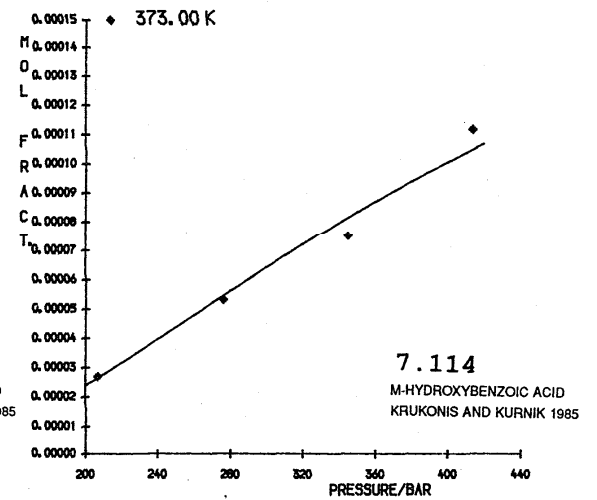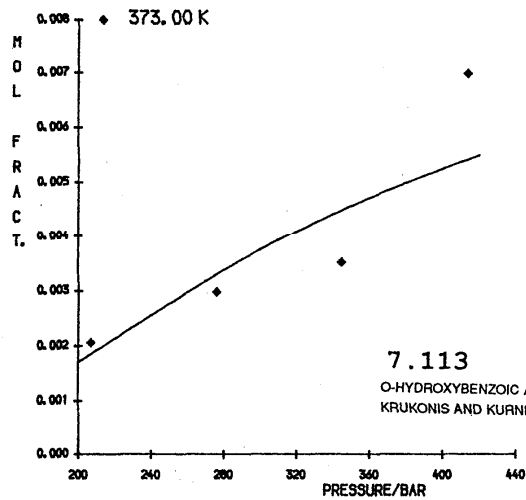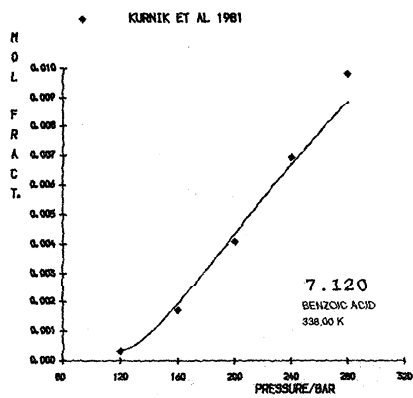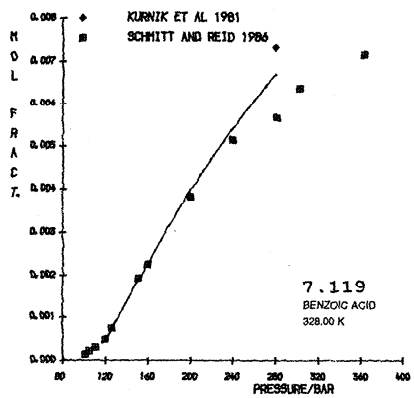| Compound	T (K)	P (bars)	A	$B \times 10^3$ $(m^3\ kg^{-1})$	Reference
Acridine	308.0	100–360	− 13.4711*	13.39	59
	308.0	120–350	− 10.2254*	9.82	63
	318.0	100–360	− 9.9604	10.34	59
	328.0	100–360	− 8.7478	9.66	59
	343.0	100–400	− 7.7046	9.57	59
Adamantane	343.0	130–660	− 3.2223	5.32	50
	362.5	150–750	− 2.3603	5.23	50
	382.0	180–750	− 1.5552	5.07	50
	402.0	170–600	− 1.1149	5.52	50
2-Aminobenzoic acid	308.0	120–350	− 11.8151	9.29	63
2-Aminofluorene	318.0	110–370	− 15.2469	14.02	59
	328.0	110–370	− 11.9043	11.29	59
	343.0	110–370	− 9.9369	10.32	59
5-Aminoindole	308.2	100–190	− 10.0399	6.98	41
Anthracene	303.0	100–420	− 14.2435	10.95	56
	308.0	100–280	− 16.5693	14.36	31
	308.0	120–350	− 11.5029*	8.32	62
	308.0	140–480	− 11.8762	7.84	49
	313.0	100–200	− 10.0052*	6.43	27
	313.0	100–300	− 11.0643	7.39	49
	318.0	100–280	− 12.6634*	10.68	31
	318.0	100–280	− 12.7553	9.84	49
	323.0	100–420	− 12.1867*	10.41	56
	323.0	100–380	− 11.9161	9.25	49
	323.0	100–620	− 9.7933	7.00	85
	343.0	110–420	− 9.1781*	8.43	56
	343.0	110–1060	− 8.2466	6.36	49
	348.0	100–1100	− 7.9587*	6.32	49
	353.0	100–1200	− 7.5684*	6.16	49
	353.0	200–900	− 7.9508	6.75	85
	373.0	100–470	− 7.7461	8.00	85
	403.0	120–340	− 6.6287	8.75	85
	423.0	100–240	− 6.0238	10.07	85
Behenic acid	313.0	100–260	− 8.0300	5.16	43
	333.0	100–210	− 6.2551	3.55	43
Benzoic acid	308.0	100–370	− 10.6194*	11.39	59
	308.0	120–280	− 10.5378	11.34	63
	318.0	120–280	− 8.7151*	10.18	23
	318.0	100–370	− 9.0029	10.45	59
	328.0	120–280	− 8.2501*	10.61	23
	328.0	100–370	− 7.4450	9.45	59
	338.0	120–280	− 7.3430	10.41	23
	343.0	100–370	− 6.6632	9.93	59
Biphenyl	308.8	100–440	− 5.2613	7.32	12
	318.4	150–450	− 4.7963	7.68	12
	322.5	150–470	− 4.4365	7.73	12
	328.2	100–490	− 5.2316	9.55	12
	330.5	350–430	− 10.6870	15.73	12
Brassylic acid	328.0	150–370	− 12.2633	10.32	67
	343.0	150–370	− 10.5682	9.61	67
Carbazole	313.1	100–200	− 10.4181	5.75	27
p-Chlorophenol	309.0	100–240	− 7.9162	11.14	22
Cholesterol	313.0	100–210	− 18.7304	18.95	43
	333.0	120–210	− 18.2216	21.57	43
	353.0	150–210	− 16.8527	22.73	43
Decane	343.0	110–130	− 5.3432	18.39	50
	362.5	120–150	− 3.8180	15.77	50
	382.0	120–170	− 3.3014	16.27	50
	402.0	120–180	− 2.2291	14.82	50
1,10-Decanediol	318.0	200–310	− 10.1280	8.95	58
	323.0	130–310	− 9.9801	9.50	58
	328.0	130–310	− 8.5464	8.34	58
Dibenzothiophene	309.2	100–280	− 11.4979	11.86	68
	328.2	100–280	− 7.0188	7.98	68
	338.2	100–280	− 7.1954	9.05	68
2,4-Dichlorophenol	309.0	100–210	− 7.2329	11.84	22
Di-N-Dodecylamine	310.0	110–210	− 12.2529	10.64	67
	320.0	110–210	− 10.9314	9.91	67
Didodecylphosphine	320.0	120–150	− 8.3668	9.14	67

TABLE 4. Correlation constants A and B in Eq. (4) calculated from literature solubility data—Continued

Compound	T (K)	P (bars)	A	$B \times 10^3$ (m^3 kg^{-1})	Reference
Didodecylthioether	310.0	110–200	− 12.4260	13.77	67
	320.0	110–200	− 10.7812	12.52	67
2,3-Dimethylnaphthalene	308.0	100–280	− 7.8840*	9.20	23
	308.2	100–280	− 7.9335	9.25	26
	318.0	100–280	− 5.6941	7.27	23
	328.0	100–280	− 4.9307	7.02	23
2,6-Dimethylnaphthalene	308.0	100–280	− 8.5371	9.52	23
	318.0	100–280	− 6.6992	8.34	23
	328.0	100–280	− 5.1027	7.16	23
Dioctylether	320.0	100–140	− 7.6615	14.00	67
Diphenylamine	305.4	100–170	− 8.7591	9.77	55
	310.2	100–220	− 8.1720	9.64	55
n-Docosane	310.0	110–210	− 17.5744	22.11	67
	320.0	110–190	− 12.6631	16.86	67
n-Dotriacontane	308.0	100–160	− 11.3146	8.23	82
Eicosane	310.0	110–280	− 9.4365	11.77	67
	320.0	110–280	− 8.2179	11.11	67
Fluorene	303.0	100–350	− 9.7359	9.77	56
	308.0	100–420	− 8.6441	8.95	56
	313.1	100–200	− 6.6763	6.98	27
	323.0	100–420	− 6.5610	7.68	56
	343.0	100–420	− 6.0193	8.57	56
Hexachloroethane	308.0	100–280	− 3.8398	5.98	23
	318.0	100–280	− 2.6556	5.32	23
	328.0	100–280	− 2.5590	5.98	23
1-Hexadecanol	318.0	150–420	− 9.0257	11.52	69
	328.0	140–420	− 8.5080	11.84	69
	338.0	140–380	− 7.5966	11.43	69
Hexamethylbenzene	303.0	100–350	− 8.7410	8.43	56
	308.0	150–350	− 7.1496	7.07	39
	323.0	100–350	− 6.3018	7.25	56
	343.0	100–490	− 5.2286	7.34	56
5-Hydroxyindole	308.2	100–190	− 11.6896	9.43	41
m-Hydroxybenzoic acid	373.0	200–420	− 9.0621	7.73	72
o-Hydroxybenzoic acid	373.0	200–420	− 4.2468	6.59	72
p-Hydroxybenzoic acid	373.0	200–420	− 10.3969	9.09	72
Indole-3-aldehyde	308.2	100–160	− 11.6202	6.45	41
Indole-3-carboxylic acid	308.2	100–200	− 12.0067	6.82	41
Lauric acid	313.0	100–250	− 13.1461	17.64	34
5-Methoxyindole	308.2	100–190	− 7.9283	7.95	42
5-Methoxy-1-tetralone	308.0	100–280	− 6.4528	7.52	57
6-Methoxy-1-tetralone	308.0	100–280	− 10.5271	12.75	57
7-Methoxy-1-tetralone	308.0	100–280	− 10.2554	14.45	57
Methyl-m-nitrobenzoate	308.0	100–280	− 9.3690	12.07	57
Methyl-o-nitrobenzoate	308.0	100–280	− 8.8871	12.48	57
Methyl-p-nitrobenzoate	308.0	100–280	− 9.5920	11.98	57
Monocrotaline	308.2	100–280	− 16.4638	12.80	33
	318.2	100–280	− 11.7091	7.95	33
	328.2	100–280	− 9.1428	5.39	33
Mono-olein	308.0	100–180	− 14.7600	13.39	82
	333.0	130–190	− 11.9936	11.20	82
Myristic acid	313.0	100–250	− 11.5409	14.23	34
Naphthalene	308.0	100–330	− 5.7394*	8.00	15
	308.0	120–240	− 5.5861	7.82	39
	308.0	100–250	− 6.1017	8.50	12
	308.0	100–280	− 6.4679	8.86	68
	308.0	120–200	− 6.0850	8.45	84
	308.0	100–130	− 7.5834	10.16	82
	318.0	100–310	− 3.6958*	6.50	15
	318.0	100–280	− 3.3817	6.07	57
	323.0	100–380	− 3.4633	6.70	20
	328.0	100–290	− 3.5284*	7.50	12
	328.0	110–280	− 3.8078	7.84	57
	328.0	120–320	− 3.6695	7.59	20
	328.0	100–280	− 3.8227	7.91	68
	328.0	100–320	− 3.4745	7.41	15
	331.5	120–500	− 3.8054	8.02	20
	333.4	100–290	− 3.6167	8.50	12
	337.9	140–230	− 3.6285	8.77	12

SOLUBILITIES OF COMPOUNDS IN SUPERCRITICAL CARBON DIOXIDE

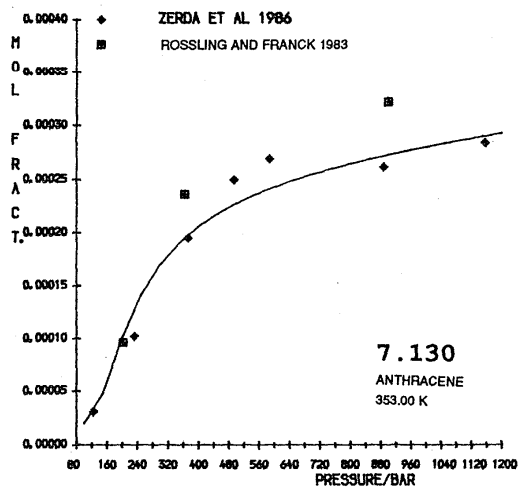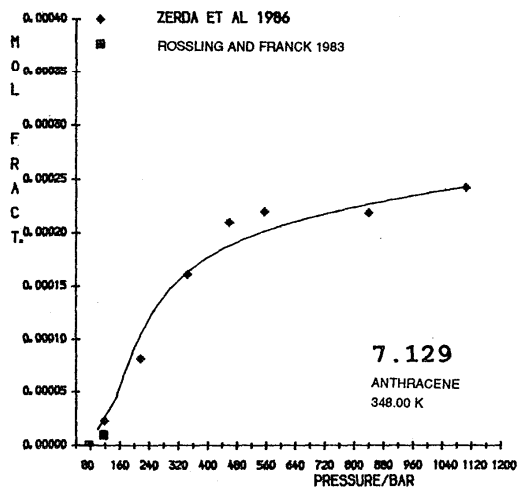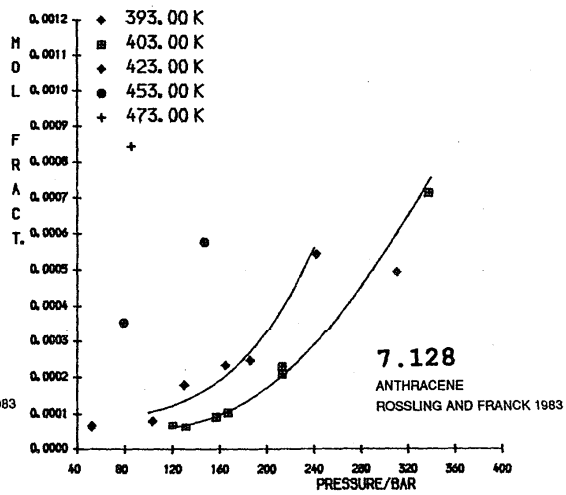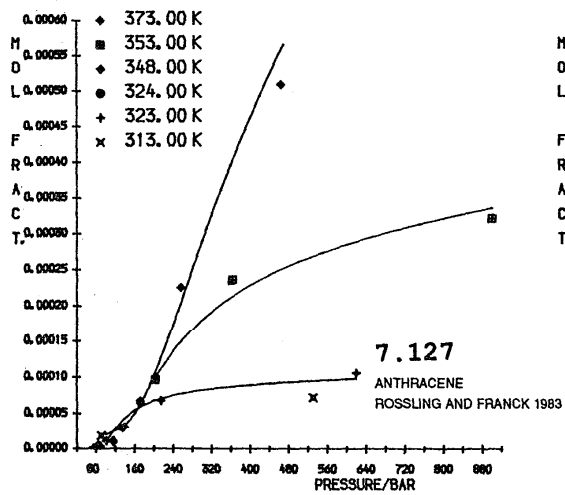TABLE 4. Correlation constants A and B in Eq. (4) calculated from literature solubility data—Continued

Compound	T (K)	P (bars)	A	$B \times 10^3$ (m^3 kg^{-1})	Reference
α-Naphthol	308.0	100–160	− 8.1013	7.89	32
	318.0	100–150	− 6.6145	6.84	32
	328.0	100–170	− 5.8110	6.57	32
β-Naphthol	308.0	100–360	− 10.4090*	9.50	63
	308.0	100–160	− 10.1571	9.30	32
	308.0	100–370	− 13.6898	13.07	59
	318.0	100–370	− 9.4624*	9.09	59
	318.0	100–150	− 7.7998	7.30	32
	328.0	100–370	− 7.8206*	8.00	59
	328.0	100–170	− 7.2368	7.66	32
	343.0	100–370	− 7.0293	8.14	59
Naphthoquinone	318.0	100–370	− 6.8600	8.29	59
	328.0	100–370	− 6.6700	8.75	59
	343.0	100–370	− 6.2421	9.50	59
Nonadecane	310.0	110–210	− 11.9233	15.34	67
	320.0	110–210	− 7.1305	9.64	67
Nonadecanenitrile	320.0	110–210	− 9.8521	13.68	67
2-Nonadecanone	320.0	110–150	− 7.8886	11.50	67
Octacosane	307.9	120–280	− 9.0389	6.07	30
	318.6	120–290	− 9.2625	8.16	30
	323.4	120–330	− 8.9944	8.91	30
	323.7	200–490	− 5.3007	4.64	50
	325.2	120–290	− 9.0172	9.36	30
	343.2	200–810	− 8.2050	10.00	50
	362.5	240–570	− 8.9345	12.32	50
Octadecane	310.0	120–210	− 15.2936	20.59	67
	320.0	140–200	− 12.4901	18.23	67
1-Octadecanol	310.0	110–280	− 8.7462	8.20	67
	320.0	110–280	− 8.2865	9.48	67
Octadecylmercaptan	310.0	110–210	− 12.6438	15.29	67
	320.0	110–210	− 8.5600	11.14	67
Oleic acid	308.0	100–180	− 11.1388	11.11	82
	313.0	100–260	− 12.4173*	13.02	43
	333.0	130–180	− 9.0620	9.79	82
	333.0	100–260	− 10.2540	14.57	43
Oxindole	308.2	100–190	− 10.7912	9.66	41
Palmitic acid	298.0	100–190	− 13.3962	10.77	24
	313.0	100–250	− 11.5194*	11.52	34
	313.0	100–170	− 7.2038	6.00	24
	318.0	140–360	− 11.7847	14.00	69
	328.0	140–580	− 10.7342	13.95	69
	338.0	140–580	− 10.0706	14.16	69
Phenanthrene	303.0	100–420	− 10.6591	10.23	56
	308.0	100–350	− 10.0056	9.95	39
	313.0	100–550	− 11.4694*	12.36	65
	313.1	100–200	− 6.7724	6.39	27
	318.0	120–280	− 7.9321	8.50	23
	323.0	100–420	− 8.0300	8.89	56
	328.0	120–280	− 7.2147	8.48	23
	338.0	120–280	− 6.4214	8.18	23
	343.0	100–420	− 7.7438	9.84	56
Phenol	309.0	100–250	− 4.9257	7.16	22
	333.0	110–240	− 2.8248	6.55	22
Phenol blue	308.0	100–300	− 14.5107	10.91	66
Phthalic anhydride	308.0	120–350	− 10.3563	11.05	63
Pyrene	308.0	100–350	− 12.5753	10.73	56
	323.0	110–350	− 10.9059	10.09	56
	343.0	100–420	− 10.2415	11.05	56
Skatole	308.2	100–190	− 6.7598	7.32	42
Squalane	320.0	110–240	− 9.6692	11.43	67
	323.6	120–900	− 9.3449	11.34	50
	328.5	310–890	− 7.5097	9.93	50
	343.2	170–400	− 10.4032	14.41	50
	362.8	200–370	− 10.1945	15.79	50
	382.3	260–370	− 10.2417	17.36	50
Stearic acid	310.0	110–370	− 5.5392	3.07	67
	313.0	100–260	− 6.9297	5.00	43
	320.0	110–370	− 8.8289	8.73	67

TABLE 4. Correlation constants A and B in Eq. (4) calculated from literature solubility data—Continued

Compound	T (K)	P (bars)	A	$B \times 10^3$ ($m^3\ kg^{-1}$)	Reference
	333.0	100–260	− 3.3157	3.30	43
n-Tetracosane	310.0	110–260	− 7.4810	6.68	67
	320.0	110–260	− 12.1224	15.20	67
Titanium tetrachloride	328.0	60–85	− 1.0296	15.07	25
	349.0	60–105	− 0.8803	13.36	25
	368.0	60–140	0.0524	8.18	25
α-Tocopherol	298.0	100–160	− 9.3689	7.57	24
	313.0	100–190	− 19.8253	21.79	24
	313.0	100–260	− 14.5140*	13.66	43
	333.0	100–260	− 12.3815	16.00	43
	353.0	100–260	− 10.4634	18.61	43
Tributyrin	313.0	100–210	− 11.5596	14.61	43
	333.0	120–260	− 10.2935	16.27	43
Trihexylamine	310.0	110–140	− 15.5076	22.23	67
	320.0	110–160	− 7.8968	13.07	67
Trilaurin	313.0	100–260	− 16.1804	18.11	34
Trimyristin	313.0	100–310	− 14.7328	14.20	34
Trioctylamine	320.0	110–240	− 8.9313	11.43	67
Trioctylphosphine	320.0	110–260	− 8.5935	10.98	67
Trioctylphosphine oxide	310.0	110–210	− 13.9645	17.27	67
	320.0	110–210	− 11.2762	14.52	67
Triolein	313.0	100–260	− 11.1770	9.43	43
	323.0	100–260	− 8.6291	11.39	43
	343.0	100–260	− 9.8101	9.45	43
	353.0	100–260	− 7.8700	12.09	43
Tripalmitin	298.0	100–190	− 10.0929	3.61	24
	313.0	110–160	− 10.0195	3.70	24
	313.0	100–260	− 9.8100*	6.48	43
	313.0	120–300	− 20.2696	17.14	34
	333.0	100–260	− 9.2243	7.02	43
	353.0	100–260	− 7.9711	6.41	43
Triphenylamine	320.0	110–210	− 14.4011	15.57	67
Triphenylmethane	303.0	100–420	− 11.1948	10.89	56
	313.0	100–350	− 9.1482	9.50	56
	323.0	100–420	− 8.6541	9.50	56
Triphenylphosphate	310.0	110–280	− 10.7632	11.82	67
	320.0	110–280	− 10.1354	11.57	67
Triphenylphosphine	310.0	110–280	− 10.6076	10.86	67
	320.0	110–280	− 9.2576	10.16	67
Tristearin	313.0	100–210	− 19.1540	15.57	43
	333.0	120–260	− 17.8755	16.52	43
Water	304.0	100–560	− 6.6600	7.50	80
	323.0	100–720	− 2.6177*	4.16	80
	323.0	100–260	− 2.0226	2.98	43
	348.0	100–720	− 1.0174	3.41	80
	353.0	100–260	− 1.0428	3.30	43

TABLE 5. Densities of pure carbon dioxide in mol dm^{-3} from the Ely equation of state.[16]

P(bars)	100	150	200	250	300	350	400
T(K)							
308	16.253	18.555	19.706	20.511	21.141	21.665	22.115
313	14.379	17.764	19.117	20.018	22.525	21.270	21.750
318	11.441	16.897	18.500	19.510	20.263	20.869	21.381
323	8.809	15.939	17.853	18.988	19.811	20.464	21.009
328	7.414	14.888	17.177	18.452	19.351	20.054	20.634
333	6.604	13.769	16.472	17.902	18.884	19.639	20.256
338	6.052	12.633	15.744	17.341	18.411	19.221	19.877
343	5.639	11.547	15.002	16.770	17.932	18.800	19.496
348	5.312	10.572	14.257	16.194	17.450	18.377	19.113
353	5.042	9.738	13.524	15.616	16.966	17.952	18.731

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