Solubility Phenomena in Dense Carbon Dioxide Gas in

the Range 270–1900 Atmospheres

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A high-pressure gas chromatographic instrument has been used to measure the density dependent solubility of Carbowax 4000, Carbowax 1000, 1-octadecanol, and stearic acid in compressed CO_2 at 40°. It is shown that maxima exist in all these solubility curves at between 300 and 2500 atm, depending on the solute. This result is consistent with a form of regular solution theory developed for dense gaseous solvents. A comparison of theory and experiment relative to a number of parameters shows generally excellent qualitative agreement and in some instances a quantitative predictability.

Introduction

The enhancement of volatility caused by the presence of a dense gaseous atmosphere has been noted on many occasions.¹⁻¹³ Compression appears to give to the gas a positive solvent power not possessed in its normal, lowpressure state. This solvent power increases substantially with increasing compression. Studies of the phenomenon, which extend back to the last century,¹ are mainly limited to solute molecules of small and medium size and to pressures under 200 atm. Recently we have reported data on the solubility of biochemicals and polymers (molecular weight to 4×10^{5}) in dense NH₃ gas at 200 atm and dense CO₂ gas at pressures to 1560 atm.^{12,13} Here we extend this work by obtaining solubilities as a function of CO₂ density for Carbowax 4000, Carbowax 1000, 1-octadecanol, and stearic acid in CO_2 in the pressure range 270–1900 atm at 135-atm intervals. We show that there are maxima in the solubility curves not seen before and indeed not present in the low-pressure range. In our cases, the maxima for different solutes occur anywhere from 300 to 2040 atm. The existence of the maxima is predicted, and their locations well approximated, by the application of a form of regular solution-solubility parameter theory.

The impetus for recent studies in dense gas solubility comes from the realization that these gaseous "solvents" may be of unique value in enhancing the volatility of complex molecules so that they can be gas chromatographed.¹⁰⁻¹⁴ The sensitivity of solubility to pressure provides a rapid mechanical means for manipulating solubility both in chromatographic and in other systems. Experiments have borne out the fruitfulness of this approach.

Efforts to describe the solvent power of nonideal gases in quantitative, mathematical form have almost entirely used the virial approach. This direction has been followed for both chromatographic^{11,15–22} and nonchromatographic^{23–27} work. The virial treatment is rigorous, but is inapplicable at pressures much beyond 100 atm because of difficulties in evaluating higher virial coefficients and series convergence problems.⁹ Hence

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this method, which approaches dense gases from the ideal gas side, is not valid for the high densities studied here.

More likely to succeed, under the circumstances, would be an approach based on liquid solubility phenomena. Densities of practical interest are usually in the range 0.3–0.9 times the equivalent liquid density, while gases at 1 atm pressure, already showing measurable nonideal effects, are removed in density by several hundredfold from this range.

The principal difficulty with following the general path of liquid solution is that the latter are themselves imperfectly understood.²⁸ However, it is clearly more suitable to use approximate methods where the approximations are in accord with the physical situation than to stretch an exact theory (virial) far beyond its reasonable limit of application.

For the above reasons, we previously suggested and developed approximate methods for applying solubility parameter concepts to dense gaseous solutions.¹³ Some aspects of this approach will be tested here.

The key results of the theory are given in the following two equations. First the solubility parameter is a function only of density ρ , approximated by the linear relationship

$$\delta_{\rm g} = \delta_{\rm liq} [\rho / \rho_{\rm liq}] \tag{1}$$

and therefore reaches the value, δ_{liq} , characteristic of the parent liquid when the gas is compressed to the liquid density, ρ_{liq} . Solubility enhancement is related to this by

$$\ln I = (V_0 \delta_0^2 / RT) \Delta (2 - \Delta)$$
⁽²⁾

where I is the solubility enhancement, the solute concentration at saturation relative to its ideal gas value, V_0 and δ_0 are solute molar volume and solubility parameter, respectively, and Δ is the reduced solubility parameter of the compressed gas, δ_g/δ_0 .

The direct measurement of I is impractical for large solute molecules since ideal vapor pressures are immeasurably low (estimates of I will be given later). Instead, solubility relative to the maximum value is more appropriate here. From eq 2 this is

$$\ln (I/I_{\rm max}) = -(V_0 \delta_0^2 / RT) (\Delta - 1)^2$$
(3)

The above equations are approximations which do not adequately allow for density-dependent entropy effects, pressure-volume effects, and the various molecular subtleties which render regular solution theory itself inexact. They are looked to more as a guide to qualitative effects and to rough quantitative estimates, both presently needed in this field.

Experimental Section

The high-pressure apparatus used in this study was basically like that described elsewhere.^{12,29} A schematic diagram which helps illustrate the procedure is



Figure 1. Schematic of high-pressure unit: 1, 2, 3, on-off valves; A, B, sample chambers; P, pyrolysis unit; V, pressure reducing valve; D, detector.

given in Figure 1. Modifications to the previous apparatus are as follows.

Pyrolysis Unit. It has been pointed out often that the dissolved molecules become thermodynamically unstable upon decompression and tend to condense out.^{7,8,12,30} This leads to line clogging and consequently to alteration or stoppage of flow to the detector. It was suggested that pyrolysis at the downstream end of the column prior to decompression may eliminate this difficulty.¹² For this reason a pyrolysis unit was incorporated into the system.

The structure of the pyrolysis unit is shown in Figure 2. It consists of approximately 20 cm of 0.015-cm i.d. stainless steel tubing which is heated to about 650°. The outer tubing acts both as a form on which the heating wire is wound and also as a guard in the event of rupture of the inner tubing. From our experience, such a unit can withstand pressures up to 30,000 psi without failure. This, however, is not true for ammonia, where a few leaks have been encountered.

Pressure Reducing Valve. A new type of valve has been constructed which maintains very stable flow for long periods of time. A detailed description of this valve will appear elsewhere.

Splitter. The splitter and the back pressure regulator have been eliminated because of the availability of controlled flow. Under these conditions the entire sample is swept into the detector.

Detection System. The detector was a Beckman GC-4 flame ionization detector. Provisions were made to ensure constant air and hydrogen supply to the detector. The detector signal was fed into a Cary Model 31 electrometer which was coupled to a Speedomax Type G

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Figure 2. The pyrolysis unit: A, stainless steel tube, 0.006 in. i.d.; B, Fiberglas insulation; C, heating wire; D, thermocouple; E, outer tubing.

recorder. The voltage to the detector was supplied by a 300-V battery. All experiments were carried out at $40 \pm 1^{\circ}$.

Solutes. The stearic acid was obtained from Merck and Co., Inc., and the 1-octadecanol from Eastman Kodak. These compounds were recrystallized three times from hot water; only the first portion of solute to crystallize was used. The solutes were then dried, melted, and cooled under vacuum.

The two Carbowaxes (1000 and 4000) were supplied by Applied Science Laboratory.

Experimental Procedure. Prior to each experiment, sample chambers A and B and the tubing between valves 1 and 2 (see Figure 1) were washed with organic solvents, ethanol, and finally distilled water. After drying, the sample chambers were installed and pressurized to 1900 atm. By using valves 1, 2, and 3, the gas was directed through the sample loop and finally into the detector. When the recorder signal dropped to the limit of detectability, it was assumed that organic impurities were adequately purged. The sample chambers were then removed from the system for charging with solute. The sample chambers were filled to capacity, this requiring about 1 cm³ of solute. They were then returned to the system and pressurized to 1900 atm. Extreme care was taken to avoid contamination during filling.

A plug of solute vapor can be obtained by momentarily routing the gas flow through the sample loop. Plug sampling, however, introduced too much uncertainty into the data. Even with considerable care the peak size varied $\pm 6\%$.

A superior way for determining solute concentration in the dense gas is by the constant plateau method. Here the carrier gas is flowed steadily through the sample loop for 15–20 min. The recorder trace showed a steep rise followed by a constant plateau. The height of the plateau is proportional to the solute concentration in the carrier gas and to the flow rate, and thus can be used to measure equilibrium concentrations.

The plateau method can be used to check on and correct for the presence of impurities and the possible lack of solubility equilibrium.

Impurities (light hydrocarbons, etc.) were apparent on several occasions, particularly with octadecanol. They were observed and allowed for as follows. Following 30 min of static equilibration, flow causes a steep signal rise, a short plateau, and a slow signal decay to a

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new plateau. With repetition of this process the initial rise becomes progressively smaller until a true and reproducible plateau trace is obtained. Apparently at this point the volatile impurities have been extracted. This repetition test was made for all systems.

Lack of solubility equilibrium is indicated by a sharp rise, a short plateau, and a decay. Repetition does not lead to a steady plateau. Saturation could be improved by reducing the flow, but this reduces the detector signal. One could also increase the size or length of the sample chamber and sample, thus giving a longer contact time with the carrier gas. It is for this reason that two sample chambers were joined in series in the present study. Sample chamber A can be thought of as a presaturator. Satisfactory saturation was thus achievable with all compounds attempted except Carbowax 6000; the latter was thus not studied further.

Calibration Procedure. To estimate the absolute values of solubilities in compressed gases, the signal size requires calibration. Since the detector responses for the compounds used in this work are unknown, approximate calibration is achieved using the principle that the signal from a flame ionization detector is roughly proportional to the flux of carbon atoms into the flame. A relative response factor, or equivalently, an effective carbon atom number, which accounts for the bonding of carbon atoms to noncarbon atoms, must be employed.

Propane was used as the reference compound. Ten $60-\mu$ l peaks were passed through the detector. Assuming the ideal gas law, each peak contained 2.10×10^{-6} mol of propane or 6.29×10^{-6} g-atoms of carbon. From this and the mean area per peak, it was determined that the number of effective gram-atoms of carbon in unit time was equal to

$$\frac{m}{t} = 0.90 \times 10^{-2}R \times E \tag{4}$$

where R is the recorder response in tenths of an inch and E the electrometer setting in millivolts. The outlet gas flow rate was held constant at 39 cc/min. Assuming the CO₂ to be ideal under outlet (atmospheric) conditions, this corresponds to a CO₂ flux of 2.3 \times 10⁻⁵ mol/sec. Thus the mole fraction of solute in the dense gas is simply

$$X_2 = 3.0 \times 10^{-8}R \times E/\theta \tag{5}$$

where θ is the number of effective carbon atoms in the molecule in relationship to detector response.

Pyrolysis Products. The products of the high pressure pyrolysis of Carbowax 4000 were examined by sampling the column effluent into a low-pressure Poropak Q-S column. Pyrolysis constituents were identified by relative retention times.

Results and Discussion

Density Dependence of Solubility. The accurate mea-

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Figure 3. Detector response $(R \times E)$ and relative solubility $(X_2/X_{2,\max})$ at 40° as a function of CO₂ density, ρ , solubility parameter, δ , and pressure, P.

surement of relative solubility changes in dense gases by our procedure hinges on the assumption that essentially all the solute reaches the detector in some form. However, without pryolysis or with only partial pyrolysis, the dissolved solute would be inclined thermodynamically to condense upon decompression and would perhaps not reach the detector. This tendency has been observed many times.^{5,7} Evidence against any significant condensation in our case is the failure of the small flow lines to the detector to plug after prolonged use, including that with a continuous 2-hr, high level Carbowax 4000 plateau at 1900 atm. However, with the pyrolyzer unit unheated the detector signal was very small and the flow fell off rapidly, presumably due to Thus we conclude that, with pyrolysis, the clogging. solute reaches the detector in some form in nearly quantitative amounts.

Figure 3 shows the logarithmic variation of detector response $(R \times E)$ with CO₂ density for the four compounds. The curves are also shown as log (I/I_{max}) + constant, equivalent to log $(X_2/X_{2,\text{max}})$ + constant, where $(X_2/X_{2,\text{max}})$ is the mole fraction of solute relative to its maximum volume and the constant represents vertical displacement depending on θ , eq 5. The heights at the signal maxima are seen to be fairly close to one another.

Also on the abscissa of Figure 3 is a solubility parameter scale and entries for pressure. The pressuredensity conversion was made using data for CO_2 found in the literature.³¹⁻³⁵

The gaseous solubility parameter was calculated from eq 1. When δ_{liq} is approximated by $1.25P_o^{1/2}$ (with P_o in atmospheres) the value 10.7 $(cal/cm^3)^{1/2}$ is obtained. With $\rho_{liq} = 1.25$ g/cm³, we have $\delta =$ 8.54ρ . This coefficient may be in error up to 10% due to uncertainties in δ_{liq} and ρ_{liq} .

The reproducibility and precision of the data were checked by obtaining two independent sets of data for Carbowax 4000 and stearic acid. As shown in Figure 3, the duplicated experiments yield points lying essentially on top of one another. This is in accord with our observation that the solubility plateau was steady with little tendency to drift.

Equations 2 and 3 are effective expressions for solubility (or solubility enhancement) in volume concentration while our experiments, because a constant mass flux of solvent gas is employed, lead directly to mole fraction solubilities. While the two are not exactly proportional to one another because of variable gas density, a virtual proportionality exists within experimental limits. This occurs because a hundredfold solubility change is induced by a density change of only 5-30%. Therefore we expect, providing solubilities remain fairly small, a parabolic expression for log ($E \times R$) or log (X_2), *i.e.*

$$\log X_2 = a\delta^2 + b\delta + C \tag{6}$$

This equation has been fit to the data, yielding the solid lines in Figure 3. The function seems certainly of the right general form. A comparison of coefficients in eq 2 and 6 yields the apparent molar volume and solubility parameter for solute

$$V_0 = -2.3RTa \tag{7}$$

$$\delta_0 = -b/2a \tag{8}$$

In Table I these experimentally derived quantities are shown in comparison with values obtained independently. This comparison is of some significance and will be discussed at length in the next subsection.

The most novel feature of the results in Figure 3 is the decrease in the solubility of octadecanol and stearic

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P* (previ-

ous).

atm

190

115

P*

atm

162

91

76

Table I:	Solubility	Propertie	s of the Four	Solutes in	CO ₂ at 40°	5			
Sol	ute	$\delta_0({ m eq~8}), ({ m cal}/{ m cm^3})^{1/2}$	$\delta_0(\text{calcd}),$ $(\text{cal/cm}^3)^{1/2}$	V₀(exptl), cm ³	V₀(calcd), cm ³	$\epsilon = \frac{V_0(\text{exptl})}{V_0(\text{caled})}$	I_{\max}	X_{\max}	${f Mol} {f wt}$

2800

865

329

328

0.186

0.238

0.780

0.416

 5.6×10^{54}

 1.1×10^{21}

 1.7×10^{17}

 6.7×10^{8}

520

206

257

136

acid with increasing pressure. This effect, consistent with eq 2 and 3, has not been previously observed.

 10.7 ± 0.9

 10.7 ± 0.8

8.5

8.6

10.8

10.9

7.9

7.6

The apparent existence of maxima in the continuous solubility-density curves of Figure 3 which lead to this peculiar phenomenon are, in fact, analogous to the formation of maxima in solubility-polarity plots with liquid mixtures. The explanation is presumably the same. The excess energy of mixing is a minimum when the cohesive energy densities are roughly equal for solute and solvent. Therefore the dense gas solubility parameter at a given maximum should equal the solubility parameter of the particular solute. This is in accord with eq 2 and 3, and, as we shall see in the next subsection, can be broadly confirmed for our specific group of solutes. Since these solutes have different solubility parameters, the maxima in Figure 3 are horizontally displaced from one another.

Although the present experimental pressure range, 270-1900 atm, is rather broad, it covers a relatively incompressible region well above the critical pressure. Thus the density and solubility parameter vary only about 25% in our experiment. While this has a very large effect on solubility, as Figure 3 illustrates, the limited range makes it difficult to show a clear solubility maximum with both descending branches distinctly exhibited. Nonetheless, the existence of a maximum is rather certain from (a) the shape of the curves in the experimental range, and (b) the fact that octadecanol and stearic acid are effectively nonvolatile at low pressures and must therefore have a descending branch on the left to complement the observed one on the right. In fact, previous work has been done with octadecanol on other instrumentation which shows a threshold pressure of 98.7 atm.¹³ This is equivalent to another point (actually a cluster of points) on the plot at (0, 4.8). Such an addition clearly requires a maximum in the solubility curve.

Figure 3 shows that the solubility peaks differ in width. From eq 2 it can be shown that the half-width is

$$\delta_{\rm g} - \delta_{\rm g,max} = \left[\frac{2.3RT}{V_0} \left(\log I_{\rm max} - \log I\right)\right]^{1/2}$$
(9)

so that the width at any level below the peak maximum is related to solute mole volume as $V_0^{-1/2}$. Thus larger molecules have narrower solubility peaks, as strikingly

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confirmed by the Carbowax 4000 and 1000 peaks in Figure 3. This is another instance where liquid and dense gas solubility phenomena follow parallel trends.

 2.4×10^{-4}

 1.5×10^{-3}

 1.6×10^{-3}

 1.5×10^{-3}

Solubility Enhancement. The enhancement in solubility (or volatility) relative to that for the ideal gas reaches very large proportions. At the solubility maxmum it is given by

$$I_{\rm max} = \exp(V_0 \delta_0^2 / RT) \tag{10}$$

3350

1000

284

270

Values of I_{max} are tabulated in Table I. For Carbowax 4000 the maximum enhancement is seen to be in excess of 10⁵⁰, reflecting mainly its extremely low vapor pressure under ideal conditions.

Absolute Solubility. The absolute magnitude of the equilibrium solute concentration can be approximated using the calibration procedure mentioned earlier. However, some uncertainty exists because of the need to estimate effective carbon numbers (θ in eq 5). For stearic acid and octadecanol we assumed θ as the number of carbon atoms in the molecule minus one, the excluded one corresponding to a carbon presumably tied up in nondetectable form (CO₂ or CO) in the pyrolysis products. For Carbowax 4000 (mean molecular weight, 3350) we assumed $\theta = 75$, the other half of the carbon atoms again presumably tied up in nondetectable form.

The results for the mole fraction of solute at the solubility peak, X_{max} , calculated from eq 5, are shown in Table I. Solubilities at other δ values may be calculated from eq 6 or obtained from the relative solubility plots in Figure 3.

Threshold Pressures. Of great experimental importance, particularly to gas chromatography, is the threshold pressure, P^* , the applied pressure which is barely sufficient to bring volatility to a measurable level. Since the solubility is an extremely steep function of pressure for large molecules, this parameter is nearly constant with reasonable variations in the sensitivity of the detection device.

For the present system, $R \times E = 1$ serves as the lowest limit of detection. Since none of the measurements was made near the threshold level, the latter was calculated assuming a parabolic dependence of the solubility signal on δ as in eq 6. Conversion from the obtained δ value to density and then to pressure yields the P^* values shown in Table I. Values obtained pre-

Carbowax 4000

Carbowax 1000

1-Octadecanol

Stearic acid

viously on a different apparatus are shown in the subsequent column. The agreement is satisfactory.

It is interesting that the present theory predicts two threshold pressures, only the lower of which has been observed. Gas densities necessary to reach the upper threshold are impractical with most systems, but clearly exceptions exist which should be experimentally tractable.

Pyrolysis Products. Methane was the major detectable pyrolysis product for Carbowax 4000. The methane peak was followed by ethane and ethylene peaks in slightly smaller amounts. There were then several minor peaks of propane, propylene, etc. Only slight shifts in the pyrolysis pattern were noted with a twofold change in flow. The pattern was also rather stable with changes in the age of the pyrolyzer.

Effective Solubility Parameters and Volumes. The solubility parameters in columns 2 and 3 of Table I are obtained from eq 8 in combination with the experimental data and from independent calculations, respectively. The calculated δ_0 for stearic acid was obtained from data given by Beerbower and Dickey;³⁶ values for 1-octadecanol and the Carbowaxes were calculated by known procedures.^{37, 38} The Carbowax δ_0 's appear as a range because of the uncertainty in the oxygen contribution. Small suggests a contribution of 70 (cal ml)^{1/2}.³⁷ Available V_0 and δ_0 values³⁷⁻³⁹ suggest that the ether oxygen contribution varies drastically with molecular size and shape. Molecules such as dioxane and triethylene glycol suggest values in the neighborhood of 140 (cal ml)^{1/2}. Use of 70 and 140 (cal ml)^{1/2} gives the lower and upper limits, respectively, of δ_0 (calcd) for the Carbowaxes in Table I. The agreement between experimental and calculated δ_0 values is excellent considering the inherent uncertainties in both values and in the underlying theory. In particular the relative displacement of the Carbowax maximum upscale from that for 1-octadecanol and stearic acid in Figure 3 is exactly as predicted.

The agreement on molar volume, columns 4 and 5 of Table I, is far less satisfactory. To a degree such discrepancies are consistent with studies of liquid mixtures. "Effective volume" parameters have been used to account for molecular shape differences. Martire defines the parameter ϵ where $\epsilon = V_0^*/V_0$, the ratio of effective to actual volumes.^{40, 41} His ϵ values for several solutes were in the range 0.74–1.0. Values less than unity also occur for our solutes, column 6.

A plot of log ϵ vs. (mol wt)⁻¹, shown in Figure 4, yields a straight line, again with the exception of stearic acid. If stearic acid were "normal" on this plot its ϵ value would be 0.390 and its "experimental" volume thus 129 cm³. Actual values are twice this, suggesting dimer formation in the dense gas phase. The stearic acid points in Figure 4 are based on the assumption of dimer formation.

The reason for the considerable departure of ϵ from

unity is not clear. Martire⁴⁰ found this parameter to be independent of the particular solvent in a given class. He also attempted to correlate the ϵ values with the solution process. From solution-density measurements carried out at various concentrations, he showed that the partial molar volumes at infinite dilution were close to the pure solute molar volumes and that no apparent correlation existed with the ϵ values.

The present results, Figure 4, indicate that the ϵ values do not vary in a random manner for the large solute species dealt with here, and that they can be related to the molecular weight. However there is no obvious theoretical basis for the empirical straight line correlation between log ϵ and (mol wt)⁻¹.



Figure 4. Correlation of $\epsilon = [V_0(\text{exptl})/V_0(\text{calcd})]$ with molecular weight.

It is possible that ϵ is consistently less than unity for large molecules because the latter, in a poor solvent, will tend to form intramolecular contacts in place of solute-solvent contacts. A reduced energy of mixing will be associated with the reduced number of contacts, leading to enhancement of the expected solubility. This is precisely the effect of $\epsilon < 1$. In the limit the solute molecules will assume a spherical form, and since intermolecular energy can be associated with inter-

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facial contacts,⁴² ϵ may approach the ratio of the respective surface areas of a sphere and an extended chain. In this case ϵ should be in proportion to (mol wt)^{-1/3} and a plot of log ϵ vs. log M should form a straight line of slope $-1/_3$. Figure 4, in which the dashed line has $-1/_3$ slope, demonstrates reasonable agreement with this hypothesis. However, more evidence is needed before any firm conclusions about the phenomenon can be made.

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