

Table I: Solubility Properties of the Four Solutes in CO₂ at 40°

Solute	$\delta_0(\text{eq 8}),$ (cal/cm ³) ^{1/2}	$\delta_0(\text{calcd}),$ (cal/cm ³) ^{1/2}	$V_0(\text{exptl}),$ cm ³	$V_0(\text{calcd}),$ cm ³	$\epsilon =$ $V_0(\text{exptl})/V_0(\text{calcd})$	$I_{\max}$	$X_{\max}$	Mol wt	$P^*,$ atm	P^* (previous), atm
Carbowax 4000	10.8	10.7 ± 0.9	520	2800	0.186	5.6 × 10 ⁵⁴	2.4 × 10 ⁻⁴	3350	162	190
Carbowax 1000	10.9	10.7 ± 0.8	206	865	0.238	1.1 × 10 ²¹	1.5 × 10 ⁻³	1000	91	115
Stearic acid	7.9	8.5	257	329	0.780	1.7 × 10 ¹⁷	1.6 × 10 ⁻³	284	76	
1-Octadecanol	7.6	8.6	136	328	0.416	6.7 × 10 ⁸	1.5 × 10 ⁻³	270		

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

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

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

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

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.

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

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

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-

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 $\log \epsilon$ 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 $\log \epsilon$ and (mol wt)⁻¹.

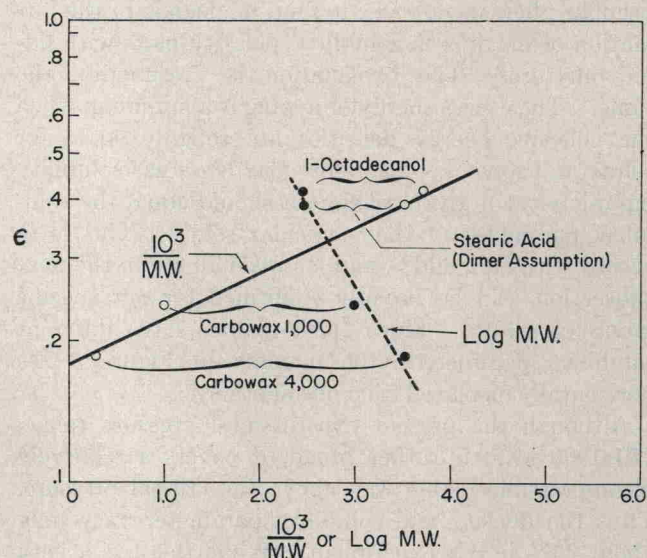


Figure 4. Correlation of $\epsilon = [V_0(\text{exptl})/V_0(\text{calcd})]$ with molecular weight.

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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