

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 cm<sup>3</sup> 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

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 pre-saturator. 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  $2.10 \times 10^{-6}$  mol of propane or  $6.29 \times 10^{-6}$  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

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

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 CO<sub>2</sub> to be ideal under outlet (atmospheric) conditions, this corresponds to a CO<sub>2</sub> flux of  $2.3 \times 10^{-5}$  mol/sec. Thus the mole fraction of solute in the dense gas is simply

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

where  $\theta$  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-



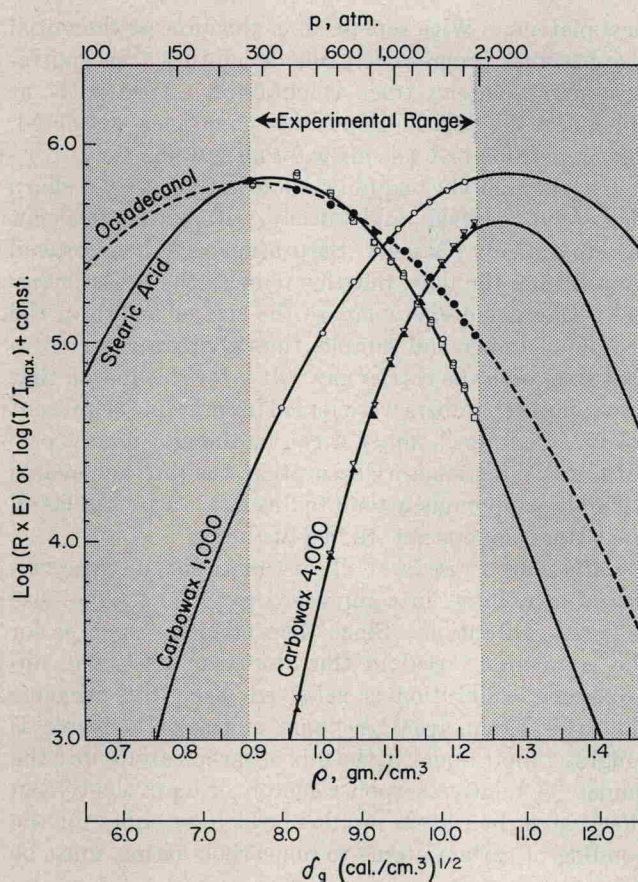


Figure 3. Detector response ( $R \times E$ ) and relative solubility ( $X_2/X_{2,\max}$ ) at  $40^\circ$  as a function of CO<sub>2</sub> density,  $\rho$ , solubility parameter,  $\delta$ , and pressure,  $P$ .

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 pyrolysis 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.<sup>5,7</sup> 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 clogging. Thus we conclude that, with pyrolysis, the solute reaches the detector in some form in nearly quantitative amounts.

Figure 3 shows the logarithmic variation of detector response ( $R \times E$ ) with CO<sub>2</sub> density for the four compounds. The curves are also shown as  $\log (I/I_{\max}) + \text{constant}$ , equivalent to  $\log (X_2/X_{2,\max}) + \text{constant}$ , where ( $X_2/X_{2,\max}$ ) is the mole fraction of solute relative to its maximum volume and the constant represents vertical displacement depending on  $\theta$ , 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 pressure-density conversion was made using data for CO<sub>2</sub> found in the literature.<sup>31-35</sup>

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

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.

$$\log X_2 = a\delta^2 + b\delta + C \quad (6)$$

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

$$V_0 = -2.3RTa \quad (7)$$

$$\delta_0 = -b/2a \quad (8)$$

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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