Figure 3. Detector response $(R \times E)$ and relative solubility $(X_2/X_{2,max})$ at 40° as a function of CO_2 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 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.[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 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_2 density for the four compounds. The curves are also shown as $\log (I/I_{max})$ + constant, equivalent to $\log (X_2/X_{2,max})$ + 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 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 pressure–density 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 $1.25 P_c^{1/2}$ (with P_c in atmospheres) the value 10.7 $(cal/cm^3)^{1/2}$ is obtained. With $\rho_{liq} = 1.25$ g/cm³, we have $\delta = 8.54\rho$. 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.

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

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

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

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

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

(31) E. W. Washburn, C. J. West, N. E. Dorsey, F. R. Bichowsky, and A. Klemenc, "International Critical Tables," Vol. 3, McGraw-Hill, New York, N. Y., 1928, p 11.

(32) A. Michels and C. Michels, *Proc. Roy. Soc., Ser. A*, **153**, 201 (1935).

(33) A. Michels, C. Michels, and H. Wouters, *ibid.*, **153**, 214 (1935).

(34) G. C. Kennedy, *Amer. J. Sci.*, **252**, 225 (1954).

(35) A. Michels, A. Botzen, and W. Schuurman, *Physica*, **23**, 95 (1957).