

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.

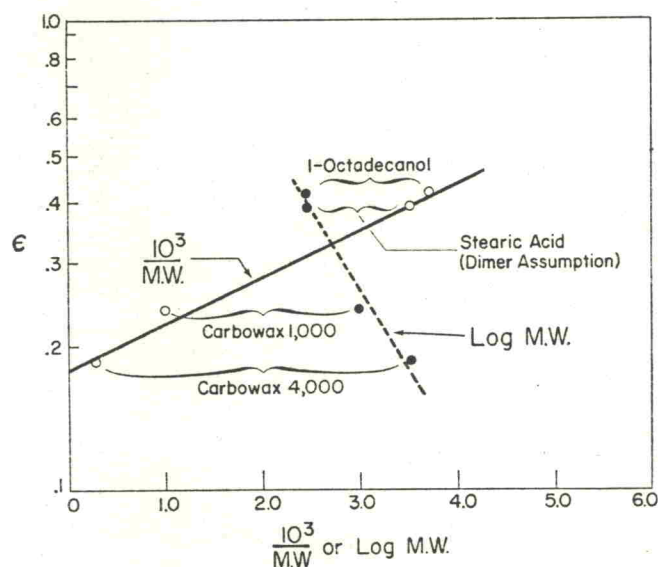


Figure 4. Correlation of $\epsilon = [V_0(\text{exptl})/V_0(\text{calcd})]$ with molecular weight.

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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