# Cryoscopic Studies of High Boiling Fluids in Benzene

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THE MOLECULAR weights of high boiling fluids are often determined by freezing point depression or boiling point elevation. Previous investigations (*8*, *9*) have shown that these apparent weights usually depend on concentration. When accurate values are desired, freezing point depressions must be determined at several concentrations and the data extrapolated to infinite dilution to eliminate solute-solvent interaction effects. The present investigation was undertaken to determine the nature of the concentration effects for solutions of high molecular weight fluids (300 to 1000) of various structures and compositions in benzene. The results should serve as a guide in establishing the reliability of cryoscopic molecular weights of petroleum fractions, polymer fluids, and high molecular weight esters of several types.

The cryoscopic data can also be used to characterize solutions in terms of conformation or departure from ideal behavior. Thus, it is possible to distinguish between negative and positive deviations and to determine quantitatively the magnitude of the deviations. This provides a means of relating the composition of solute and solvent to solution behavior.

## EXPERIMENTAL

**Materials Used.** The benzene used as solvent was Mallinckrodt C. P., thiophene free. It was purified further by freezing it completely and then discarding the first 10% which melted. The remainder was distilled from phosphorous pentoxide through a Vigreaux column. The first 10% to distill over was discarded and the middle fraction which distilled at a temperature of 79.9 ±0.1° C. at 756.2 mm. of mercury was retained for the cryoscopic studies.

The high boiling fluids were obtained from various sources. Mineral oil A, paraffinic, aromatic free, viscosity 31 centistokes at 25° C., from Esso Standard Oil Co. Mineral oil B, paraffins, aromatic free, viscosity 83 centistokes at 25° C., from Esso. Mineral oil C, paraffinic, aromatic free, viscosity 142 centistokes at 25° C., from Esso. Naphthenic base petroleum oil D, viscosity 68 centistokes at 25° C., from Sun Oil Co. Naphthenic base petroleum oil E, viscosity 68 centistokes at 25° C., from Texaco Inc. Alkylated naphthalene, viscosity 322 centistokes at 25° C., from Shell Oil Co. Diundecyl sebacate, distilled at 185° C. at 0.3mm. of mercury in a spinning blade still, $n_D^{25}$ 1.4501, prepared at General Electric Research Laboratory, Schenectady, N. Y. 2,2,3-Trimethyl-1,3-pentanediol dilaurate, $n_D^{25}$ 1.4509, from Tennessee Eastman Co. Pentaerythritol ester (Hercoflex 600), from Hercules Power Co. 2,2-Dimethylhydracrylate phosphoric acid ester, $n_D^{25}$ 1.4409, from Tennessee Eastman Co. Di(1,1,7-trihydroperfluoroheptyl) *dl*-camphorate, $n_D^{25}$ 1.3699, from E. I. du Pont de Nemours and Co. Poly(alkalene glycol), (Ucon D-50-HB-160-E), from Union Carbide Corp. Poly-(alkalene glycol) (Ucon 50-HB-260), from Union Carbode. Poly(*sec*-butyl silicate), viscosity 55 centistokes at 25° C., from Montrose Chemical Co. Poly(trifluorovinyl chloride) (Fluorolube MO-10), from Hooker Electrochemical Co.

**Freezing Point Apparatus.** The freezing points were determined with a modified Beckman apparatus (*2*). A mechanical stirrer uniformly agitated the benzene or solution. Cooling was accomplished by a glass double-wall water bath containing a copper coil through which cold water was circulated. The operation of the circulating pump was controlled by a thermo-regulator. Thus, the temperature differential between the air-jacketed freezing tube and the cooling bath was kept at about 1° C. Supercooling was minimized by allowing the glass stirring rod to strike against the wall of the freezing tube. The freezing tube was sealed at all times except when additions of solutes were made. This prevented moisture from condensing in the solutions. The stirrer shaft was introduced through a long, close-fitting sleeve which provided an effective seal when properly lubricated.

**Solutions and Measurements.** Dry benzene (20 cc.) was transferred quantitatively to the freezing tube which was immediately stoppered and cooled. The freezing point of the pure benzene was determined; it was allowed to melt, and the desired amount of liquid solute was added through the side arm of the freezing tube with a small pycnometer. The low vapor pressure of the solutes facilitated the accurate determination of the quantities added.

The freezing point of the benzene solution was then determined. This measurement was repeated until good agreement (±0.002° C.) was achieved in two consecutive determinations. Two measurements usually sufficed, and no continuous changes were observed in these repeated measurements. Subsequent additions of high boiling solute were made to the same solution until freezing point data had been determined for four or five concentrations.

## TREATMENT OF DATA

The equation for the activity of a solid at temperatures near its melting point is given by Lewis and Randall (*7*).

$$\ln a_s = \frac{1}{RT_0^2}\left[ L_s + \left(\frac{L_s}{T_0} - \frac{\Delta C_p}{2}\right)\theta^2 + \left(\frac{L_s}{T_0^2} - \frac{2\Delta C_p}{3\,T_0}\right)\theta^3 + \ldots\right] \tag{1}$$

where $a_s$ is the activity of the solid, $T_0$ is the absolute freezing point, $L_s$ is the molal heat of solidification at the freezing point, $\theta$ is a small temperature increment below the freezing point—i.e., the freezing point depression—and $\Delta C_p$ is the molal heat capacity of the solid less that of the liquid.

According to Bury and Jenkins (*1*) the values for pure benzene are $T_0 = 278.6$, $\Delta C_p = 28.3 - 31.0 = -2.7$ gram calories, and $L_s = -2349.4$ gram calories. As a check on the difference in molal heat capacity of solid and liquid benzene (−2.7 gram calories) the data of Huffman, Parks, and Daniels (*4*) for the specific heat capacity of crystalline and liquid benzene were extrapolated to 278.6° K. The discontinuity in the two curves indicates a difference in molal heat capacities of about −0.6 gram calories. Fortunately the $\Delta C_p$ term makes but a small contribution to the higher order $\theta$ coefficients of Equation 1. For small values of $\theta$, the differences resulting from the use of −2.7 or −0.6 are negligible.

The values of Bury and Jenkins were substituted into Equation 1. For an ideal solution, the activity of the solvent can be replaced by its mole fraction. Then

$$\text{Log } X_1 = 2.8156 \times 10^{-6}(-2349.4\theta - 7.08290^2 - 0.02381\theta^3 + \ldots) \tag{2}$$

For small values of θ (less than 2°), the third and higher order θ terms become negligible and

$$\log(1 - 0.7811\, w_2/M_2) = 0.006615\theta - 0.000020\theta^2 \qquad (3)$$

This equation applies to 100 grams of benzene and the moles of solute, $w_2/M_2$, are regarded as negiligible with respect to the moles of solvent.

To expedite calculations, the working equation can be put into an exponential form: $w_2/M_2 = \frac{1 - 10^{-(a\theta + b\theta^2)}}{c}$ where $a = 0.006615$, $b = 0.000020$, and $c = 0.7811$. A computer then readily solves this equation for $w_2/M_2$ for all values of θ in the range 0.010 to 2.000 at increments of 0.001. Thus, the value of $w_2/M_2$ can be obtained from a table for any value of θ. $M_2$ is calculated by expressing the weight of the solute in grams per 100 grams of benzene.

## RESULTS AND DISCUSSION

Table I summarizes the results: $w_2$ is the grams of solute per 100 grams of benzene, θ is the depression of the freezing point, and $M_2$ is the apparent molecular weight as calculated from Equation 3. The covariance of $M_2$ and $w_2$ is established, and the regression line is extrapolated mathematically to the intercept $w_2 = 0$. This value of the molecular weight at infinite dilution, $M_0$, is used to calculate the molality of the solution, $m$. These data, as well as the $\theta/m$ ratio, are given in Table I.

The values of $M_0$, the slopes of the regression lines and the standard deviations of the intercepts, $S_a$, are given in Table II. The last named values are of interest because they are a measure of uncertainty of $M_0$. For comparative purposes, these probable errors are also expressed as percentages of the $M_0$ values.

Solution behavior is interpreted by studying the covariance of the $\theta/m$ ratio with $m$. Bury and Jenkins plotted $\theta/m$ as a function of θ in their work. The substitution of $m$ for θ enhances the physical significance of the results. The graphs reflect the rate of change of the freezing point depression with concentration expressed as a function of the concentration.

The relation for an ideal solution is readily computed from Equation 3 and is shown in Figure 1, curve *B*. This curve departs very slightly from linearity and is almost parallel to the $m$-axis. It intersects the $\theta/m$ axis at 5.12. The behavior of several nonideal solution "types" is also illustrated in Figure 1. Solutions exhibiting "normal" positive deviations from Raoult's law extrapolate to the

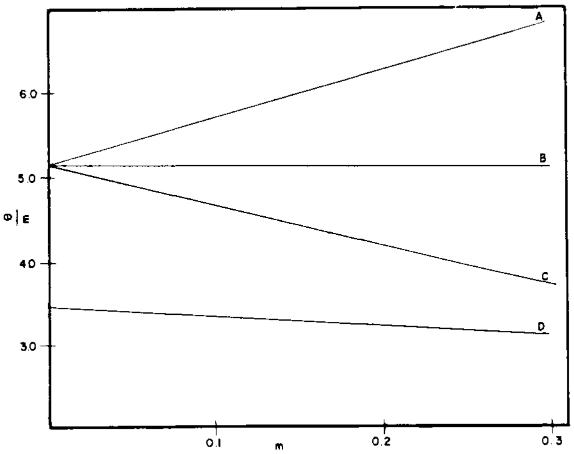


Figure 1. Freezing point behavior of typical benzene solutions

*A* Negative deviations
*B* Ideal solution
*C* Positive deviations
*D* Solid solution

Table I. Cryoscopic Data for Benzene Solutions[a]

| $w_2$ | θ | $M_2$ | $m$ | $\theta/m$ |
|---|---|---|---|---|
| | | Petroleum Oil A | | |
| 0.9967 | 0.176 | 290.7 | 0.0352 | 5.00 |
| 1.9429 | 0.342 | 291.8 | 0.0686 | 4.99 |
| 3.1670 | 0.539 | 302.1 | 0.1118 | 4.82 |
| 4.1225 | 0.690 | 307.4 | 0.1456 | 4.74 |
| 5.1634 | 0.849 | 313.1 | 0.1823 | 4.67 |
| | | | $M_0 = 283.2 \pm 0.8$[b] | |
| | | Petroleum Oil B | | |
| 1.6175 | 0.247 | 336.2 | 0.0515 | 4.80 |
| 1.7755 | 0.258 | 353.3 | 0.0565 | 4.57 |
| 3.1148 | 0.430 | 372.2 | 0.0992 | 4.33 |
| 3.5167 | 0.475 | 380.5 | 0.1120 | 4.24 |
| 5.0069 | 0.637 | 404.3 | 0.1594 | 4.00 |
| | | | $M_0 = 314.1 \pm 2.7$ | |
| | | Petroleum Oil C | | |
| 1.1636 | 0.159 | 375.6 | 0.0321 | 4.95 |
| 2.5187 | 0.307 | 421.3 | 0.0694 | 4.42 |
| 4.1178 | 0.488 | 433.7 | 0.1135 | 4.30 |
| 5.2486 | 0.594 | 454.4 | 0.1446 | 4.11 |
| | | | $M_0 = 362.9 \pm 5.7$ | |
| | | Petroleum Oil D | | |
| 1.5386 | 0.245 | 322.4 | 0.0485 | 5.05 |
| 3.8072 | 0.592 | 330.8 | 0.1200 | 4.93 |
| 5.8788 | 0.912 | 331.9 | 0.1853 | 4.92 |
| 7.6163 | 1.160 | 338.5 | 0.2401 | 4.83 |
| 10.3476 | 1.530 | 349.3 | 0.3262 | 4.69 |
| | | | $M_0 = 317.2 \pm 1.3$ | |
| | | Petroleum Oil E | | |
| 1.5901 | 0.293 | 278.7 | 0.0584 | 5.02 |
| 4.0433 | 0.684 | 304.0 | 0.1486 | 4.60 |
| 6.3430 | 1.024 | 319.2 | 0.2331 | 4.39 |
| 8.6884 | 1.371 | 327.0 | 0.3193 | 4.29 |
| | | | $M_0 = 272.1 \pm 3.0$ | |
| | | Alkylated Naphthalene | | |
| 1.5832 | 0.304 | 267.4 | 0.0596 | 5.10 |
| 3.4954 | 0.679 | 264.8 | 0.1316 | 5.16 |
| 6.2749 | 1.217 | 265.9 | 0.2363 | 5.15 |
| 8.2092 | 1.592 | 266.4 | 0.3091 | 5.15 |
| 9.5243 | 1.834 | 268.6 | 0.3586 | 5.11 |
| | | | $M_0 = 265.6 \pm 0.7$ | |
| | | Diundecyl Sebacate | | |
| 1.2467 | 0.167 | 383.1 | 0.0335 | 4.99 |
| 2.4052 | 0.302 | 409.0 | 0.0647 | 4.67 |
| 3.6298 | 0.437 | 426.8 | 0.0977 | 4.47 |
| 4.8475 | 0.578 | 431.3 | 0.1304 | 4.43 |
| | | | $M_0 = 371.7 \pm 3.9$ | |
| | | Dilaurate Ester | | |
| 1.2002 | 0.154 | 399.9 | 0.0301 | 5.12 |
| 3.2423 | 0.364 | 457.6 | 0.0814 | 4.47 |
| 4.6905 | 0.521 | 462.6 | 0.1177 | 4.43 |
| 6.3257 | 0.700 | 464.8 | 0.1587 | 4.41 |
| | | | $M_0 = 398.5 \pm 9.6$ | |
| | | Pentaerythritol Ester | | |
| 1.9843 | 0.220 | 463.0 | 0.0424 | 5.19 |
| 3.7102 | 0.392 | 486.3 | 0.0792 | 4.95 |
| 5.6621 | 0.585 | 497.5 | 0.1209 | 4.84 |
| 8.1076 | 0.856 | 487.5 | 0.1732 | 4.94 |
| 9.7386 | 1.017 | 493.3 | 0.2080 | 4.89 |
| | | | $M_0 = 468.2 \pm 4.9$ | |
| | | Phosphate Ester | | |
| 1.6691 | 0.174 | 492.4 | 0.0334 | 5.21 |
| 3.9391 | 0.394 | 513.6 | 0.0789 | 4.99 |
| 6.2366 | 0.599 | 535.3 | 0.1249 | 4.80 |
| 8.2598 | 0.820 | 518.5 | 0.1654 | 4.96 |
| 9.8346 | 0.985 | 514.4 | 0.1970 | 5.00 |
| | | | $M_0 = 4.99.3 \pm 6.6$ | |
| | | Fluoroalkyl Camphorate | | |
| 0.9034 | 0.077 | 601.9 | 0.0146 | 5.27 |
| 2.3347 | 0.160 | 748.8 | 0.0378 | 4.23 |
| 4.9060 | 0.304 | 828.7 | 0.0794 | 3.83 |
| 7.2766 | 0.418 | 894.5 | 0.1178 | 3.55 |
| 9.2712 | 0.504 | 945.6 | 0.1501 | 3.36 |
| | | | $M_0 = 617.7 \pm 19.1$ | |

### Table I. Continued

| $w_2$ | $\theta$ | $M_2$ | $m$ | $\theta/m$ |
|---|---|---|---|---|
| Poly(alkalene Glycol) (Ucon D-50-HB-160-E) | | | | |
| 3.8024 | 0.233 | 837.7 | 0.0413 | 5.64 |
| 5.6123 | 0.361 | 798.6 | 0.0610 | 5.92 |
| 7.0671 | 0.477 | 761.5 | 0.0768 | 6.21 |
| 9.4724 | 0.682 | 714.4 | 0.1029 | 6.63 |
| | | | $M_0 = 920.4 \pm 1.6$ | |
| Poly(alkalene Glycol) (Ucon 50-HB-260) | | | | |
| 1.3906 | 0.080 | 892.0 | 0.0154 | 5.19 |
| 3.4640 | 0.209 | 850.7 | 0.0383 | 5.46 |
| 5.3845 | 0.317 | 872.3 | 0.0595 | 5.33 |
| 7.0910 | 0.435 | 837.6 | 0.0784 | 5.55 |
| 9.4383 | 0.608 | 798.5 | 0.1043 | 5.83 |
| | | | $M_0 = 905.0 \pm 8.1$ | |
| Poly(*sec*-butyl Silicate) | | | | |
| 3.7170 | 0.315 | 606.0 | 0.0620 | 5.08 |
| 5.6247 | 0.462 | 625.7 | 0.0937 | 4.93 |
| 7.9956 | 0.660 | 623.2 | 0.1333 | 4.95 |
| 9.8021 | 0.807 | 628.3 | 0.1634 | 4.94 |
| | | | $M_0 = 600.0 \pm 3.6$ | |
| Poly(trifluorovinyl Chloride) (Fluorolube MO-10) | | | | |
| 1.2706 | 0.117 | 557.3 | 0.0236 | 4.96 |
| 3.5352 | 0.302 | 601.1 | 0.0656 | 4.60 |
| 4.6262 | 0.369 | 644.0 | 0.0858 | 4.30 |
| 5.9242 | 0.469 | 649.2 | 0.1098 | 4.27 |
| | | | $M_0 = 539.3 \pm 8.5$ | |

[a] The number of significant figures in the calculation is determined by $\theta$. All values of $M_2$ are expressed in four digits but are not all significant.

[b] Uncertainties in $M_0$ values are standard deviations of the intercepts of the $M_2 - w_2$ lines.

ideal solution value of $\theta/m$ as illustrated by line *C*. Positive deviations can be ascribed to nonspecific interactions resulting from internal pressure differences (*3*). Negative deviations from Raoult's law are represented by curve *A* and result when the components of the solution have abnormally great attraction for each other. This specific interaction may be due to high polarity, hydrogen bonding, or "positive-negative"—for example, acid-base—character of the components. When the solute and solvent form solid solutions on freezing, the straight line *D* intersects the $\theta/m$ axis at some distance from that predicted for the ideal solution. Other, more complex deviations from ideal solution behavior can be expected in the study of real solutions.

It is instructive to group the fluids according to their composition. Group I fluids are obtained by fractional distillation of complex mixtures of hydrocarbons. Group II fluids are synthesized by polymerization reactions, usually followed by fractionation to obtain a well-defined range of products. Group III consists of pure compounds, each fluid comprised of a single molecular species.

**Group I.** Petroleum oils A-E, alkylated naphthalene.

**Group II.** Poly(*sec*-butyl silicate); poly(alkalene glycol), Ucon D-50-HB-160-E; poly(alkalene glycol); Ucon 50-HB-260; poly(trifluorovinyl chloride), Fluorolube MO-10.

**Group III.** Pentaerythriol ester, diundecyl sebacate, fluoroalkyl camphorate, dilaurate ester, phosphate ester.

The plots of $\theta/m$ *vs.* $m$ for each of these groups are shown in Figures 2, 3, and 5. In each instance the ideal solution curve is included for comparison.

Figure 2 reveals that the alkylated naphthalene-benzene solutions closely approximate ideal solution behavior. This is due to structural similarities between solute and solvent because both are principally aromatic compounds. The difference in molar volumes (89 cc. for benzene; 287 cc. for alkylated naphthalene) apparently is not a significant factor in determining the behavior of these solutions.

### Table II. Covariance of Apparent Molecular Weight and Concentration

| Fluid | Intercept, $M_0$ | Slope | Std. Dev. of Intercept ($s_a$) | $\frac{S_a \times 100}{M_0}$ |
|---|---|---|---|---|
| Petroleum oil A | 283.2 | 5.77 | 0.83 | 0.29 |
| Petroleum oil B | 314.1 | 18.36 | 2.69 | 0.86 |
| Petroleum oil C | 362.9 | 17.88 | 5.67 | 1.56 |
| Petroleum oil D | 317.2 | 2.95 | 1.28 | 0.40 |
| Petroleum oil E | 272.1 | 6.80 | 2.96 | 1.09 |
| Alkylated naphthalene | 265,6 | 0.159 | 0.70 | 0.26 |
| Diundecyl sebacate | 371.7 | 13.46 | 3.94 | 0.11 |
| Dilaurate ester | 399.5 | 12.34 | 9.50 | 2.38 |
| Pentaerythritol ester | 468.2 | 2.96 | 4.94 | 1.06 |
| Phosphate ester | 499.3 | 2.59 | 6.58 | 1.32 |
| Fluoroalkyl camphorate | 617.7 | 37.71 | 19.13 | 3.10 |
| Poly(alkalene glycol) (Ucon D-50-HB-160-E) | 920.4 | − 21.93 | 1.61 | 0.18 |
| Poly(alkalene glycol) (Ucon D-50-HB-260) | 905.0 | − 10.24 | 8.10 | 0.90 |
| Poly(*sec*-butyl silicate | 600.0 | 3.06 | 3.63 | 0.61 |
| Poly(trifluorovinyl chloride) | 539.3 | 19.63 | 8.53 | 1.58 |

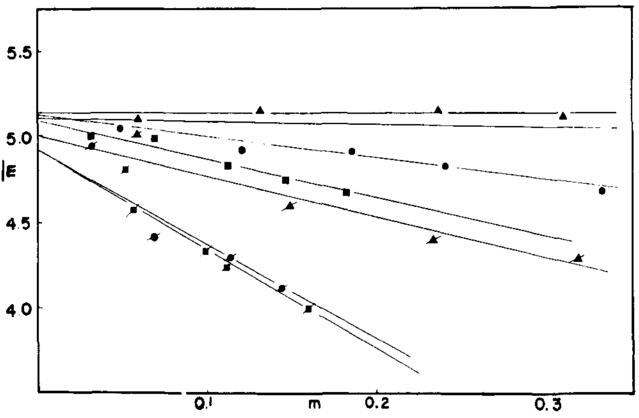


Figure 2. Freezing point data for hydrocarbons in benzene

▲ Alkylated naphthalene
● Petroleum oil D
■ Petroleum oil A
✦ Petroleum oil E
✦ Petroleum oil C
✦ Petroleum oil B
— Ideal solution

Benzene solutions of the other hydrocarbon fluids in this group exhibit positive deviations from Raoult's law. Because the solute molecules are nonpolar, specific interactions between solute and solvent are not expected, and deviations from ideal behavior should be related to the size and structure of the solute molecules. However, there is no correlation between the slope of the $\theta/m$ *vs.* $m$ line and molecular weight or molar volume. More specific structural information about the solutes is required to account for the degree of positive deviation.

The $\theta/m$ *vs.* $m$ data for all these hydrocarbon solutions obey linear relationships. Thus, if cryoscopic measurements are made at several concentrations, the data can be accurately extrapolated to zero concentration. The present studies do not consider the effect of a molecular weight distribution in the solute. This leads to low values for the number average molecular weight as compared to the weight average value.

Results for the Group II fluids are summarized in Figure 3. As in the case of the Group I fluids the $\theta/m$ *vs.* $m$ plots are generally rectilinear. There are large differences, however, in the slopes of the lines for the different solutes. The poly(*sec*-butyl silicate)-benzene solutions approach

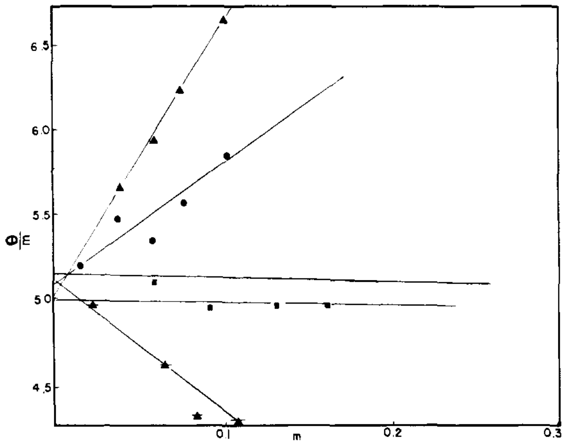


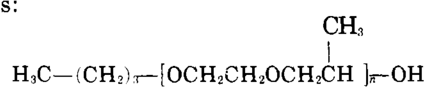
Figure 3. Freezing point data for polymer fluids in benzene

▲ Ucon D-50-HB-160-E
● Ucon 50-HB-260
■ Poly(sec-butyl silicate)
★ Fluorolube
– Ideal solution

ideal behavior. Considering the differences of polarity and size of the solute and solvent molecules, ideal solution behavior would not be expected. Opposing factors of equal intensity may cancel each other resulting in a pseudo-ideal system.

Benzene solutions of poly(trifluorovinyl chloride) gave positive deviations from Raoult's law. The results for these solutions indicate a regular concentration dependency and extrapolate to the theoretical value of $\Theta/m$ for the ideal solution at concentration $m = 0$. The deviations from ideality probably result from internal pressure differences rather than interactions between solvent-solvent or solute-solute molecules.

The poly(alkalene glycol)-benzene solutions exhibit large negative deviations from the behavior predicted by Raoult's law for ideal solutions. The infrared and near infrared spectra of these solutions were studied for evidence of new bonds or bon energy shifts. The structure of the Ucon 50-HB-260 is:



$$H_3C{-}(CH_2)_7{-}[OCH_2CH_2OCH_2\overset{\overset{\displaystyle CH_3}{|}}{C}H\ ]_n{-}OH$$

where $n$ is about 9. In the D-50-HB-160-E fluid the terminal OH group has been reacted. Absorption measurements in the regions 3500 and 7000 cm.$^{-1}$ reveal almost no free OH for this fluid. Apparently the terminal OH group is not an important factor in producing the negative deviations from Raoult's law observed for both fluids. This was confirmed by studying the spectra of three Ucon 50-HB-260-benzene solutions of different concentrations in the 7000 cm.$^{-1}$ region. This frequency corresponds to the first overtone of stretching of the OH bond. The results (Figure 4) indicate no change in the nature of the bond with changes in the concentration of the solution. The decrease of the absorption peak with concentration is as expected in the absence of other effects such as hydrogen bonding. The spectra of benzene solutions from 5000 to 670 cm.$^{-1}$ were also compared with those for the pure components. All absorption peaks in the solution spectra could be accounted for with no evidence for shift in the frequencies of the vibrations.

The cryoscopic results for these poly(alkalene glycol) solutions are similar to those observed for other high polymer solutions. Kemp and Peters (*5, 6*) reported negative deviations for benzene solutions of polystyrene above molecular weight of 1000 and for polyisobutylene above 2300. Thus, the critical molecular weight above which negative deviations are manifest varies considerably with the configuration and size of the solute molecules. These deviations, as in other polymer solutions, probably result from an anomalous entropy of mixing the long polymer chains with the relatively small benzene molecules.

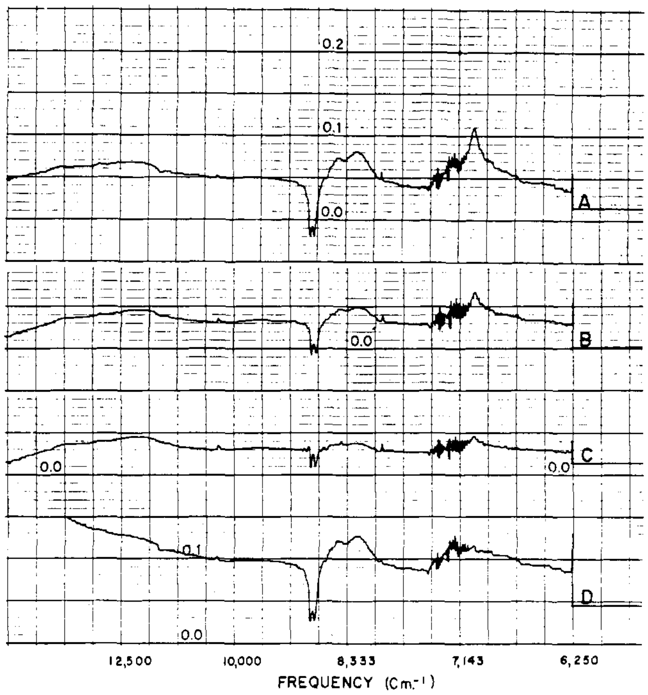


Figure 4. Infrared OH absorption for poly(alkalene glycol)–benzene solutions at 7000 cm.$^{-1}$

*A* 9% Ucon 50-HB-260
*B* 5% Ucon 50-HB-260
*C* 2% Ucon 50-HB-260
*D* 9% Ucon D-50-HB-160-E

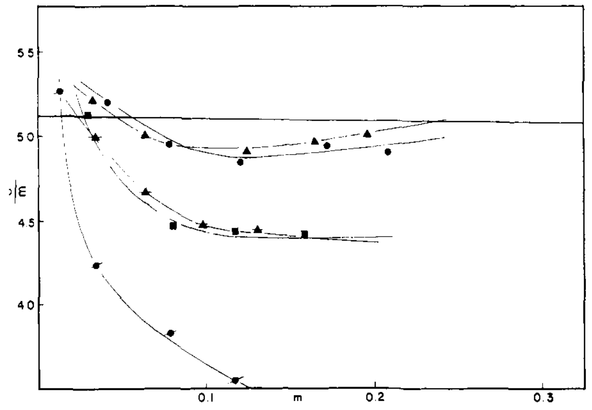


Figure 5. Freezing point data for esters in benzene

▲ Phosphate ester
● Pentaerythritol ester
■ Diundecyl sebacate
★ Dilaurate ester
● Fluoroalkyl camphorate
– Ideal solution

Results for the ester-benzene solutions are given in Figure 5. All $\Theta/m$ *vs.* $m$ plots are curvilinear and characterized by large increases in $\Theta/m$ at concentrations below 0.05 molal. Plotting the data in this manner emphasizes the large uncertainties in extrapolating these functions to infinite dilution.

The variation of the calculated molecular weight with concentration is illustrated in Figure 6. The $w_2/M_2$ covariance is linear at concentrations above about 5 grams of ester per 100 grams of benzene. The linear portions of these curves have been extrapolated to zero concentration to

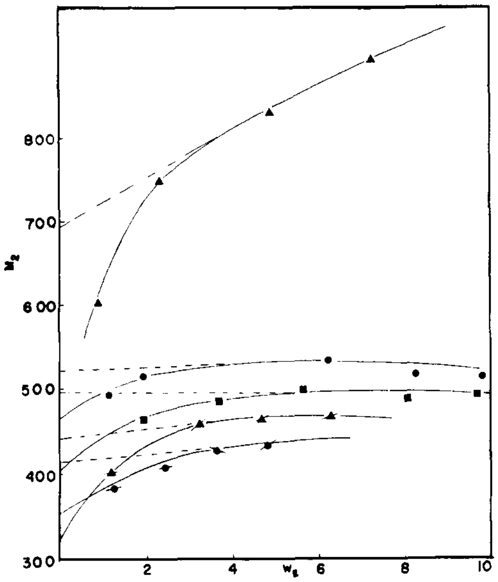


Figure 6. Apparent molecular weight of esters in benzene

▲ Fluoroalkyl camphorate
● Phosphate ester
■ Pentaerythritol ester
★ Dilaurate ester
✱ Diundecyl sebacate

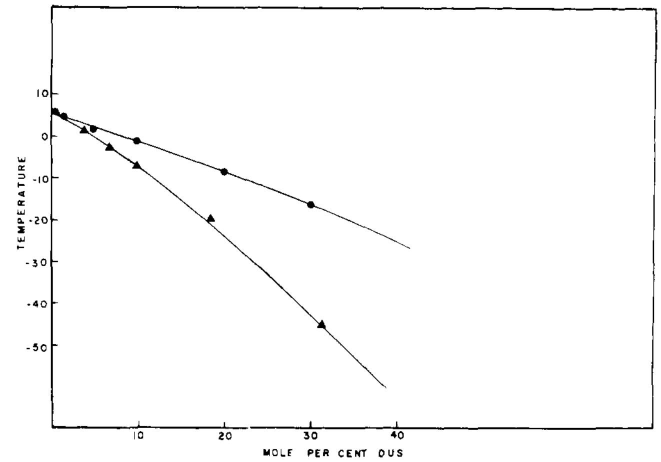


Figure 7. Freezing points of benzene solutions of high solute concentration

● Ideal solution ▲ Diundecyl sebacate

Table III. Molecular Weight Comparisons

| Fluid | Calcd. Molecular Wt. | $M_0$ | % Difference from Calcd. | $M_e$ | % Difference from Calcd. |
|---|---|---|---|---|---|
| Diundecyl sebacate | 510.8 | 371.7 | 27.2 | 415 | 18.8 |
| Dilaurate ester | 510.8 | 398.5 | 22.0 | 440 | 13.9 |
| Pentaerythritol ester | | 468.2 | | 496 | |
| Phosphate ester | 566.7 | 499.3 | 11.9 | 521 | 8.1 |
| Fluoroalkyl camphorate | 828.4 | 617.7 | 25.4 | 691 | 16.6 |

obtain a value for the molecular weight ($M_e$). This molecular weight is independent of the factors responsible for the large increase in $\theta/m$ for dilute benzene solutions. In Table III the experimental molecular weights are compared with the values calculated by summing the atomic weights for the esters of known structure. The $M_e$ values are in better agreement with the calculated molecular weights but are still 8 to 16% low.

The freezing point depressions observed for low concentrations of these esters in benzene represent a radical departure from the cryoscopic behavior of conventional solutions. The increasingly large values of $\theta/m$ at low concentrations lead to low values for the molecular weights of the solutes and suggest an effective decrease in solvent concentration. Such an effective decrease would result if the attractive forces between the ester solutes and benzene solvent were sufficiently strong to reduce the solvent activity. For the solutions studied, such an interaction could exist between electron depleted hydrogens on the benzene ring and the electron dense region in the carbonyl groups of the ester linkages. The large size of the ester molecules in comparison with the benzene, along with the fact that several of the esters are polyfunctional, could account for the magnitude of the interactions.

The freezing points of a series of concentrated solutions of diundecyl sebacate in benzene were studied to obtain evidence for or against the postulated interaction. The results are given in Figure 7. The freezing points of these solutions lie well below those predicted for the ideal benzene solution. This type of deviation occurs when the solute and solvent combine partially in the liquid mixture (*10*). In the extreme case, when the forces of attraction are very strong, it leads to compound formation. In milder cases, such as that postulated for the ester-benzene solutions, it is sometimes called solvation. These results lend further support to the postulated interaction mechanism.

The freezing points of a series of solutions of diundecyl sebacate in 1,4-dioxane were also studied. Like benzene, 1,4-dioxane is essentially nonpolar, the dipole moments being zero and 0.4 Debye units respectively (*11*). The structures of these two solvents, however, are basically different. The $\theta/m$ *vs.* $m$ curve for the dioxane solutions was similar to that observed for benzene solutions, again showing a large rise in $\theta/m$ for concentrations below 0.05 molal. This is evidence that the mode of solute-solvent interaction is not sensitive to structural features of the solvent molecules. The influence of the large ester molecules, with their polar functional groups, apparently extends nonspecifically to affect a large number of the small, nonpolar solvent molecules.

## ACKNOWLEDGMENT

The author acknowledges the assistance of David Stafford in carrying out the experimental work.

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RECEIVED for review June 1, 1959. Accepted August 26, 1959. Presented in part before the Division of Physical and Inorganic Chemistry, 133rd Meeting, ACS, San Francisco, Calif., April 1958.