Application of the Prigogine Solution Theory to the Heats of Mixing of Some Polymer-Solvent Systems

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Using the Tian-Calvet microcalorimeter, the heats of mixing at infinite dilution have been determined for the following sets of binary systems comprising an amorphous high polymer and solvents from a homologous series: polydimethyl-siloxane+n-alkanes, polydimethylsiloxane+oligomers of dimethylsiloxane, polyisobutylene+dialkyl ether and polyisobutylene+ethyl esters of the aliphatic acids. The results of the first two sets of systems provide confirmation of the Prigogine solution thermodynamics which gives a simple relation between the thermodynamic quantities for a polymer in solvents whose molecules are chains of identical segments. The solvents of the last two sets have one group different from the others, and the results confirm a more general relation.

Although the currently accepted polymer solution thermodynamics has had many successes, there are various phenomena which it does not explain, e.g., (*a*) the lower critical solution temperatures (l.c.s.t.) recently found by Freeman and Rowlinson [1] to be of general occurrence in polymer solutions, (*b*), the negative (exothermic) heats of mixing found at room temperature for such non-polar systems as polystyrene+benzene,[2] +toluene,[2] polyisobutylene (PIB)+cyclohexane,[3] PIB with the lower normal alkanes up to tetradecane [4] and various branched alkanes,[4] and (*c*) the negative volumes of mixing frequently found for non-polar polymer solutions. All of these phenomena are related to the large difference in coefficients of thermal expansion between the polymer and the solvent. The relatively " expanded " state of the solvent at high temperatures results in negative contributions to ΔS_M, ΔH_M and ΔV_M on mixing the solvent with the " compact " polymer. The contributions to the above three thermodynamic quantities are respectively the causes of the three phenomena mentioned above, but cannot be predicted by the usual polymer solution thermodynamics which assumes a rigid lattice model. On the other hand, the molecular theory of polymer solutions [5] due to Prigogine and his collaborators is based on a deformable lattice, and can be used [4] to give a quantitative explanation of the experimental values of the l.c.s.t. in the PIB+pentane, +hexane, +heptane and +octane systems, and also of the heats of mixing in solutions of PIB in the n-alkanes from pentane to hexadecane.

Thus, not only does the Prigogine theory give a better temperature dependence of the thermodynamic parameters of polymer-solvent interaction, but also enables one to correlate parameters obtained for a polymer and different members of a homologous solvent series. In the present work, we test this latter feature of the theory for heats of mixing at infinite dilution of polydimethylsiloxane (PDS) with two quite different series: the n-alkanes from pentane to hexadecane, and the shorter dimethylsiloxane oligomers starting with hexamethyldisiloxane. We have also determined the heats of mixing of PIB with two less simple series of solvents: the dialkyl ethers from diethyl to dihexyl and the esters from ethyl hexanoate to ethyl hexadecanoate, and the results have been treated allowing for different kinds of segments in the solvent molecule.

EXPERIMENTAL

MATERIALS

POLYMERS

The PIB of $M_v \simeq 30{,}000$ was previously fractionated[6] from a sample of commercial Vistanex LM-MH-225 given by Enjay Co., Inc. The polydimethylsiloxanes were commercial samples of DC 200 silicone fluids obtained from Dow Corning Silicones Ltd., and no attempt was made to neutralize the small residual amount of catalyst. The molecular weights of the various fractions range from 20,000 to 100,000. The various polymers were heated under vacuum to rid them of any volatile material.

SOLVENTS

Except for the hexadecane from Fisher Scientific Co., the n-alkanes were all obtained from Phillips Petroleum Co., and were of " pure " grade (99 % pure); they were refluxed with sodium, distilled, and passed through a silica gel column. The total impurity content of the alkanes up to decane was estimated by vapour-phase chromatography to be less than $\simeq$0·1 %. The lower oligomers of dimethylsiloxane were obtained as commercial Dow Corning DC 200 silicone fluids. The oligomers of 0·65, 1·0, 1·5 and 2·0 centistokes (cs) viscosity contain respectively two, three, four and five silicone atoms in the chain, i.e., they are hexamethyldisiloxane (MM), octamethyltrisiloxane (MDM), etc. The commercial liquids are of 90-95 % purity and were further purified by distillation. The silicone fluid of 25 cs is a mixture of oligomers but with an average molecular weight$\simeq$1900 or $\simeq$25 silicon atoms in the molecule. It was used without any treatment. The ethers and esters were " highest purity " Fisher reagents except for a few of " practical " grade which were distilled.

APPARATUS AND RESULTS

The heats of mixing were determined at 24·5°C using a Tian-Calvet microcalorimeter. A description of this type of instrument may be found elsewhere,[7] while the mixing cell and experimental procedure are the same as in our previous work.[4] The heat of setting off the mixing and of stirring are negligible even compared with the small heat effects observed—from 0·015 to 1 joule and evolved over periods of time ranging from 1 h for PDS in the alkanes to 3-5 h for PIB in the esters. The correction for the small vapour space in the cell was of negligible importance since the concentration of the final polymer solution was always small (<3 %).

Tables 1 and 2 give the average values of the heats of mixing expressed per g of polymer and corrected to infinite dilution. Varying the molecular weight of the PDS between 20,000 and 100,000 produced no observable effect on the heats.

Fig. 1, 2 and 3 show the experimental points for calorimetric determinations of ΔH_M with the solvents of the homologous series. The absolute " scatter " of the points is $\simeq$15 J/base mole for PDS+alkanes, $\simeq$5 J/base mole for PDS+oligomers. The precision for the

TABLE 1.—HEATS OF MIXING FOR PDS+ALKANES AND PDS+OLIGOMERS SYSTEMS

solvent	ΔH_M J/(base-mole)ϕ_B	solvent	ΔH_M J/(base-mole)ϕ_B
n-pentane	− 70	n-tetradecane	+375
n-hexane	+ 50	n-hexadecane	+410
n-heptane	+145		
n-octane	+190		
n-nonane	+250	2 Si chain atoms	− 90
n-decane	+285	3 „	− 45
n-undecane	+315	4 „	− 33
n-dodecane	+330	5 „	− 21
n-tridecane	+355	25 „	− 3·7

TABLE 2.—HEATS OF MIXING FOR PIB+ETHERS AND PIB+ESTERS SYSTEMS

solvent	ΔH_M J/(base-mole)ϕ_B	r_B	solvent	ΔH_M J/(base-mole)ϕ_B	r_B
esters			ethers		
ethyl hexanoate	375	5	diethyl ether	155	3
ethyl heptanoate	315	5·5			
ethyl octanoate	255	6	dipropyl ether	98	4
ethyl nonanoate	207	6·5	dibutyl ether	69	5
ethyl decanoate	170	7	diamyl ether	59	6
ethyl tetradecanoate	99	9	dihexyl ether	48	7
ethyl hexadecanoate	72	10			

base mole = 56 g

PIB+esters and PIB+ethers systems is estimated to be rather better than for the PDS+alkanes systems.

Following a previous discussion[4] of possible sources of error in using the microcalorimeters, we believe that the accuracy should be of the same order as the precision.

THEORY AND DISCUSSION

RESULTS OF THE PRIGOGINE THEORY

The excess thermodynamic functions of a mixture of N_A r_A-mers and N_B r_B-mers are related to characteristic constants expressing differences between the two types of segments:

$$\begin{aligned}\delta &= \varepsilon^*_{BB}/\varepsilon^*_{AA}-1,\\ \rho &= r^*_{BB}/r^*_{AA}-1,\end{aligned} \qquad (1)$$

where $-\varepsilon^*_{ij}$ and r^*_{ij} are the minimum potential energy and distance at this minimum between segments of type i and j. $3c$, the number of external degrees of freedom[8] of an r-mer enters the theory through the ratio c/q where q is defined by

$$qz = r(z-2)+2,$$

and z is the lattice co-ordination number.

The Prigogine "average potential" theory with, for definiteness, the smoothed potential model can be used to give the following expression for the heat of mixing:

$$\frac{\Delta H_M}{(N_Aq_A+N_Bq_B)X_AX_B/N} = z\varepsilon^*_{AA}N\left[\frac{\delta^2}{8}+\frac{9}{2}\rho^2\right] - \frac{10{\cdot}5Nk^2T^2}{z\varepsilon^*_{AA}}\left[\left(\frac{c_A}{q_A}-\frac{c_B}{q_B}+\frac{3}{2}\delta\frac{c_A}{q_A}\right)\left(\frac{c_A}{q_A}-\frac{c_B}{q_B}+\frac{\delta}{2}\frac{c_A}{q_A}\right)-9\rho^2\left(\frac{c_A}{q_A}\right)^2\right]. \qquad (2)$$

Here, third and higher orders of the quantities δ, ρ and $C_A/q_A-C_B/q_B$ have been neglected, and the geometric mean combining rule used, i.e.,

$$\varepsilon^{*2}_{ij} = \varepsilon^*_{ii}\varepsilon^*_{jj}. \qquad (3)$$

N is Avogadro's number so that the heat is expressed per mole of segments, and X_A and X_B are the site fractions defined by

$$X_A = q_AN_A/(q_AN_A+q_BN_B). \qquad (4)$$

In (2), the ratios c/q depend on the lengths and flexibilities of the molecules A and B. In particular, assuming free rotation between segments gives[8] $3c = r+3$. With the Flory approximation ($z \to \infty$), $q = r$ so that $c/q = 1/3+1/r$. Assigning these same flexibilities to both r-mers in (2), and then letting $r_A \rightarrow \infty$, we have for a high polymer A in a chain-molecule solvent B:

$$\frac{\Delta H_M}{(N_A r_A + N_B r_B)\phi_A \phi_B / N} = A - BT^2\left[\left(\frac{1}{r_B} - \frac{\delta}{2}\right)\left(\frac{1}{r_B} - \frac{\delta}{6}\right) - \rho^2\right], \tag{5}$$

where we have put

$$A = z\varepsilon^*_{AA}N\left[\frac{\delta^2}{8} + \frac{9}{2}\rho^2\right]. \tag{6}$$

$$B = 10{\cdot}5k^2N/z\varepsilon^*_{AA}, \tag{7}$$

and ϕ_A and ϕ_B are the volume fractions. With δ and ρ neglected in the calculation of the second, " structural ", term,

$$\frac{\Delta H_M}{(N_A r_A + N_B r_B)\phi_A \phi_B / N} = A - B\frac{T^2}{r_B^2},$$

or

$$\frac{\Delta H_M}{(\text{no. base moles polymer})\ \phi_B} = A - B\frac{T^2}{r_B^2}. \tag{8}$$

The structural term of (8) allows the heat to become negative at high temperature, and predicts a variation of ΔH_M with length of the solvent molecule (as seen in the results of tables 1 and 2), whereas the usual theory would predict only a positive contribution as given by the first, temperature-independent term.

A more general discussion of the Prigogine type of treatment of polymer solution thermodynamics will be published in the *Official Digest of the Federation of Societies or Paint Technology (U.S.).*

END-EFFECTS ON THE HEAT OF MIXING

If, however, the solvent molecules have end-groups different from their interior groups, the temperature-independent term as calculated by even the rigid lattice theory[9, 10] depends on $1/r_B$. More generally, suppose that there are p segments, not necessarily the ends, of type B′, the remaining $r_B - p$ being of type B. We then have the following expression for T^*_B:

$$T^*_B = \frac{kT\left(\dfrac{c_B}{q_B}\right)}{2z\left[\dfrac{p}{r_B}\varepsilon^*_{B'B'} + \left(1 - \dfrac{p}{r_B}\right)\varepsilon^*_{BB} - 2\dfrac{p}{r_B}\left(1 - \dfrac{p}{r_B}\right)\left\{\dfrac{1}{2}(\varepsilon^*_{B'B'} + \varepsilon^*_{BB}) - \varepsilon^*_{BB'}\right\}\right]}. \tag{9}$$

A similar expression for T^*_M can be written, and defining

$$(\varepsilon^*_{B'B'}/\varepsilon^*_{BB}) - 1 = \delta',$$

ΔH_M may be worked out ignoring powers of $1/r_B$, δ and δ' higher than the second. Grouping terms in powers of $1/r_B$, we have

$$\begin{aligned}\frac{\Delta H_M}{(N_A r_A + N_B r_B)\phi_A \phi_B / N} = z\varepsilon^*_{AA}N\left(\frac{\delta^2}{8} + \frac{9}{2}\rho^2\right) - BT^2\left(\frac{\delta^2}{12} - \rho^2\right) + \\ \frac{1}{r_B}\left[z\varepsilon^*_{AA}N\frac{p\delta\delta'}{4} + BT^2\delta\left(\frac{2}{3} - \frac{p\delta'}{6}\right)\right] - \\ \frac{1}{r_B^2}\left[BT^2\left(1 - \frac{p\delta'}{2}\right)\left(1 - \frac{p\delta'}{6}\right) - z\varepsilon^*_{AA}N\frac{(p\delta')^2}{8}\right].\end{aligned} \tag{10}$$

PDS + n-ALKANE SYSTEMS

Due to the Si—O bond, the polymer contains permanent dipole moments which have been measured [11] for the lower oligomers. It is suggested that with lengthening of the chain the moment per segment decreases due to an internal compensation effect, and the polar character of the polymer does not seem very pronounced. In any case, we apply the above theoretical results ignoring the possibility of special dipole effects.

Reasons have been given [12, 13] for taking a segment or base molar unit of the n-alkane chain to correspond to two methylene groups with $r_B = \frac{1}{2}(n+1)$, where n is the number of carbon atoms. We have correspondingly chosen the $Si(CH_3)_2O$ group to correspond to a segment of PDS. Due to the presence of the methyl side-groups, the volume of a segment of PDS is far from being equal to that for a segment of n-alkane, and strictly speaking, the Prigogine theory can only be applied when the segment sizes are approximately equal. A test of eqn. (8) is shown in fig. 1

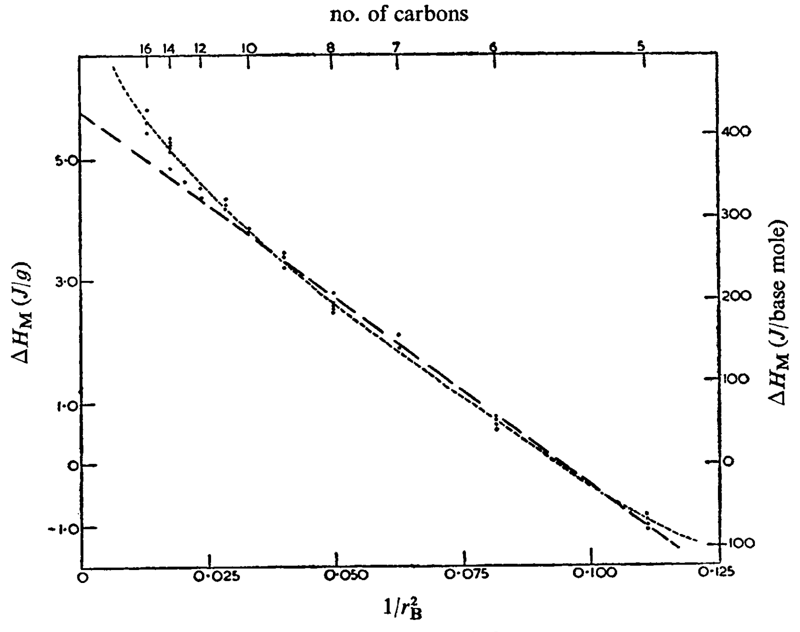

FIG. 1.—Heats of mixing (corrected to infinite dilution) for PDS+alkane systems as a function of $1/r_B^2$.

where the heats of mixing per base mole, divided by ϕ_B to correct to infinite dilution, are plotted against $1/r_B^2$, each point corresponding to a separate determination. The simple straight line predicted by (8) is seen to give, within experimental error, a fair representation of the results except for the higher alkanes, with values of A and B equal to 430 J/base mole and $5{\cdot}1 \times 10^{-2}$ J/deg.^{2} base mole respectively. For PIB+alkanes,[4] $A = 42$ J/base mole and $B = 2{\cdot}5 \times 10^{-2}$ J/deg.^{2} base mole. The relatively large value of A for the present systems reflects the large difference in force fields between the alkane and PDS segments relative to that between alkane and PIB segments. It is apparent, however, that the Prigogine structural term is important, and suffices to make ΔH_M negative for PDS+pentane. (For PIB+alkanes, all the heats for solvents shorter than tetradecane are negative.)

It would seem, however, that the dotted curve in fig. 1 is in better agreement with the data than the straight line; it has been drawn using eqn. (10) fitted to the results at three points. The upward curvature is brought about by a negative term multiplying $1/r_B$ in (10), and since for PDS+alkanes, $\delta>0$, we must have $\delta'<0$. Thus, the interaction energy of two end segments of an alkane should be less than that for two interior segments. Such an end-effect has, in fact, been found [13] in an analysis of equations of state of the pure n-alkanes, and apparently arises from the total polarizability of a —CH_2—CH_2— group, or interior segment, being greater than that of the end —CH_3 group. It may therefore be that our speculative interpretation is correct, but a detailed treatment along these lines would be unwarranted.

PDS+DIMETHYLSILOXANE OLIGOMER SYSTEMS

Fig. 2 shows the observed heats per base mole against $1/r_B^2$ with the same choice of segment for the oligomers as made for the polymer. M_2 (two chain silicons) is taken to correspond to 2·5 segments, MDM to 3·5 and so on. This choice of number of segments was made from volume considerations, but the straight line of fig. 3 is not sensitive to the exact choice of numbers of segments. We find $A = -3$ J/base mole and $B = 4{\cdot}9\times10^{-3}$ J/deg.^{2} base mole. A is almost negligible as one might expect for a mixture of a polymer with its oligomers. However, the discrepancy between the values of B found for PDS in the PDS+oligomer and PDS+alkane cases seems striking. Furthermore, a calculation using eqn. (2) and allowing a greater flexibility and smaller cohesive energy for PDS than for the alkanes increases the difference in B between the two cases.

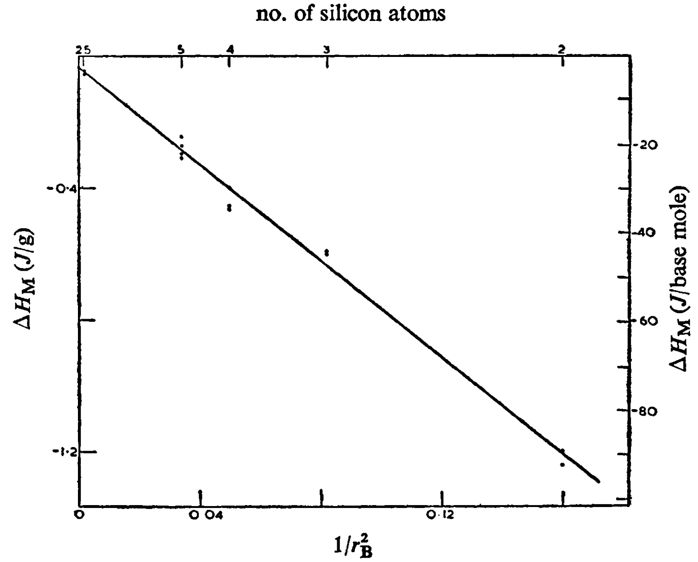

FIG. 2.—Heats of mixing (corrected to infinite dilution) for PDS+dimethylsiloxane oligomer systems as a function of $1/r_B^2$.

A possible explanation is suggested by a decrease of the average value of ε_{BB}^* for oligomers of increasing molecular weight as calculated [14] from their coefficients of thermal expansion. This may indicate the presence of end-effects ($\delta'>0$); in the alkanes a similar change of ε_{BB}^*, but of opposite sign, is found.[13] Taking eqn. (10), and putting $\delta = 0$, $\rho = 0$, i.e., no difference between the force fields of the interior groups of PDS and the oligomers, we have

$$\frac{\Delta H_M}{(N_A r_A + N_B r_B)\phi_A \phi_B / N} = -\frac{1}{r_B^2}\left[BT^2\left(1-\frac{p\delta'}{2}\right)\left(1-\frac{p\delta'}{6}\right) - z\varepsilon_{AA}^{*} N \frac{(p\delta')^2}{8}\right]. \tag{11}$$

Thus a lowering of the effective value of B is obtained by the presence of the end-effects, and in fact the experimental result is obtained for $p\delta' \simeq 0{\cdot}3$. However, such a treatment must be considered as speculative, especially in view of the difficulty of assessing the possible effect of the polar nature of the system.

PIB+ESTERS AND PIB+ETHERS SYSTEMS

It is clear that in these sets of systems we are now dealing with solvent molecules with a constituent group which is quite different from the others. Fig. 3 shows the heats plotted against $1/r_B^2$ for each solvent series. The value of r_B has been taken to be that of an n-alkane of an equal number of atoms in the chain, i.e., r_B for diethyl ether = 3, r_B for ethyl hexanoate = 5, and so on. The heats increase with $1/r_B^2$ rather than decrease, due no doubt to the large difference in force fields between, respectively, the ester carbonyl and a PIB segment, and the ether oxygen and a PIB segment. For $1/r_B^2 \rightarrow 0$, the heats for both series must tend to the point shown on the ordinate which corresponds to the heat of mixing of PIB with an n-alkane of infinite length, i.e., the value A found for the PIB+alkanes systems, or to the expression (10) with $r_B \rightarrow \infty$. The heats may be compared with (10) but a more convenient form results from subtracting from each heat, the heat of mixing of PIB with the alkane of the corresponding length. The small effect of the alkane methyl end-groups in the PIB+alkane systems will cancel with the corresponding end-

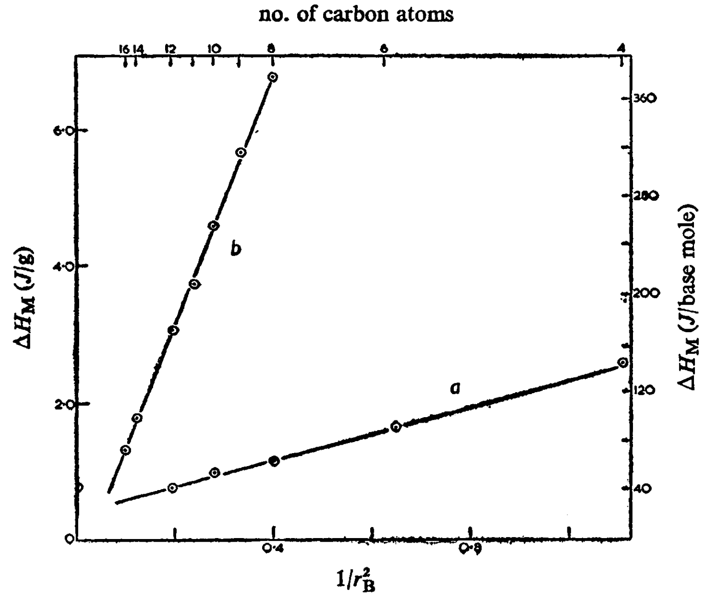

FIG. 3.—Heats of mixing (corrected to infinite dilution) for (*a*) PIB+ethers, (*b*) PIB+esters as a function of $1/r_B^2$.

effects in the present systems. Thus, the differences in heat of mixing for the PIB+ ethers or +esters and the PIB+alkanes is given by

$$\frac{\Delta H_{\mathrm{M}}(\delta')-\Delta H_{\mathrm{M}}(0)}{(N_{\mathrm{A}}r_{\mathrm{A}}+N_{\mathrm{B}}r_{\mathrm{B}})\phi_{\mathrm{A}}\phi_{\mathrm{B}}/N}=y=\frac{1}{r_{\mathrm{B}}}\left[z\varepsilon^{*}_{\mathrm{AA}}N\frac{p\delta\delta'}{4}-BT^{2}\frac{p\delta\delta'}{6}\right]+$$
$$\frac{1}{r_{\mathrm{B}}^{2}}\left[z\varepsilon^{*}_{\mathrm{AA}}N\frac{(p\delta')^{2}}{8}+BT^{2}\left(\frac{2p\delta'}{3}-\frac{(p\delta')^{2}}{12}\right)\right]. \quad (12)$$

It may be shown that the last term of each bracket is negligible in comparison with the others. $r_{\mathrm{B}}y$ is now a linear function of $1/r_{\mathrm{B}}$ with

$$\begin{aligned}\text{intercept} &= z\varepsilon^{*}_{\mathrm{AA}}Np\delta\delta'/4,\\ \text{slope} &= (z\varepsilon^{*}_{\mathrm{AA}}N(p\delta')^{2}/8)+(2BT^{2}p\delta'/3),\end{aligned} \quad (13)$$

where the factor $p\delta'$ is different in the ester and ether systems. Fig. 4 shows plots of $r_b y$ against $1/r_{\mathrm{B}}$; both esters and ethers show negative intercepts. Now δ' must

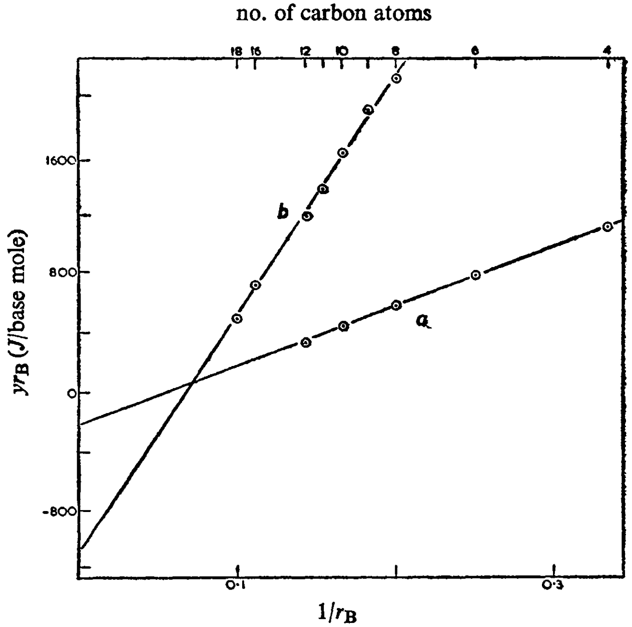

FIG. 4.—The function yr_{B} against $1/r_{\mathrm{B}}$ for (*a*) PIB+ethers, (*b*) PIB+esters showing comparison with eqn. (13).

presumably be positive since the interaction energy of two —COO— groups or two —COC— groups must be greater than between two methylene groups as attested by the high solubility parameters of the esters and ethers. Thus, for $\delta\delta'$ negative, δ must be taken negative which seems reasonable in view of the methyl side-groups on the PIB chain. Eqn. (13) show that as δ' becomes greater the slope increases and the intercept becomes more negative, as seen in fig. 4, leading to the intersection between the two straight lines for the ethers and esters. A further prediction of the relation (13) is that the slope should increase as a power of the intercept, between one and two, depending on the importance of the second term in the expression for the intercept. Experimentally, the intercepts and slopes are, for the ethers

-220 J and 4000 J, and for the esters -1100 J and 16,000 J, so that the slope in fact rises more slowly than predicted. Such a discrepancy is hardly surprising in view of the approximations in the theory, and particularly the presence of large dipole-dipole interactions in the esters and ethers for which the geometric mean rule, (3), on which eqn. (13) are based, is rather poor.

For short-range forces not obeying the geometric mean rule, the above relation between slope and intercept will not hold, although the expression $r_B y$ should still be linear in $1/r_B$.

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