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THE INTERACTION BETWEEN RUBBER AND LIQUIDS.

PART VII. THE HEATS AND ENTROPIES OF DILUTION OF NATURAL RUBBER BY VARIOUS LIQUIDS.

By (MISS) J. FERRY, GEOFFREY GEE and L. R. G. TRELOAR.

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1. Introduction.

Considerable progress has been made in interpreting the properties of polymer solutions and gels in the light of statistical calculations of the entropy of mixing of polymers with liquids.[1] The basis of most of these applications has been the assumption that the Gibbs free energy of dilution ΔG_0 of such a mixture by the liquid was expressible in terms of the entropy of dilution ΔS_0, as calculated statistically on the assumption of random mixing, and a heat of dilution ΔH_0 proportional to the square of the volume fraction v_r of the polymer. Huggins has shown that a wide variety of thermodynamic data can be represented in this way; the present paper will include a more sensitive test of the validity of the assumption.

Free energies of dilution of polymer solutions have been calculated [2] from data on vapour pressure, osmotic pressure, swelling pressure, and freezing point depression. Corresponding values for the heats of dilution are almost entirely lacking, and it is therefore impossible to check whether the quantity employed to relate the theoretical entropy to the experimental free energy is equal to the heat of dilution, or whether it contains also an empirical correction factor. The direct measurement of heats of dilution for polymer systems is exceedingly difficult; a new attempt to do so for mixtures of natural rubber + benzene is now in progress. Here we present estimates of the heats of mixing of natural rubber with a number of liquids, based on calorimetric measurements of the heats of mixing of low molecular liquid homologues of rubber with the same liquids, and of the entropies of mixing obtained by combining these with vapour pressure data.

2. Heat and Volume Changes on Mixing Dihydromyrcene and Squalene with other Liquids.

A quantity of dihydromyrcene and a much smaller amount of squalene were made available to us by Dr. E. H. Farmer, to whom our thanks are due. These substances contain respectively two and six isoprene units per molecule, and may thus be regarded as very low molecular homologues of natural rubber. The heats of mixing of dihydromyrcene with a series of liquids were measured in the calorimeter shown in Fig. 1. In order to conserve materials it was necessary to work with relatively small volumes of liquids (not more than 10 c.c. dihydromyrcene for the whole series of measurements on each liquid). The heat absorption to be measured in a typical mixing was thus of the order of 1 cal. Attempts to do this in a small vacuum jacketted calorimeter of small heat capacity were

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[1] Huggins, *J.A.C.S.*, 1942, **64**, 1712. Flory, *J. Chem. Physics*, 1942, **10**, 51. Gee, *Trans. Farad. Soc.*, 1942, **38**, 276, 418; 1944, **40**, 463, 468. *Ann. Repts. Chem. Soc.*, 1942, 7. *Recent Advances in Colloid Science*, Vol. 2 (Interscience Publishers, *in press*).

[2] Refs. 1 and especially Huggins, *Ann. N.Y. Acad. Sci.*, 1942, **43**, 1; *Ind. Eng. Chem.*, 1943, **35**, 216.

rendered inaccurate by relatively large heat losses, and the arrangement shown was finally adopted. It consisted of a thermostatted vacuum vessel almost filled with water, in which were suspended two coaxial bulbs, the tube of the inner bulb being a close fit into the outer so as to minimise loss by evaporation. The liquids A and B were in the outer and inner bulbs respectively, the lower end of the latter being sealed by a pool of mercury. Mixing of the two liquids was accomplished by raising the inner bulb out of the mercury and rotating it so that the liquid was stirred by the vanes attached to the inner bulb. Several samples of B could be added successively without removing the calorimeter from the thermostat, the inner bulb being completely emptied each time by passing a gentle stream of nitrogen through it. The water in the calorimeter was stirred by a slow stream of air presaturated with water vapour. A layer of cork, C, was found necessary in order to prevent water splashing through the exit tube. The temperature change was measured by ten copper-eureka thermocouples, T, in series, arranged at different levels, with the cold junctions in a second vacuum vessel also filled with water, and contained in the same thermostat; the connecting leads passed through a short length of lead tubing. The heater H was of *ca.* 10 ohms resistance, and permitted small measured quantities of energy to be introduced in order to determine the heat capacity. This was approximately 65 cals., so that the temperature change to be measured was of the order of a hundredth of a degree, and the thermoelectric e.m.f. a few microvolts. This was measured directly by means of a Tinsley taut suspension galvanometer, of resistance 9·5 ohms and sensitivity 180 mms. per microamp. The overall sensitivity (maximum 5 metres per degree) was determined by calibrating against Beckmann thermometers, the galvanometer deflection being very nearly proportional to the temperature difference between the hot and cold junctions.

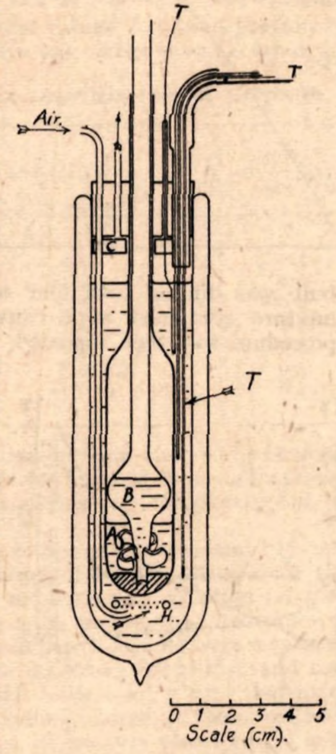

FIG. 1.—Calorimeter.

In order to make the heat interchange with the surroundings during an experiment small compared with the quantity to be measured, it was necessary that both hot and cold junctions should be very near to the thermostat temperature.* In order to ensure this, it was found desirable to check the cold junction temperature before and during an experiment by a Beckmann thermometer, and to leave the calorimeter in the thermostat overnight before making the first addition. Subsequent additions could be made after an interval of 1 to 2 hours. Under these conditions, the correction for heat interchange with the surroundings was small, and the temperature change on mixing was nearly that calculated from the maximum galvanometer deflection.

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* A further precaution was to make the thermocouples of sufficiently fine wire for heat loss by conduction to be negligible; 20 s.w.g. eureka and 38 s.w.g. copper were actually employed.

A typical series of measurements of the heat of mixing of the two liquids was performed in two parts. In the first, 5 c.c. of liquid A in the outer bulb was diluted with four successive additions of liquid B, until the mixture contained approximately equal volumes of A and B. The procedure was then repeated, with the liquids interchanged. The heat absorptions measured were used to calculate the heat of mixing ΔH^m of v_0 c.c. of liquid A with $(1 - v_0)$ c.c. of liquid B; results obtained in this way for CS_2 + dihydromyrcene are shown in Fig. 2. In accordance with the usage of earlier papers the volume fraction of dihydromyrcene (regarded as "rubber") is written v_r; that of the other liquid v_0. Points in the two halves of the experiment are differently indicated, and it will be noted that all lie on a smooth, almost parabolic curve. This curve would be exactly parabolic if Hildebrand's expression[3] for the heat of mixing was obeyed:

$$\Delta H^m = \alpha v_0 v_r \qquad . \qquad . \quad (1)$$

The deviation from this form can be represented most readily by employing each experimental point to calculate a value of α; the results for a series of liquids are shown in Fig. 3. It is evident that equation (1) is obeyed with considerable accuracy by most of the liquids examined, only acetone and chloroform showing large deviations. There appears to be a real, though small, deviation in the CS_2 data, although the extreme points are less accurate than the remainder.

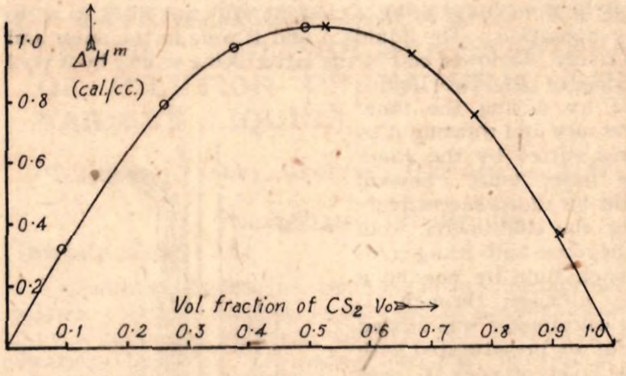

FIG. 2.—Heat of mixing of CS_2 and dihydromyrcene.

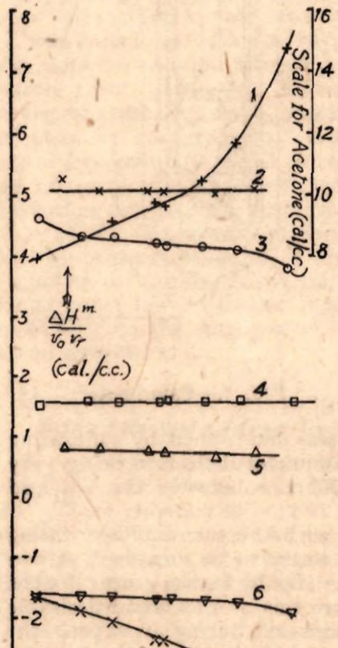

FIG. 3.—Heats of mixing of liquids with dihydromyrcene.

1. Acetone.
2. Benzene.
3. CS_2.
4. Toluene.
5. Heptane.
6. CCl_4.
7. $CHCl_3$.

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[3] Hildebrand, *Solubility* (Reinhold, 1936).

The constant α is given, according to Hildebrand's theory by

$$\alpha = (\sqrt{e_0} - \sqrt{e_r})^2 \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where e_0 and e_r are the cohesive energy densities of the liquid and of dihydromyrcene; α should thus always be positive, so that (2) evidently breaks down for $CHCl_3$ and CCl_4. By comparison with other hydrocarbons we may estimate $\sqrt{e_r}$ *for dihydromyrcene as* $7{\cdot}4_2$ (cal./c.c.)$^{\frac{1}{2}}$, *for squalene* as $7{\cdot}7_8$ (cal./c.c.)$^{\frac{1}{2}}$ while the value for natural rubber has been previously estimated[4] as $7{\cdot}9_8$. In Table I, values of α calculated from (2) are compared with the experimental values, and it is evident that while there is a rough agreement as to order of magnitude for benzene, toluene, heptane, CS_2, and acetone, the halogenated hydrocarbons fall completely out of line.

TABLE I.—HEAT AND VOLUME CHANGES IN DIHYDROMYRCENE MIXTURES.

Liquid.	$\sqrt{e_0}$.	α(cal./c.c.).		$100\,\dfrac{\Delta V^m}{v_0 v_r}$ (c.c.).
	(cal./c.c.)$^{\frac{1}{2}}$.	calc.	obs.	
Benzene . . .	$9{\cdot}1_8$	$3{\cdot}1_0$	$5{\cdot}1$	$1{\cdot}5$
Toluene . .	$9{\cdot}0_2$	$2{\cdot}5_6$	$1{\cdot}60$	$0{\cdot}2$
Heptane . .	$7{\cdot}5_0$	$0{\cdot}0_1$	$0{\cdot}7_0$	$-0{\cdot}4$
CS_2 . . .	$10{\cdot}0_5$	$6{\cdot}9$	$4{\cdot}2$	$1{\cdot}2$
CCl_4 . . .	$8{\cdot}5_5$	$1{\cdot}2_8$	$-1{\cdot}7$	$-0{\cdot}3$
Acetone . .	$9{\cdot}7_7$	$5{\cdot}5$	8 to 16	$0{\cdot}4$
$CHCl_3$ . . .	$9{\cdot}3_0$	$3{\cdot}5$	$-1{\cdot}6$ to $-3{\cdot}5$	$0{\cdot}2$

It has been suggested[5] that the general source of disagreement between calculated and experimental heats of mixing of liquids arises from the failure of the assumption involved in the derivation of equation (2) that there is no volume change on mixing. In order to test the importance of this factor in the present case the volume changes on mixing were measured in a simple modification of the apparatus described by Hildebrand and Carter.[6] It consisted of a U-tube of total volume *ca.* 7 c.c., the upper parts of the two limbs being of capillary tubing, closed at the outer ends by stoppers. The tube was filled with 3 c.c. of mercury plus 2 c.c. of each liquid under examination and thermostatted, the mercury forming a seal between the two liquids. After reading the liquid levels in the capillaries, the two liquids were mixed by allowing the mercury to flow from limb to limb and the levels again noted. The expansions observed (ΔV^m c.c./c.c. of total liquid), are given in Table I, expressed as $100\,\Delta V^m/v_0 v_r$, which is reproducible to $\pm\,0{\cdot}2$ c.c. The energy required to compress the mixture isothermally to the volume it would have if mixing occurred without change of volume is approximately $T\alpha_v \Delta V^m / 41{\cdot}3\beta$ cal. where α_v(deg.$^{-1}$), β(at$_m{}^{-1}$) are the coefficients of cubical expansion and compressibility of the mixture. For most liquids at room temperature $T\alpha_v/41{\cdot}3\beta \approx 100$ cal./c.c., so that the last column is approximately equal, numerically, to the contribution to the heat of mixing from the work done against the intermolecular forces in the observed expansion. This contribution is by no means negligible for benzene and CS_2 but the lack of correlation between the last two columns shows that it *does not account quantitatively* for the discrepancy between the calculated and observed values of α. In view of this conclusion, it was not considered worth while to investigate the constancy of the function $\Delta V^m/v_0 v_r$.

[4] Gee, *I.R.I. Trans.*, 1943, **18**, 266.

[5] Scatchard, *Trans. Farad. Soc.*, 1937, **33**, 160.

[6] Hildebrand and Carter, *J.A.C.S.*, 1932, **54**, 3592.

3. Estimation of Heats of Dilution of Rubber from Calorimetric Data.

In order to obtain the heat of dilution ΔH_0, we re-write equation (1) to give the heat absorbed ΔH, on mixing N_0 moles of liquid (molar vol. V_0) with N_r moles of rubber (molar volume V_r) in the form :

$$\Delta H = \frac{\alpha N_0 N_r V_0 V_r}{N_0 V_0 + N_r V_r} \quad . \quad . \quad . \quad . \quad . \quad (1')$$

and differentiate, to obtain $\Delta H_0 \equiv \left(\frac{\partial \Delta H}{\partial N_0}\right)_{N_r}$ . . . . . . (2)

If α is constant, the result is

$$\Delta H_0 / v_r^2 = \alpha V_0 \quad . \quad . \quad . \quad . \quad . \quad (3)$$

If α is not constant, we may still express the experimental results in terms of α, and it may then be shown that

$$\frac{\Delta H_0}{v_r^2} = V_0\left(\alpha - v_0 \frac{\partial \alpha}{\partial v_r}\right) \quad . \quad . \quad . \quad . \quad . \quad (4)$$

Using values of $\partial\alpha/\partial v_r$ from the smoothed curves of Fig. 3, we thus obtain $\Delta H_0/v_r^2$ as functions of v_r for dihydromyrcene in acetone and chloroform ; for the other liquids (3) may be used with sufficient accuracy.

We have now to consider the relation between the heats of dilution of dihydromyrcene and of rubber by the same liquid. If we denote the respective "constants" of equation (1) by α_d, α_r, (2) gives

$$\alpha_d = (\sqrt{e_0} - 7{\cdot}42)^2 ; \quad \alpha_r = (\sqrt{e_0} - 7{\cdot}98)^2,$$

whence

$$\alpha_d - \alpha_r = 1{\cdot}12(\sqrt{e_0} - 7{\cdot}70). \quad . \quad (5)$$

This equation should be true provided that the difference between the heats of dilution of dihydromyrcene and rubber can be represented completely by the difference of cohesive energy density, i.e. provided that the factors responsible for the failure of equation (2) are equally operative in both cases. This is clearly a plausible assumption, and one would expect (5) to hold much more closely than (2). A limited test of its validity has been made by comparing the heats of mixing of benzene and heptane with dihydromyrcene and squalene. Denoting the constant of mixtures with the latter by α_s, equation (5) should be replaced by

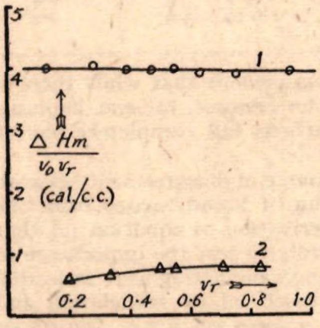

FIG. 4.—Heats of mixing of squalene with benzene (1), Heptane (2).

$$\alpha_d - \alpha_s = 0{\cdot}72\ (\sqrt{e_0} - 7{\cdot}60) \quad . \quad . \quad . \quad (5')$$

The experimental data for the squalene mixtures are given in Fig. 4, which shows equation (1) to be very well obeyed. Table II shows that the observed and calculated values of $(\alpha_d - \alpha_s)$ are in excellent agreement :

TABLE II.—HEATS OF MIXING WITH SQUALENE AND DIHYDROMYRCENE.

Liquid.	α_d.	α_s.	$\alpha_d - \alpha_s$.	
			(obs.)	(calc.)
Benzene . .	5·1	$3{\cdot}9_5$	$1{\cdot}1_5$	$1{\cdot}1_3$
Heptane . .	0·65 to 0·8	0·8 to 0·7	$\pm 0{\cdot}1_5$	0·07

Values of $\alpha_r V_0$ have therefore been computed by using the experimental values of α_d and values of $(\alpha_d - \alpha_r)$ calculated from equation (5) giving:

TABLE III.

Liquid.	$\alpha_r V_0 = \Delta H_0/v_r^2$ (cal./mole).
Benzene . . .	310
Toluene . . .	15
Heptane . . .	135
CS_2 . . .	95
CCl_4 . . .	−255

For acetone and $CHCl_3$ combination of (4) and (5) gives:

$$\Delta H_0/V_0 v_r^2 = \alpha_d - v_0\,\partial\alpha_d/\partial v_r - 1{\cdot}12\,(\sqrt{e_0} - 7{\cdot}70). \quad (6)$$

Values of $\Delta H_0/v_r^2$ plotted in Fig. 5 were calculated from this expression. These results (Table III and Fig. 5) constitute our estimates of the heats of dilution of natural rubber by the seven liquids concerned.

One rather puzzling feature is the apparent constancy of $\Delta H_0/v_r^2$ for most of the liquids, since the number of contacts between rubber and liquid will depend on their relative molecular surfaces, which will not be proportional to the volume fractions, except in the artificial case of infinite co-ordination number.[7a] It is true that this constancy has only been proved experimentally for mixtures with dihydromyrcene and squalene, but the case of benzene + squalene affords a very striking example of the disagreement between theory and experiment; according to Orr's calculations[7b] the value of $\Delta H_0/v_r^2$ at $v_r = 0$ should be only about one half of that at $v_r = 1$. The origin of the discrepancy remains obscure, but these experimental results, so far as they go, support the usual practice of assuming $\Delta H_0 \propto v_r^2$ for polymer + liquid, as well as for mixtures of two liquids.

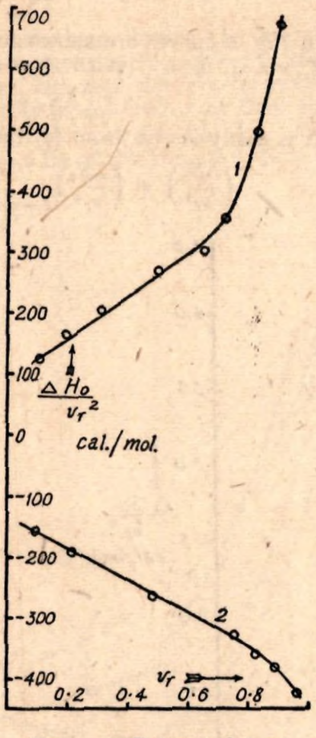

FIG. 5.—Estimated heat of dilution of natural rubber by: (1) acetone, (2) $CHCl_3$.

The heat of dilution obtained for benzene does not agree with our direct estimate reported earlier[8] according to which $\Delta H_0/v_r^2$ varies from 160 cal./mole at $v_r = 1$ to 60 cal./mole at $v_r = 0$; we wish to defer comment on this until further work on benzene, now in progress, is completed.

4. Estimation of Entropies of Dilution.

The free energy of dilution of natural rubber by each of these liquids has been calculated from the available vapour pressure data, and combined with the above thermal measurements to give an estimate of the entropy of dilution. The results are shown in Figs. 6 and 7, in which $\Delta S_0/v_r^2$ is

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[7] (*a*) Gee and Treloar, *Trans. Farad. Soc.*, 1942, **38**, 147. (*b*) Orr, *ibid.*, 1944, **40**, 320.

[8] Gee, *ibid.*, 1942, **38**, 418; *cf.* 7(*a*).

plotted against v_r, and compared with the theoretical value obtained from Miller's equation[13] *

$$\Delta S_0 = -R\left[\ln(1 - v_r) - \frac{Z}{2}\ln\left(1 - \frac{2v_r}{Z}\right)\right] \quad . \quad . \quad (7)$$

In Fig. 6 curves are shown for three values of the co-ordination number Z, viz. 4, 6, ∞. With $Z = \infty$, (7) reduces to Flory's expression :[14]

$$\Delta S_0 = -R[\ln(1 - v_r) + v_r] \quad . \quad . \quad . \quad (8)$$

It is easily shown from (7) that

$$\left(\frac{\Delta S_0}{v_r^2}\right) = \left(\frac{\Delta S_0}{v_r^2}\right)_{Z=\infty} - \frac{R}{Z}\left(1 + \frac{4}{3Z}\cdot v_r + \frac{2}{Z^2}\cdot v_r^2 + \ldots\right) \quad . \quad (9)$$

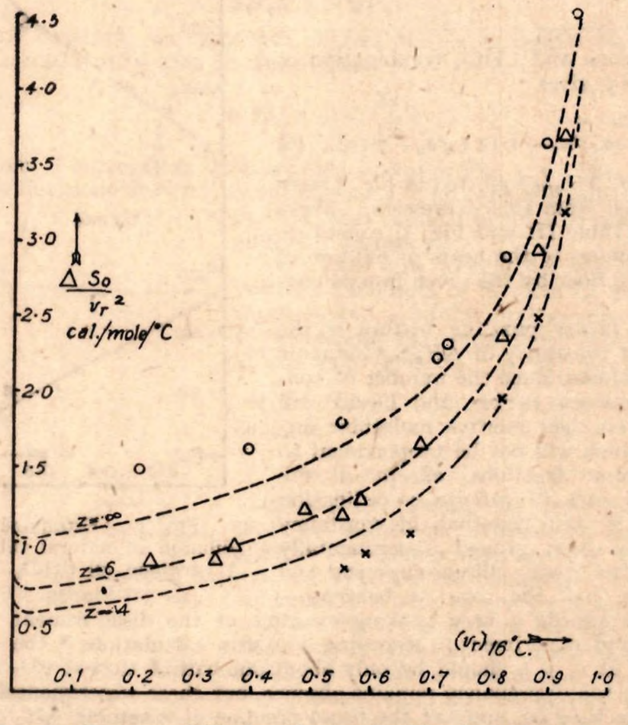

FIG. 6.—Entropy of dilution of natural rubber by hydrocarbons.
○ Benzene at 25° C.[7a] △ Heptane at 40° C.[9] × Toluene at 25° C.[10]
Dotted curves calculated from equation (7).

so that plots of $\Delta S_0/v_r^2 \sim v_r$ for different values of Z are nearly superposable by adding suitable constants. Huggins[2] has shown that a very wide range of thermodynamic data (including that used here) can be represented by an equation of the form

$$-\frac{\Delta G_0}{T v_r^2} = \left(\frac{\Delta S_0}{v_r^2}\right)_{Z=\infty} - \frac{\mu}{RT} \quad . \quad . \quad . \quad (10)$$

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[9] *Unpublished experiments.*

[10] Meyer and Boissonnas, *Helv. Chim. Acta*, 1940, **23**, 430.

[13] Miller, *Proc. Camb. Phil. Soc.*, 1943, **39**, 54, 131.

* This is a simplification of the general equation, valid for polymers of high molecular weight, except in dilute solutions.

[14] Flory, *J. Chem. Physics*, 1941, **9**, 660 ; 1942, **10**, 51.

where μ is a constant. Now, for those liquids for which $\Delta H_0 = \alpha_r V_0 v_r^2$ we have also

$$-\frac{\Delta G_0}{T v_r^2} = \frac{\Delta S_0}{v_r^2} - \frac{\alpha_r V_0}{T} \quad . \quad . \quad . \quad . \quad (11)$$

Huggins' observation thus requires that for these liquids the entropy curves should be either identical or at least superposable by adding suitable constants. This is nearly true in most cases, although the present method of plotting provides a much more severe test of equation (10) than that employed by Huggins. If equation (10) holds for liquids for which $\Delta H_0 \neq \alpha_r V_0 v_r^2$ it follows that $\Delta S_0 / v_r^2$ cannot be of the standard form.

It is evident from Figs. 6 and 7 that our estimated entropies of dilution, although generally of the expected form, do not agree quantitatively either among themselves or with the theoretical equation. It is unlikely that the free energies deduced from vapour pressure data can be seriously in error for $v_r > 0{\cdot}5$, but the lower points are much less certain. Some part at least of the disagreement may arise from errors in the heats of dilution; this cannot at present be checked. Discussion of the origin of these different entropies of dilution must therefore be somewhat tentative at present.

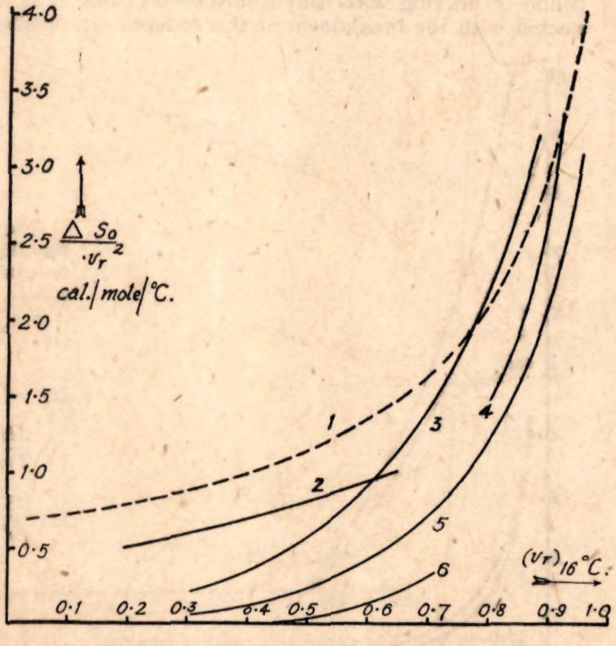

FIG. 7.—Entropy of dilution of natural rubber by polar liquids.

Curve 1. Theoretical ($Z = 6$).
2. CS_2 at 25° C.[11]
3. CCl_4 at 35° C.[12]

Curve 4. Acetone at 35° C.[12]
5. $CHCl_3$ at 35° C.[12]
6. $CHCl_3$ at 25° C.[11]

The first point to be noted is that equation (7) was deduced on the assumption of random mixing, so that it can only be expected to apply accurately to athermal mixtures. The nearest approach to this condition is provided by toluene, heptane and CS_2, and it is satisfactory to note that these three liquids give entropy curves in fair agreement with theory, assuming low co-ordination numbers (4 to 6). There is, of course, no reason to suppose that the co-ordination number will be the same for all mixtures of rubber + liquid, or even that it will necessarily be independent of concentration in any particular mixture. The effect of finite heats

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[11] Stamberger, *J.C.S.*, 1929, 2323.

[12] Lens, *Rec. trav. chim.*, 1932, **51**, 971.

of mixing on the entropy of dilution has been estimated by Orr,[7b] and shown to be small for heats of mixing of the order found experimentally for most of the liquids with which we have worked, the only possible exception being acetone. The effect vanishes for $Z = \infty$, and for finite values of Z is positive at low v_r, negative at high. Using Orr's equation, the theoretical entropy of dilution of rubber by benzene, taking $N_w = 310$ cal.; $Z = 6$ is 2·08 cal./mole/°C. at $v_r = 0{\cdot}8$, which is almost identical with the value calculated for athermal mixing. The high entropy found experimentally for benzene appears to be a specific effect, and is probably due to the fact that this liquid is known from other evidence to be rather highly ordered,[15] due no doubt to a tendency for the flat molecules to pack with the planes of adjacent molecules parallel. The very large expansion found on mixing with dihydromyrcene (Table I) is almost certainly connected with the breakdown of this ordered arrangement.

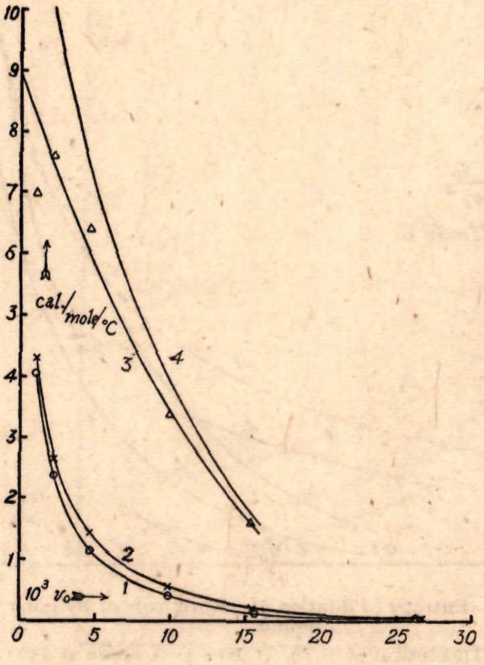

FIG. 8.—Thermodynamic functions for the system natural rubber + methyl alcohol.

(1) $-\dfrac{\Delta G_0}{T v_r^2}$ at 25° C.

(2) $-\dfrac{\Delta G_0}{T v_r^2}$ at 35° C.

(3) $\dfrac{\Delta H_0}{T v_r^2}$ at 30° C. from (1) and (2).

(4) $\dfrac{\Delta S_0}{v_r^2}$ at 30° C. from (1), (2) and (3).

Acetone is an example of a liquid possessing a rather large heat of mixing with rubber, the two materials being only partially miscible. The tendency towards separation into two phases is shown by the rapid fall of both $\Delta H_0/Tv_r^2$ and $\Delta S_0/v_r^2$ as the acetone content is increased, indicative of increasingly non-random mixing. Although in the direction indicated by Orr's analysis, both effects are considerably greater than would be given by the theory. Taking $N_w = 1000$ cal., $Z = 6$, the calculated values at $v_r = 0{\cdot}8$ are $\Delta H_0/v_r^2 = 680$ cal./mole; $\Delta S_0/v_r^2 = 1{\cdot}86$ cal./mole/°C. The maximum inbibition of acetone by rubber at 35° C. should be only about 8 % by volume, compared with the experimental value of ca. 20 %. It is evident therefore that neither the crude theory, as developed by Flory and Huggins, nor Orr's refinement of it, applies quantitatively to this system.

CCl_4 and $CHCl_3$ present a different kind of departure from the simple theory; the entropy of mixing is again small, but for these liquids ΔH_0

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[15] Scatchard, Wood and Mochel, *J. Physic Chem.*, 1939, **43**, 119.

is negative, indicating a tendency towards complex formation between the liquid and rubber. The very small entropies of dilution at low liquid concentrations affords further evidence of order in the mixture, associated with complex formation.

5. Thermodynamics of the System Rubber + Methyl Alcohol.

The evidence presented above shows that, while the statistical thermodynamic theory of polymer solutions holds reasonably well for normal mixtures it is less satisfactory when the heat of mixing is large. In order to test the usefulness of the present theories in an extreme case, we have studied the thermodynamic properties of mixtures of rubber + methyl alcohol. Only about 2 % of methyl alcohol is imbibed by rubber at room temperature, so that a very limited concentration range is available for study. Vapour pressures were measured at 25° C. and 35° C. by a method previously described [7a] and used to calculate the free energy and heat of dilution. The results are shown in Fig. 8, from which the following points may be noted :—

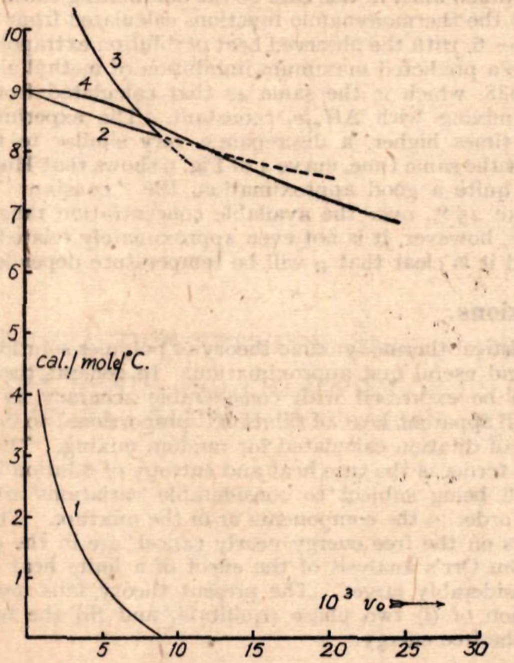

FIG. 9.—Theoretical thermodynamic functions for rubber and methyl alcohol at 30° C.

$$\left.\begin{array}{ll}\text{Curve 1.} & -\dfrac{\Delta G_0}{Tv_r^2}\\ \text{2.} & \dfrac{\Delta H_0}{Tv_r^2}\\ \text{3.} & \dfrac{\Delta S_0}{v_r^2}\end{array}\right\}\text{Theoretical for }\begin{cases}Z = 6.\\ N_w = 2{\cdot}72\text{ k. cal.}\end{cases}$$

$$\text{4.}\quad \left(\frac{\Delta G_0}{Tv_r^2}\right)_{\text{expt.}} + \left(\frac{\Delta S_0}{v_r^2}\right)\text{ theoretical for }\begin{cases}\Delta H_0 = 0.\\ Z = 6.\end{cases}$$

(i) $\Delta H_0/v_r^2$ falls very rapidly as the alcohol content of the mixture increases. This behaviour is paralleled by the heats of solution of alcohols in low molecular hydrocarbons,[16] and must be ascribed to the almost complete association of alcohols except in the most dilute solution. The very large heat of dilution as $v_0 \rightarrow 0$ represents the energy of the hydrogen bonds, and is of the same order for methyl alcohol in rubber as for a range of alcohols in hexane and benzene.

(ii) ΔS_0 is very much less than its theoretical value, except at very small v_0, and it is evident that mixing is far from random.

(iii) These deviations are far larger than would be expected on the basis of Orr's calculation of the effect of a heat of mixing.[7b] The discrepancy is not surprising, since the theory does not make allowance for association, which must in this case be the dominating cause of irregularity. Fig. 9 shows the thermodynamic functions calculated from Orr's equation, assuming $Z = 6$, with the observed heat of dilution extrapolated to $v_0 = 0$. They lead to a predicted maximum imbibition of methyl alcohol at 30° C. of $v_0 = 0{\cdot}0088$, which is the same as that calculated from the entropy of random mixing with $\Delta H_0/v_r^2$ constant. The experimental value is some three times higher, a discrepancy very similar to that found for acetone. At the same time, curve 4 of Fig. 9 shows that Huggins' equation (10) is still quite a good approximation, the "constant" μ varying by no more than 25 % over the available concentration range. Over most of this range, however, it is not even approximately related to the heat of dilution, and it is clear that μ will be temperature dependent.

6. Conclusions.

The statistical thermodynamic theory of polymer solutions is confirmed as a valid and useful first approximation. In general, the free energy of dilution can be expressed with considerable accuracy as the difference between an "apparent heat of dilution," proportional to v_r^2, and T times the entropy of dilution calculated for random mixing. The identification of these two terms as the true heat and entropy of dilution is not generally correct, both being subject to considerable variations arising from the existence of order in the components or in the mixture. These variations, whose effects on the free energy nearly cancel, are in the direction to be expected from Orr's analysis of the effect of a finite heat of mixing, but may be considerably larger. The present theory fails most seriously in the estimation of (i) two phase equilibria, and (ii) the temperature coefficient of the free energy.

Summary.

Calorimetric measurements of the heats of mixing of seven liquids with dihydromyrcene are used to estimate the heats of dilution of rubber by these liquids. Combining the results with free energies calculated from vapour pressure gives entropies of dilution which show significant deviations from the present statistical theory.

A thermodynamic study of rubber + methyl alcohol shows similar but larger deviations.

This work forms part of a programme of fundamental research on rubber undertaken by the Board of the British Rubber Producers' Research Association.

British Rubber Producers' Research Association,
48 *Tewin Road, Welwyn Garden City, Herts.*

[16] Wolf, Pahlke and Wehage, *Z. physik. Chem.*, 1935, **28**, 1.

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