Reprinted from the *Transactions of the Faraday Society*, No. 255,
Vol. XXXVIII, Part 9, September, 1942.

THE INTERACTION BETWEEN RUBBER AND LIQUIDS

III. THE SWELLING OF VULCANISED RUBBER IN VARIOUS LIQUIDS

THE INTERACTION BETWEEN RUBBER AND LIQUIDS.

III. THE SWELLING OF VULCANISED RUBBER IN VARIOUS LIQUIDS.

BY G. GEE.

Received 19th *July*, 1942.

The swelling of a vulcanised rubber in a wide range of liquids has been studied by Whitby and co-workers,[1] and a number of interesting regularities pointed out. It has been suggested[2] that a correlation should exist between the swelling power of a liquid for rubber and its cohesive energy density. The purpose of the present paper is to develop this idea a little further, and to show how it can be used to interpret Whitby's data.

It has already been pointed out[3] that the swelling and dissolution of raw rubber is best considered as the problem of the miscibility of two liquids. Vulcanised rubber differs from raw essentially in that it possesses a structure which cannot be broken down completely by any solvent: the material therefore swells but cannot be dispersed unchanged.[*] In order to describe this behaviour thermodynamically we require to know the partial molar entropy ΔS_0 and heat ΔH_0 of swelling of the rubber by liquid. No thermodynamic study has yet been made of the system vulcanised rubber + liquid, but it is reasonable to assume that vulcanised rubber will differ from raw only when a considerable amount of liquid has been imbibed. This is confirmed by the very similar swelling of raw and vulcanised rubbers in liquids of not too great swelling power. At low solvent concentrations, ΔS_0 is therefore taken to have the values found for raw rubber + benzene.[4] As before,[3] we assume ΔS_0 to be the same for all liquids, and seek to explain their different swelling powers in terms of their heats of swelling. Clearly—if we neglect any liquids which may evolve heat on swelling—the maximum degree of swelling will be found when $\Delta H_0 = 0$. Since the condition for equilibrium between swollen rubber and pure liquid is that the Gibbs free energy of swelling $\Delta G_0 = 0$, it follows that, for the *best* swelling agent, the equilibrium condition may also be written $\Delta S_0 = 0$. Whitby's data[1] suggest a maximum swelling Q of ca 5 (c.c. liquid/c.c. rubber) and we therefore take $\Delta S_0 = 0$ when v_0 (vol. fraction of liquid) $= 0{\cdot}833$. One other point on the entropy curve for vulcanised rubber is obtained by making the further assumption that the heat of swelling of vulcanised rubber by benzene is the same as that of raw rubber. Taking $Q = 3{\cdot}94$ for the maximum swelling of benzene,[*] we

---

[1] Whitby, Evans and Pasternack. *This vol.*, 269.

[2] Gee, *ibid.*, 282.

[3] Gee, *ibid.*, 276; *cf.* also Flory, *J. Chem. Physics*, 1942, **10**, 51.

[*] Examples quoted by Whitby of the ultimate dissolution of vulcanised rubber must be ascribed to degradation—probably by oxidation—unless evidence can be brought to show that the vulcanised rubber can be recovered unchanged from solution.

[4] Gee and Treloar, *Trans. Faraday Soc.* *This vol.*, 147.

[*] Whitby's data do not give any equilibrium values of Q. If the present theory is correct there must be a definite limit to swelling, and our experience suggests that for the small specimens used by Whitby equilibrium would be attained within a day or so. We therefore accept Scott's suggestion[5] that further swelling is spurious, arising most probably from oxidation, and estimate equilibrium values of Q by extrapolating Q roughly to $t = 0$. Values obtained in this way are used throughout this paper.

calculate from our previous data[4] $\Delta H_0 = T\Delta S_0 = 2{\cdot}6$ cal/mole at $v_0 = 0{\cdot}798$. These three conclusions about the entropy of swelling have been combined as shown in Fig. 1, in which $\dfrac{T\Delta S_0}{(1 - v_0)^2}$ is plotted as a function of v_0 for raw and vulcanised rubber. The curve for the latter is drawn through the above two points so as to merge with the curve for raw rubber in benzene at low values of v_0. It is clear that the resulting curve is only a first approximation and that it applies only to the specimen of vulcanised rubber used by Whitby.†

We have now to consider how the heats of swelling of rubber by the various liquids may be related with some known property of the liquids. The heats of mixing of most normal liquids are related to the difference between their cohesive energy densities[7] by an equation of the form

$$\Delta H_0 = kV_0\left\{\sqrt{\frac{E_0}{V_0}} - \sqrt{\frac{E_1}{V_1}}\right\}^2(1 - v_0)^2 \quad . \quad . \quad . \quad (1)$$

where ΔH_0 is the partial molar heat of dilution of the mixture (composition v_0) by liquid$_0$, V_0 V_1 are the molar volumes of the liquids, and E_0 E_1 are the molar cohesive energies of the liquids. According to the simple theory $k = 1$, but larger values are usually found experimentally, even for mixtures of hydrocarbons.[8] Values of E_0 are obtained from $E_0 = L_0 - \boldsymbol{R}T$, where L_0 is the molar latent heat of evaporation, and is to be calculated from the temperature coefficient of the vapour pressure at the temperature T (= 298° K). Precise values of E_0 are known for very few liquids, so that

$$\left\{\sqrt{\frac{E_0}{V_0}} - \sqrt{\frac{E_1}{V_1}}\right\}^2$$

is subject to large uncertainties. If we assume equation (1) to apply to swelling of vulcanised rubber, where the subscript $_1$ is taken to denote rubber, it is evident that $\sqrt{E_1/V_1}$ must be treated as a constant α, independent of the nature of the liquid, and having a value of the order 8 (cal./c.c.)$^{1/2}$ to bring it in line with known $\sqrt{E/V}$ values for hydrocarbons;[7] k may be regarded as an adjustable parameter, but must be of the order of magnitude of unity.

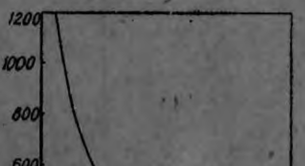

FIG. 1.—Entropy of dilution of rubber by liquids.

The condition for the equilibrium swelling of vulcanised rubber in a liquid$_0$ is now written $T\Delta S_0 = \Delta H_0$, or :

---

† The heat and entropy of dilution of raw rubber by benzene used in deriving Fig. 1 differ somewhat from those given previously,[5] owing to the correction of the latter for the departure of benzene vapour from perfect gas behaviour. Employing the correcting factors of Eucken and Mayer[6] the Gibbs free energy of dilution remains substantially unchanged, but the heat of dilution is considerably reduced. The revised values can be represented by $\Delta H_0 = 78\Delta h_0 = 156\left(\dfrac{W_r}{1{\cdot}7 - 0{\cdot}7W_r}\right)^2$, where W_r = weight fraction of rubber. This equation has been used in place of no. (20) in ref. 4. The conclusions drawn there are, of course unchanged by the correction.

[5] Scott. *This vol.*, 284.

[6] Eucken and Mayer, *Z. physik. Chem. B*, 1929, **5**, 452.

[7] Hildebrand, *Solubility* (Reinhold, 1936), p. 73; Scatchard, *Chem. Rev.*, 1931, **8**, 321; *J.A.C.S.*, 1934, **56**, 995.

[8] Scatchard, *J. Physic. Chem.*, 1939, **43**, 119.

$$\sqrt{\frac{x}{V_0}} = \sqrt{k}\left(\sqrt{\frac{E_0}{V_0}} - \alpha\right) \quad . \quad . \quad . \quad . \quad (2)$$

where
$$x = \frac{T\Delta S_0}{(1 - v_0{}^*)^2} \quad . \quad . \quad . \quad . \quad . \quad (3)$$

and $v_0{}^*$ is the volume fraction of liquid when the rubber is fully swollen by that liquid. Fig. 1 gives directly x as a function of $v_0{}^*$ for a series of liquids, and it is evident from (2) that $\sqrt{x/V_0}$ should be a linear function of $\sqrt{\frac{E_0}{V_0}}$. Whitby's data give Q and therefore $v_0\left(= \frac{Q}{1 + Q}\right)$, so that they can be used to test the validity of equation (2). The results are shown in Fig. 2, which includes the whole of Whitby's data on liquids for which E_0/V_0 could be calculated, with the exception of the alcohols and acids. These are omitted, since it is clear that the above theory cannot be expected to apply to such highly associated liquids. It is evident that equation (2) does not hold precisely for the whole range of liquids examined, but the more normal aliphatic liquids lie reasonably well on a line. Indeed, bearing in mind the uncertainties both in Q (and therefore in x) and in E_0/V_0, the agreement must be regarded as satisfactory. Dr. Whitby has very kindly allowed me to examine his unpublished data covering a further series of liquids. Few of these have known cohesive energies, but the line drawn in Fig. 2A is in good agreement with his results for some simple esters, for ethyl ether and for *iso*butylamine. It may therefore be taken as representative of the normal behaviour of aliphatic liquids, and a special explanation must be sought for any *large* deviation from it. The constants given by this line are of the expected order : $\alpha = 8{\cdot}15$, $k = 3{\cdot}0$, the former giving a cohesive energy density for rubber of 66 cal/c.c. Whitby has pointed out [1] that aromatic liquids show much larger swelling than aliphatic compounds containing the same polar group. It is now found that the swelling is also larger at a given E_0/V_0. This difference may arise either from a different entropy or a different heat of swelling, or both. Having assumed ΔS_0 to be the same for all liquids, the whole of the discrepancy has to be ascribed to ΔH_0. In Fig. 2B it is seen that equation (2) holds quite well for aromatic liquids, with the same value of $\alpha = 8{\cdot}15$, but giving this time $k = 0{\cdot}65$. There is as yet no experimental evidence as to the validity of this method of separating aliphatic and aromatic compounds.

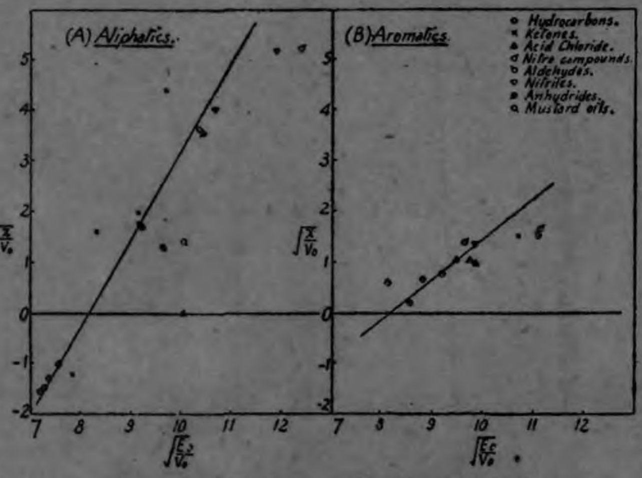

FIG. 2.—Entropy of dilution as a function of cohesive energy.

It is now possible to calculate the swelling power Q of a liquid from its cohesive energy and molecular volume, from the expression

$$x = kV_0\left\{\sqrt{\frac{E_0}{V_0}} - 8\cdot15\right\}^2 = f(Q) \quad . \quad . \quad . \quad (4)$$

where $k = 3\cdot0$ for aliphatic, $0\cdot65$ for aromatic liquids, and $x = f(Q)$ is defined by Fig. 1. In Fig. 3 (A) and (B) the lines drawn give values of Q calculated in this way as functions of $V_0\{\sqrt{E_0/V_0} - 8\cdot15\}^2$, while the points show the extent of the agreement with experiment. On the whole, this is considered satisfactory, especially when we note the sensitivity (except for small Q) of Q to small errors in x. It is clear that there is at least a close correlation between Q and $V_0\{\sqrt{E_0/V_0} - 8\cdot15\}^2$. This is all that would be expected from this treatment.

The causes of some of the major discrepancies may now be briefly considered. Most striking is the anomalously high swelling power of acids and alcohols, which undoubtedly arises from their high degree of association. The full effect of the polar group is not shown, since the liquids tend to remain associated even when present in quite low concentration in the rubber.* Whitby's unpublished data show that chlorinated hydrocarbons also possess high swelling powers, and here the explanation probably lies in a smaller ΔH_0 than would be calculated from the cohesive energy. It is well known that chlorinated hydrocarbons (especially $CHCl_3$) tend to show negative, or only slightly positive, values of ΔH_0 on mixing with a wide range of liquids, including hydrocarbons.

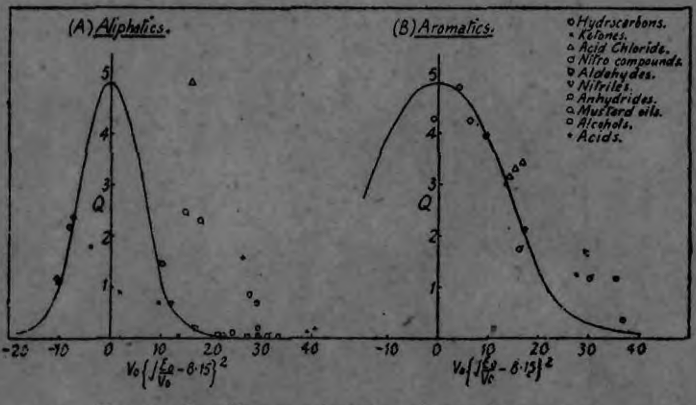

FIG. 3.—Swelling as a function of cohesive energy.

Summary.

The entropy of swelling of vulcanised rubber is estimated, and assumed independent of the nature of the swelling liquid. The heat of swelling is related to the cohesive energy of the liquid, and a value of 66 cal./c.c. deduced for the cohesive energy density of rubber. The swelling power of a liquid can be approximately calculated if its cohesive energy and molecular volume are known. Substantial agreement with theory is

---

* This behaviour is shown very strikingly by a thermodynamic study of the system rubber + MeOH which has been carried out by Dr. Treloar. The results will be described in a subsequent paper of this series.

found in most cases, although it is necessary to consider aliphatic and aromatic liquids separately. The anomalously high swelling power of acids and alcohols arises from their association.

I am grateful to Dr. Whitby for permission to refer to his unpublished results in this paper, which is based on work carried out under the programme of fundamental research on rubber undertaken by the Board of the British Rubber Producers' Research Association.

48 *Tewin Road,*
Welwyn Garden City,
Herts.

PRINTED IN GREAT BRITAIN AT
THE UNIVERSITY PRESS
ABERDEEN