COHESIVE ENERGY DENSITIES OF POLYMERS

PART I.—COHESIVE ENERGY DENSITIES OF RUBBERS BY SWELLING MEASUREMENTS

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Swelling measurements have been made on vulcanized natural rubber and eight synthetic rubbers in a wide range of solvents, and values for χ (or μ), the interaction parameter, derived by application of the Flory-Rehner theory. From an analysis of these values, cohesive energy densities have been assigned to the rubbers. The limitations on the assigned cohesive energy densities for the prediction of polymer + solvent behaviour are discussed.

For the mixing of liquids in which only intermolecular dispersion forces are operative, Hildebrand[1, 2] and Scatchard[3] have deduced that the heat ΔH_m of mixing per unit volume is positive, and related to the cohesive energy densities of the liquids, that is, their energies of vaporization per unit volume at the relevant temperature, by

$$\Delta H_m = v_1 v_2 (\delta_1 - \delta_2)^2, \tag{1}$$

where v_1 and v_2 are the volume fractions and δ_1 and δ_2 are the square roots of the cohesive energy densities (c.e.d.). As c.e.d. terms customarily involve these square roots, they have been termed for convenience the " solubility parameters " of the liquids. The analysis leading to (1) involves a simplifying assumption and so it is not surprising that it is found to give calculated heats of mixing only in fair agreement with experiment. However, due to its form and the relative magnitudes of δ_1 and δ_2, the equation gives in many cases values of δ_2 from measured ΔH_m and δ_1 values closely in accord with direct measurement.

Since the behaviour of polymers in liquids reflects in part their heats of mixing, the c.e.d. of liquids have been taken as a guide to liquids which are likely to be solvents for a given polymer or which will swell cross-linked networks of the polymer. In first suggesting an analogy of polymer + liquid and liquid + liquid systems, Gee treated the former by assigning a c.e.d. to the polymer.[4]

The c.e.d. of a high polymer cannot be obtained directly from vaporization experiments. From vapour-pressure measurements on volatile compounds, Small[5] has assigned c.e.d. terms for various molecular groups, and used these to estimate c.e.d. values for high polymers. Experimental procedures used to date have been interpretations of degrees of swelling of rubber networks in several liquids of known c.e.d.[4, 6] Since Gee's early work the Flory-Huggins[7, 8] treatment of polymer solutions in which polymer-solvent interaction is described by a parameter χ(or μ) has been extended by Flory and Rehner[9, 10] to enable polymer swelling also to be described by this parameter, or conversely to provide a determination of χ from swelling. A necessary preliminary to obtaining reliable values of χ from swelling measurements by the Flory-Rehner treatment has been the determination of the degree of cross-linking of the network. Methods for this purpose have recently been described.[11, 12]

This paper presents extensive series of swelling measurements on networks of natural and synthetic rubbers. The recent treatments have been utilized to give values for χ for each of the polymer + liquid mixtures. An interpretation of χ on the basis of current (not wholly satisfactory) polymer + liquid theory, then yields estimates of the solubility parameter δ_2 for the polymer.

EXPERIMENTAL AND RESULTS

MATERIALS

Rubber networks.—A sample of high-grade (Yellow-Circle) smoked sheet was lightly milled to ensure homogeneity and absence of gel. Its osmotic molecular weight in benzene was $2{\cdot}23 \times 10^5$. The smoked sheet was then cross-linked by incorporation of 3 % dicumyl peroxide on a twin-roll mill followed by heating at 140°C for 50 min in a rubber mould. The 2-mm thick sheets so obtained were extracted with boiling acetone for 24 h then dried for 24 h at 40°C under a pressure of 10^{-2} mm Hg. The density of this material was 0·91 g ml^{-1}.

Stress-strain measurements gave values of 1·37 and $0{\cdot}80 \times 10^6$ dyne cm^{-2} for the elasticity constants, C_1 and C_2, respectively.[13] The value for the constant C (cf. eqn. (2)) was taken as described previously,[14] as $C_1 + v_2^{4/3}C_2$. For the synthetic rubbers the constant C was equated to the elasticity constant C_1, since the possible errors of less than 0·01 introduced into the values of χ by this approximation were too small to cause significant deviations in the values of δ_2 which were sought.

Butyl 400 of the Polymer Corporation, Sarnia, was mixed with the vulcanization recipe (in parts per hundred by weight of the rubber) zinc oxide 5, sulphur 2, tetramethylthiuram disulphide 1, stearic acid 1·5, and phenyl-β-naphthylamine 1, and vulcanized as 2-mm thick sheet in a rubber mould under pressure for 50 min, at 140°C. The density and elasticity constant C_1 of the acetone-extracted and dried vulcanizate were 0·91 g ml^{-1} and $1{\cdot}075 \times 10^6$ dyne cm^{-2} respectively.

Neoprene WRT of DuPont de Nemours and Co., was vulcanized by adding the recipe, zinc oxide 5, magnesium oxide 4, sulphur 0·5, diphenyl guanidine 0·5, tetramethyl thiuram monosulphide 0·5 and mercaptoimidazoline 0·5, and heating for 20 min at 140°C to give a 2-mm sheet having, after acetone extraction, a density of 1·24 g ml^{-1} and C_1 of $1{\cdot}38 \times 10^6$ dyne cm^{-2} respectively.

Butadiene + styrene copolymer samples containing 96, 87·5 and 71·5 % polymerized butadiene, and butadiene + acrylonitrile samples having 82, 70 and 61 % butadiene were kindly supplied by Dr. L. Williams of the Polymer Corporation, Sarnia. Vulcanization was effected by the addition of zinc oxide 5, sulphur 2, mercaptobenzthiazole 1·5, and tetramethylthiuram disulphide 0·15, followed by heating in the mould for 40 min at 153°C. The densities and C_1 values of the vulcanizates were, in the same order as that given above, 0·971, 0·996, 1·008, 1·010, 1·051, 1·071 g ml^{-1} and 1·29, 1·50, 1·635, 1·655, 2·11, $2{\cdot}43 \times 10^6$ dyne cm^{-2}.

Solvents.—The solvents were reagent-grade materials which were dried and redistilled. Solubility parameters δ_1 at 25°C were obtained from

$$\delta_1 = \left[\frac{\Delta H_1^v - RT}{V_1}\right]^{\frac{1}{2}}$$

and

$$\Delta H_1^v = g\left[\frac{RT^2\, \partial \ln p}{\partial T}\right],$$

where p is the vapour pressure and V_1 the molar volume at 25°C. Values for ΔH_1^v at 25°C were obtained either from the literature or from $\ln p$ against $1/T$ plots. The gas imperfection correction factor g was evaluated by the method used by Gee.[4] As these calculations are rather tedious, and cohesive energy densities of liquids may be of more general interest and use, values for δ_1 and related data are given in table 1.

Swelling procedure.—Equilibrium swelling values for the vulcanizates were obtained by immersing rectangular pieces of *ca.* 0·2 g in the solvent at 25°C for 3 days. The vulcanizates were then surface dried and weighed in closed vessels. The volume fraction v_2 of rubber in the swollen material was calculated using the densities given above and assuming no volume change on swelling, making a correction for the volume of non-rubber constituents remaining in the vulcanizate after acetone extraction.[11] Values for v_2 are given in tables 2, 3, 4.

TABLE 1.—SOLUBILITY PARAMETERS FOR SOLVENTS AT 25°C

solvent	ΔH_1^v cal/mole	V_1 cm³/mole	s	δ_1 (cal/cm³)$^{\frac{1}{2}}$
*iso*pentane	5,878	117·4	0·975	6·625
2 : 2 : 4-trimethyl pentane	8,396	166·0	0·998	6·849
2 : 2 : 3-trimethyl butane	7,657	146·1	0·997	6·942
n-pentane	6,316	114·2	0·981	7·012
n-hexane	7,540	131·6	0·993	7·242
n-heptane	8,735	147·5	0·998	7·423
n-octane	9,915	163·5	1·000	7·554
n-decane	12,270	195·9	1·000	7·722
diethyl ether	6,984	104·7	0·982	7·743
methyl cyclohexane	8,451	128·4	0·998	7·816
*iso*butyl *n*-butyrate	10,860	167·8	1·000	7·822
n-dodecane	14,574	228·5	1·000	7·832
n-hexadecane	19,090	294·2	1·000	7·930
cyclohexane	7,895	108·7	0·997	8·182
ethyl *n*-butyrate	9,619	133·0	1·000	8·238
n-butyl acetate	9,630	132·5	1·000	8·283
1 : 1 : 1-trichloroethane	7,949	100·4	0·996	8·544
carbon tetrachloride	7,770	97·1	0·996	8·582
n-propyl acetate	9,313	115·7	0·999	8·678
n-butyl formate	9,273	115·3	0·999	8·696
toluene	9,080	106·9	0·999	8·907
n-propyl formate	8,454	98·4	0·997	8·925
ethyl propionate	9,938	115·5	0·999	8·990
methyl ethyl ketone	7,980	90·2	1·000	9·038
ethyl acetate	8,672	98·5	0·997	9·044
1 : 1-dichloroethane	7,617	84·8	0·993	9·073
ethyl bromide	6,789	75·1	0·985	9·119
di-*iso*propyl ketone	12,380	141·7	1·000	9·123
methyl *n*-amyl ketone	12,340	140·8	1·000	9·134
benzene	8,090	89·4	0·997	9·147
mesityl oxide	10,390	115·6	1·000	9·207
chloroform	7,510	80·7	0·995	9·240
cyclohexanone	9,513	104·2	1·000	9·255
tetrahydrofuran	7,672	81·5	0·995	9·317
ethyl iodide	7,929	81·1	0·995	9·490
chlorobenzene	9,810	102·1	1·000	9·505
methyl *iso*butyl ketone	12,050	124·9	1·000	9·577
cis-1 : 2: -dichloroethylene	7,746	76·0	0·993	9·667
1 : 2-dibromoethane	8,715	86·6	1·000	9·687
acetone	7,460	74·0	0·993	9·712
dioxane	8,715	85·7	0·999	9·732
methylene chloride	7,004	64·5	0·982	9·879
1 : 2-dichloroethane	8,422	79·5	0·997	9·910
methyl *iso*propyl ketone	11,000	105·7	0·999	9·917
methyl *n*-butyl ketone	12,820	124·2	1·000	9·923
methyl *n*-propyl ketone	11,310	107·5	0·999	9·980
diethyl ketone	11,300	106·4	0·999	10·03
nitrobenzene	~ 12,000	102·7	1·000	10·4
bromoform	10,385	87·9	1·000	10·56
pyridine	9,656	80·9	0·999	10·58
methylene iodide	—	81·0	—	11·8 *
acetonitrile	7,976	52·9	0·997	11·80
allyl alcohol	10,920	68·4	0·999	12·30

* estimated by Hildebrand.[1]

TABLE 2.—SWELLING OF RUBBER VULCANIZATE IN SOLVENTS

solvent	v_2	χ
iso-pentane	0·3390	0·585
2 : 2 : 4-trimethylpentane	0·3003	0·513
n-pentane	0·3165	0·565
n-hexane	0·2506	0·474
n-heptane	0·2326	0·433
n-octane	0·2710	0·475
n-decane	0·2725	0·450
diethyl ether	0·2899	0·545
methyl cyclohexane	0·1901	0·374
*iso*butyl *n*-butyrate	0·2770	0·481
n-dodecane	0·2874	0·448
n-hexadecane	0·3226	0·458
cyclohexane	0·1866	0·399
ethyl *n*-butyrate	0·3175	0·555
n-butyl acetate	0·3236	0·561
1 : 1 : 1-trichloroethane	0·1799	0·396
carbon tetrachloride	0·1508	0·334
n-propyl acetate	0·4065	0·649
n-butyl formate	0·3535	0·606
toluene	0·1837	0·391
ethyl propionate	0·3676	0·612
methyl ethyl ketone	0·5794	0·835
ethyl acetate	0·5282	0·771
1 : 1-dichloroethane	0·2155	0·482
ethyl bromide	0·1984	0.465
di-*iso*propyl ketone	0·3322	0·565
methyl *n*-amyl ketone	0·3610	0·594
benzene	0·1931	0·437
chloroform	0·1558	0·383
tetrahydrofuran	0·1923	0·452
methyl *iso*butyl ketone	0·4184	0·656
cis-1 : 2-dichloroethylene	0·1876	0·452
1 : 2-dibromoethane	0·2886	0·557
acetone	0·8307	1·361
methylene chloride	0·2347	0·525
1 : 2-dichloroethane	0·3401	0·608
methyl *iso*propyl ketone	0·5492	0·794
methyl *n*-butyl ketone	0·3559	0·598
methyl *n*-propyl ketone	0·4405	0·694
diethyl ketone	0·4098	0·656

DISCUSSION

Gee [4] concluded from eqn. (1) that maximum swelling would occur when $\delta_1 \simeq \delta_2$ for liquids mixing with polymers without specific interaction. Hence a plot of swelling against δ_1 for liquids behaving according to (1) should give a smooth curve when allowance is made for the effect of molar volume, V_1 with a maximum at $\delta_1 = \delta_2$. Chance selection of solvents unfortunately gives no such smooth curve. Gee therefore restricted his solvents mainly to esters and other simple aliphatic compounds which he judged to be least likely to have any specific chemical interaction or complexing with the rubber. In view of the limited number of such solvents of known c.e.d., Gee assumed a Gaussian shape for the swelling against δ_1 curve from which to estimate δ_2. The statistical theory developed after Gee's work indicates that factors other than those of eqn. (i) are important in swelling even by liquids giving heats of mixing with polymers in accord with (1). The interplay of these various factors is well shown in the swelling of polymers by *n*-paraffins.

TABLE 3.—SWELLING OF VULCANIZATES IN SOLVENTS

solvent	butyl		butadiene/styrene					
			96/4		87·5/12·5		71·5/28·5	
	v_2	χ	v_2	χ	v_2	χ	v_2	χ
2 : 2 : 4-trimethyl pentane	0·3175	0·565	0·4320	0·679	0·5225	0·790	0·5580	0·789
n-pentane	0·3616	0·627	0·3953	0·649	0·4797	0·721	0·4892	0·729
n-hexane	0·2670	0·516	0·3247	0·575	0·3984	0·639	0·4226	0·656
n-heptane	0·2320	0·475	0·2933	0·533	0·3491	0·582	0·3713	0·589
n-decane	0·2930	0·519	0·3466	0·568	0·4167	0·631	0·4593	0·671
methyl cyclohexane	0·1959	0·435	—	—	—	—	—	—
n-hexadecane	0·2886	0·465	—	—	—	—	—	—
cyclohexane	0·1818	0·436	0·2155	0·465	0·2448	0·489	0·2462	0·482
carbon tetrachloride	0·1942	0·466	0·1656	0·390	0·1768	0·394	0·1718	0·362
toluene	0·2786	0·557	—	—	—	—	—	—
ethyl bromide	0·2907	0·581	0·2045	0·490	0·2132	0·486	0·2052	0·466
benzene	0·3891	0·657	0·1846	0·446	0·1957	0·442	0·1814	0·398
chloroform	0·2361	0·532	0·1503	0·390	0·1678	0·401	0·1630	0·373
1 : 2-dibromoethane	0·7119	1·037	0·2594	0·539	0·2622	0·532	0·2391	0·497
dioxane	0·8719	1·552	0·3322	0·606	0·3257	0·593	0·2724	0·538
methylene chloride	0·2778	0·579	0·2090	0·508	0·2151	0·504	0·1986	0·474
bromoform	0·6820	0·988	0·1721	0·418	0·1786	0·411	0·1664	0·369
pyridine	0·8439	1·418	0·3145	0·594	0·2833	0·558	0·2666	0·535
acetonitrile	—	—	0·9568	2·273	0·9524	2·303	0·9337	2·038

TABLE 4.—SWELLING OF VULCANIZATES IN SOLVENTS

solvent	neoprene		butadiene/acrylonitrile					
			82/18		70/30		61/39	
	v_2	χ	v_2	χ	v_2	χ	v_2	χ
2 : 2 : 4-trimethyl pentane	—	—	0·6272	0·883	—	—	0·9925	3·945
n-pentane	0·7538	1·129	0·7320	1·078	—	—	0·9760	2·880
n-hexane	0·6260	0·891	0·6897	0·990	—	—	0·9737	2·798
n-heptane	0·5966	0·850	0·6706	0·955	0·9198	1·879	0·9895	3·625
n-octane	0·7601	1·138	0·7369	1·080	—	—	—	—
n-decane	0·7648	1·147	0·7768	1·175	0·9760	2·872	0·9926	3·942
n-dodecane	0·7886	1·210	0·8020	1·247	—	—	—	—
n-hexadecane	0·8606	1·477	0·8688	1·515	0·9839	3·222	—	—
cyclohexane	0·4357	0·686	0·4587	0·700	0·8467	1·421	0·9672	2·605
carbon tetrachloride	0·1812	0·414	0·2355	0·478	0·4501	0·686	0·5862	0·831
1 : 1-dichloroethane	0·1988	0·463	—	—	—	—	—	—
ethyl bromide	0·1955	0·471	0·1767	0·416	0·2062	0·426	0·2522	0·489
benzene	0·1767	0·263	0·1789	0·390	0·2561	0·486	0·3311	0·564
chloroform	0·1530	0·384	0·1261	0·251	0·1337	0·207	0·1510	0·241
ethyl iodide	0·1779	0·433	—	—	—	—	—	—
cis-1 : 2-dichloroethylene	0·1635	0·415	—	—	—	—	—	—
1 : 2-dibromoethane	—	—	0·1653	0·366	0·1813	0·359	0·2062	0·362
dioxane	0·2254	0·497	0·2108	0·454	0·2436	0·455	0·2710	0·498
methylene chloride	0·1873	0·533	0·1472	0·394	0·1428	0·314	0·1563	0·323
1 : 2-dichloroethane	0·3774	0·644	—	—	—	—	—	—
nitrobenzene	0·2217	0·474	—	—	0·1761	0·300	—	—
bromoform	—	—	0·1338	0·262	0·1538	0·266	0·1781	0·316
pyridine	—	—	0·1671	0·390	0·1669	0·334	0·1637	0·294
methylene iodide	—	—	—	—	0·5022	0·745	—	—
acetonitrile	—	—	0·7385	1·098	0·5097	0·763	0·4219	0·677
allyl alcohol	—	—	—	—	0·5208	0·769	—	—

Here plots of c.e.d. against swelling (fig. 1) show maxima close to the same c.e.d. value for chemically different rubbers, and which have widely different behaviour in other liquids.

Swelling behaviour is generally expressed at present in terms of χ of the modified Flory-Rehner equation,[9, 10]

$$-RT[\ln(1-v_2)+v_2+\chi v_2^2] = 2V_1C(v_2^{1/3}-\tfrac{1}{2}v_2)\,, \tag{2}$$

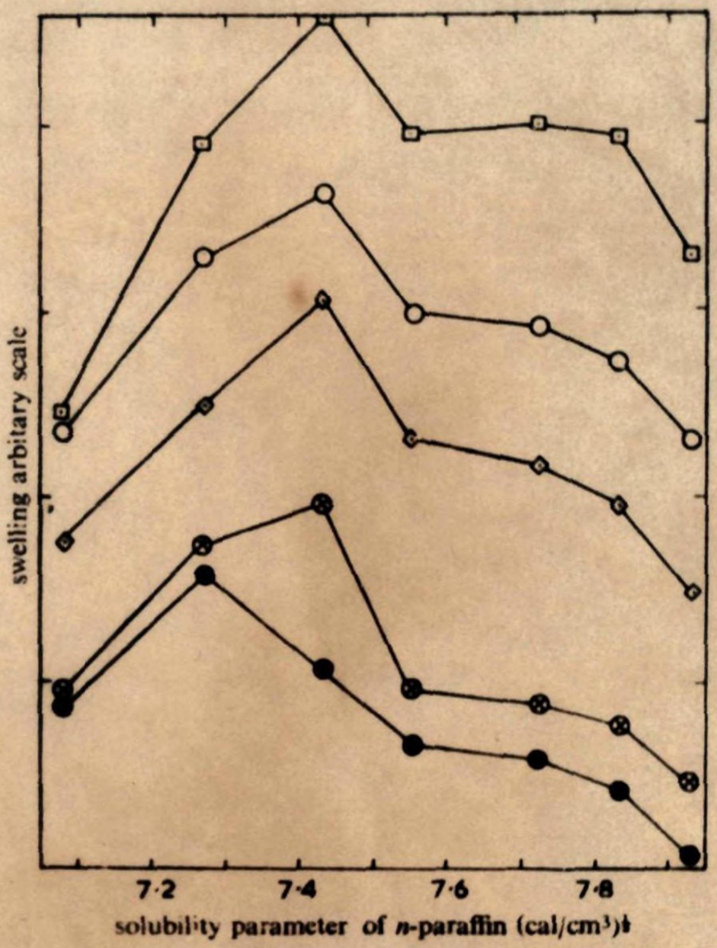

FIG. 1.—Swelling of rubbers in *n*-paraffins.

□ butyl rubber; ○ natural rubber; ◇ 70/30 butadiene + styrene rubber; ⊗ neoprene; ● radiation cross-linked polythene.

vhere C is a constant at constant temperature which can be obtained from stress-train measurements[11] and the variables have been defined previously. The nteraction parameters recorded in tables 2, 3 and 4 were calculated from eqn. (2). χ's lower by some 0·02-0·04 unit are calculated from the unmodified Flory-Rehner quation;[9] the effect of such differences on derived δ_2 values is small.) The eft-hand side of eqn. (2) gives the difference in partial molar free energy between he solvent in the swollen network and the pure solvent. The first two terms ertain to the random entropy of mixing as given by the Flory lattice treatment. nfortunately χv_2^2 cannot be taken as wholly a heat-of-mixing term due to uncertainties in the calculated entropy of mixing. From a refinement of the lattice nodel, Huggins[8] deduced that χ should be expressed approximately by

$$\chi = \beta + (V_1/RT)(\delta_1-\delta_2)^2 \tag{3}$$

ith $\beta = \frac{1}{z}\left(1-\frac{1}{m}\right)$, where z is a co-ordination number and m is the chain length of the polymer. Zimm [16] concludes from a still more refined model that β should have a value greater than the 0·1-0·2 predicted by Huggins for plausible values of z.

Eqn. (3) contains both β and δ_2 as unknowns, and hence separate values for these parameters cannot be estimated without some further assumption as to their relative magnitude. The most unsatisfactory aspect of this necessity is that the data cannot provide a critical test of the validity of (3) or of the assumptions involved in determining values for δ_2. As with the calculation of either ΔH_m or δ_2 from eqn. (1) the form of eqn. (3) is likely to lead to a more reliable calculation of δ_2 from values of χ, than *vice versa*. Nevertheless the δ_2 values assigned to the polymer by utilizing eqn. (3) have to be regarded as dependent on present, incomplete, theory or the experimental validity of an empirical equation of the form of eqn. (3) and so must be put forward with this proviso.

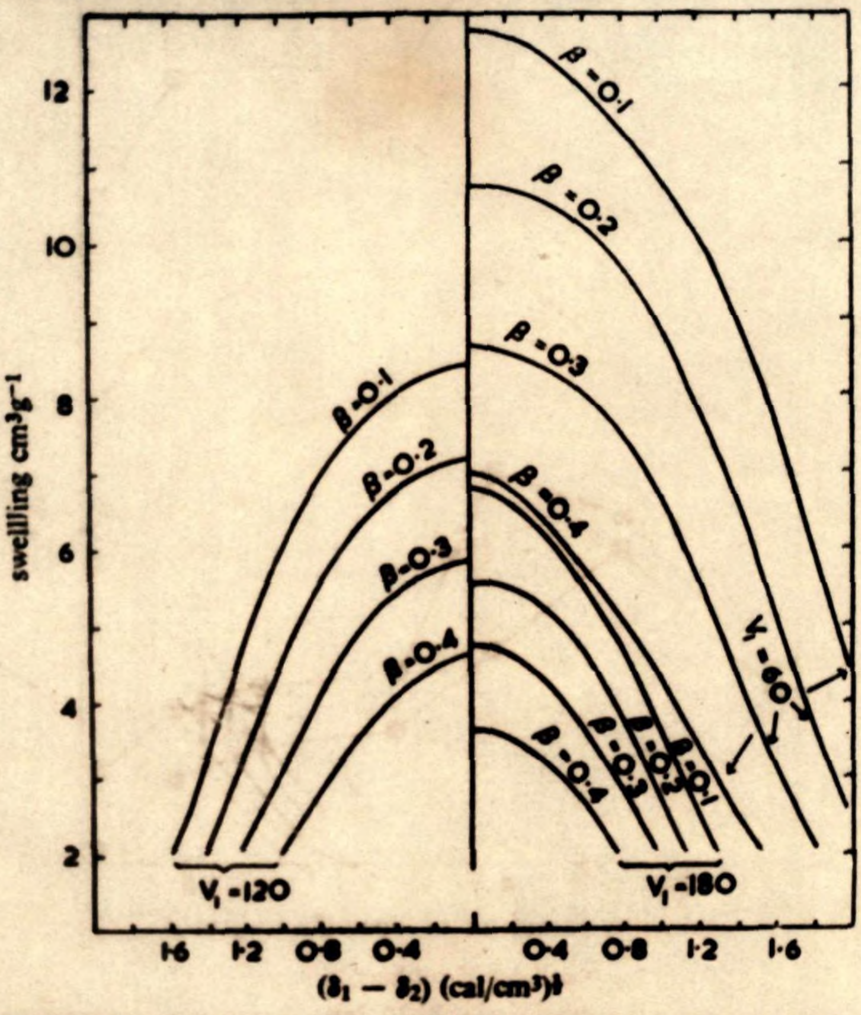

FIG. 2.—Predicted swelling curves for a rubber of given δ_2 for various values of δ_1, V_1 and β. (Only half of each symmetrical curve is shown.)

If it is accepted that equilibrium swellings can be expressed in terms of eqn. (2) and (3), then fig. 2 illustrates the dependence of swelling on the three parameters, δ_1, β and V_1 for a rubber of given δ_2. Values of $\rho = 0{\cdot}91$ and $2C/RT = 1{\cdot}14 \times 10^{-4}\ \mathrm{cm}^{-3}$ are chosen to correspond with these measured quantities for the natural rubber network examined. It is clear that all three parameters are important in interpreting swelling data. Only if β and V_1 were constant would maximum swelling occur when $\delta_1 = \delta_2$.

Scott and Magat [6] utilized eqn. (3) to interpret their swelling data by assuming a constant value of $\beta = 0{\cdot}3$ in all solvents. The above considerations suggest that this procedure is unlikely to yield reliable values for δ_2. Again, Scott and Magat had no means at that time of determining C of eqn. (2) and so had to analyze their results statistically, a value of δ_2 being chosen so as to give a minimum deviation in the calculated C for the several solvents. This analysis is not very sensitive to the value of δ_2. For their results with natural rubber, any value from 8·0 to 8·6 gives almost as small a deviation in the calculated C as the 8·35 which they favour.

Accepting that eqn. (3) represents a valid means of assignment of a constant δ_2 to the polymer, rearrangement of this equation gives

$$\frac{\delta_1^2}{RT}-\frac{\chi}{V_1}=\left[\frac{2\delta_2}{RT}\right]\delta_1-\frac{\delta_2^2}{RT}-\frac{\beta}{V_1}. \tag{4}$$

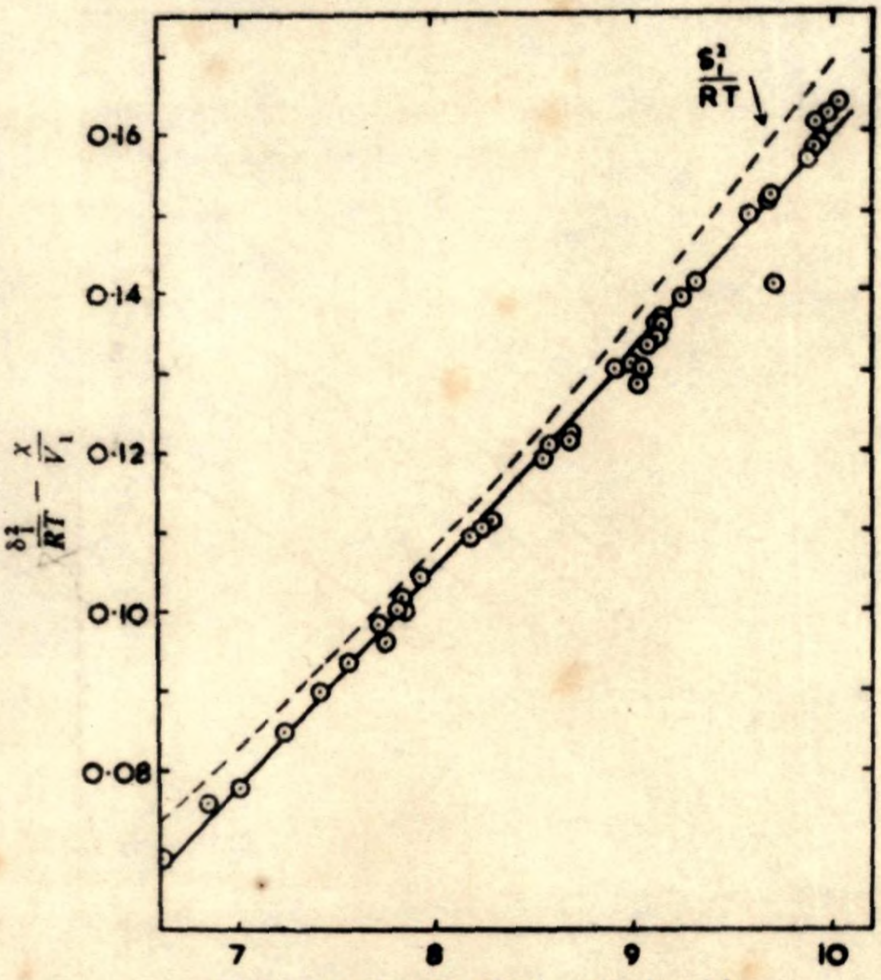

FIG. 3.—Determination of the solubility parameter for natural rubber.

Now, assuming that β is of the order of magnitude suggested by Zimm and is, in accordance with Huggin's derivation, not a function of c.e.d., β/V_1 is only some 3 % or less of δ_2^2/RT for reasonable values of δ_2 of 5-10. Hence eqn. (4) gives δ_2 from the slope and intercept on plotting the left-hand-side against δ_1.

Fig. 3 shows this plot for natural rubber with all the solvents listed in table 2. This method of representing the data, which minimizes the influence of other than c.e.d. terms, enables solvents such as chloroform, in which specific interaction effects induce very high swellings, to be recorded on the same plot as other, relatively poor, solvents. A value of $\delta_2 = 8{\cdot}1 \pm 0{\cdot}05$ is obtained from the slope. The mean intercept gives $\delta_2 = 8{\cdot}06$ and 8·12 from its identification with $(\delta_2^2/RT + \beta/V_1)$ on taking $\beta/V_1 = 0{\cdot}0020$ and 0·0035 respectively. The data are therefore consistent with eqn. (4).

The good linearity is not in itself remarkable, for neglect of χ/V_1 yields a gently curving section of a parabola over the range of δ_1 considered (fig. 3); the small χ/V_1 term merely straightens out the two ends of the parabola around the δ_2 of the rubber where the slope of the experimental plot is the same as that of the parabola.

The value of $\delta_2 = 8{\cdot}1$ compares with that of 7·9-8·0 obtained by Gee by a judicious choice of solvents. It is considerably lower than that of Scott and Magat, whose results can, however, be reconciled with it as noted above. The alternative approach to the estimation of the c.e.d. of polymers, the use of additivity terms for the various groups in the polymer as suggested by Small,[5] gives a closely similar value of 8·15 for natural rubber but in other cases, notably neoprene, the agreement is less satisfactory.

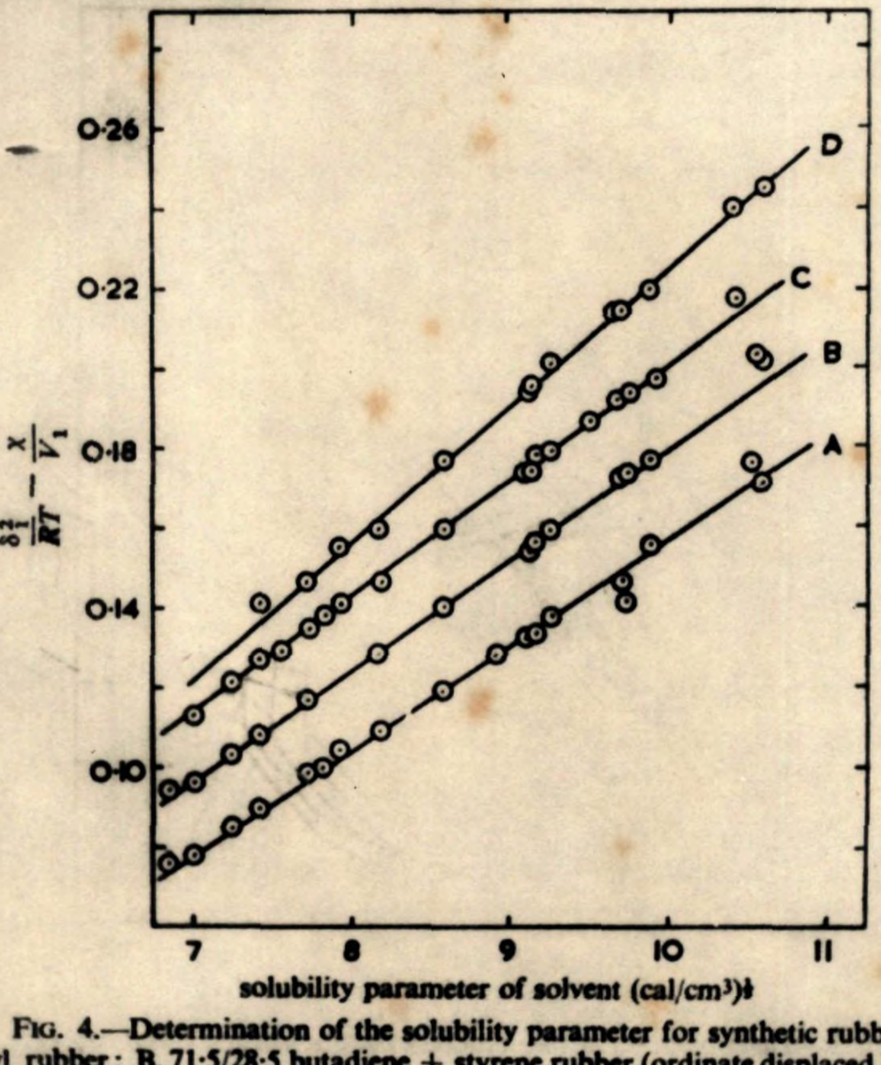

FIG. 4.—Determination of the solubility parameter for synthetic rubbers.
A, butyl rubber; B, 71·5/28·5 butadiene + styrene rubber (ordinate displaced by + 0·02); C, neoprene (ordinate displaced by + 0·04); D, 70/30 butadiene + acrylonitrile rubber (ordinate displaced by + 0·06).

Similar linear plots of eqn. (4) were obtained from the data of tables 2, 3 and 4 for the synthetic rubbers; typical examples of these plots are shown in fig. 4. Table 5 presents the δ_2 values obtained from them. The error in the δ_2 values obtained from the slopes is ± 0·1.

The solubility parameters are in agreement with general expectations based on the chemical structure of the rubbers. Butyl rubber has the lowest c.e.d., natural and butadiene + styrene rubbers are comparable, neoprene is markedly higher (in distinction from Gee's estimate), and butadiene + acrylonitrile rubbers are yet higher and depend on the acrylonitrile content as would be expected for such a highly polar constituent.

As an appraisal of the present position, solubility parameters can be assigned to polymers by measurement of swelling in a random selection of solvents. However, owing to the lack of *a priori* knowledge of non-c.e.d. factors, such values of δ_2 cannot subsequently be used to estimate the swelling in other solvents with any degree of accuracy. Nevertheless, as c.e.d. is the only available guide to polymer + liquid interaction, it is useful, for example, for suggesting possible solvents for polymers.[17] The above discussion shows that this guide is, however, very approximate as in general other important factors are involved.

TABLE 5.—COLLECTED VALUES OF THE SOLUBILITY PARAMETER δ_2 FOR RUBBERS

rubber	δ_2 from		δ_2 Gee[4]	δ_2 Scott and Magat[6]	δ_2 Small[5]
	slope	intercept			
natural rubber	8·1	8·06-8·12	7·9	8·35	8·15
butyl	7·8	7·85-7·77		8·05	7·70
neoprene	8·6	8·67-8·57	8·18	9·25	9·38
96/4 butadiene/styrene	8·1	8·13-8·04			
87·5/12·5 butadiene/styrene	8·1	8·10-8·01	8·09	8·6	8·46
71·5/28·5 butadiene/styrene	8·1	8·17-8·09		8·67 *	8·56
82/18 butadiene/acrylonitrile	8·7	8·75-8·66			
70/30 butadiene/acrylonitrile	9·9	9·90-9·83	9·38	9·5 †	9·25 †
61/39 butadiene/acrylonitrile	10·3	10·45-10·40			

* for 60/40 copolymer. † for 75/25 copolymer.

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