CCCII.—*A Study of the Vapour-pressure Diminution of Rubber Jellies.*

By PAUL STAMBERGER.

ALTHOUGH swelling-pressure measurements have been carried out by Posnjak (*Koll.-Chem. Beih.*, 1912, **3**, 417) on rubber, and theories have been put forward whereby the swelling pressure may be calculated from the vapour-pressure diminution of the solvents in the jellies, no measurements of the latter value exist (*idem, ibid.*; Katz, *ibid.*, 1918, **9**, 106).

Rubber seems to be suitable for investigations of the nature of swelling, because it combines with many organic fluids of diverse properties, and, without the action of reagents, may be made to yield jellies of widely different consistency (according to the previous mechanical treatment of the natural product): it has already been shown that the consistency of the final "solution" of rubber has no influence on its vapour pressure (Stamberger, *Rec. trav. chim.*, 1928, **47**, 316).

Measurements are now recorded of the vapour-pressure diminution of rubber jellies in three solvents, *viz.*, benzene, chloroform, and carbon disulphide, and particularly at low concentrations of rubber, so that comparison with the behaviour of molecular disperse solutions may be made.

The origins of the samples of rubber used were as follows: (1) Isolated from pure latex, freed from the protein content by centrifuging and subsequent dilution (acetone-soluble, 2·2; N, 0·12%). (2) Dutch plantation rubber (first latex crêpe) of 1926 (acetone-soluble, 3·0; N, 0·14%). (3) Plantation rubber from Ceylon (acetone-soluble, 3·6; N, 0·09%). (4) Rubber No. 2 in over-masticated condition purified by solution in benzene and precipitation with acetone (acetone-soluble, nil; N, 0·03%). (5) Rubber No. 3 in over-masticated condition. These samples, with the exception of No. 4, were used without further treatment after being dried over sulphuric acid in a vacuum desiccator for 14 days, and *no difference was found in their behaviour.* All the values were reproducible after an interval of 2 years. The vapour pressure was determined by two methods: (1) that of Gay-Lussac–van Bemmelen, which is generally used for these determinations (compare Katz, " Ergebnisse der exacten Naturwissenschaften," 1924, **3**, 317), solutions of paraffin oil of an average molecular weight of 425 being used as fluids of known vapour pressure; (2) a direct method in a modified Bremer–Frowein tensimeter. Both methods gave practically identical results. The direct measurement could not be carried out when the vapour-pressure lowering was less than 2 mm., because of experimental difficulties.

Method 1. Solutions obtained with the above-mentioned paraffin oil* of a concentration of about 2—50% were used. The vapour pressures of the solutions of low concentration (up to 10%) were calculated from the ebullioscopically-determined molecular weight of the paraffin oil (425) by means of Raoult's formula $(p_0 - p_1)/p_0 = n/(N + n)$. Above this concentration the differential vapour pressure was determined in a tensimeter (shown in Fig. 2), which was also used for measurement of the vapour pressure of jellies. From the results given in Table I it is seen that the values calculated from the molecular weight agree with those obtained directly, and if the relative vapour pressure is plotted against the concentration of paraffin oil in the solution, a linear relationship holds up to a concentration of about 40%. These results are in agreement with recent investigations on the validity of Raoult's laws (Bancroft and Davis, *J. Physical Chem.*, 1929, **33**, 361). All the measurements were carried out in a thermostat at 25° ± 0·005°, and pressures are recorded in mm. of mercury.

TABLE I.

$p_0 = 90$ mm.

Paraffin, g./100 g. solution.	$p_0 - p_1$.	$(p_0 - p_1)/p_0$. Calc.	$(p_0 - p_1)/p_0$. Found.	Paraffin, g./100 g. solution.	$p_0 - p_1$.	$(p_0 - p_1)/p_0$. Calc.	$(p_0 - p_1)/p_0$. Found.
2·47	—	0·0042	—	26·5	5·6	0·0617	0·0624
5·0	—	0·0106	—	49·7	14·0	0·159	0·154
9·1	2·2	0·0241	0·0242	60·0	18·2	0·220	0·202
13·0	3·0	0·0348	0·0334	67·0	24·2	0·275	0·268

For this type of vapour-tension measurements of jellies, Wolff and Buchner (*Z. physikal. Chem.*, 1915, **39**, 271) point out the necessity of decreasing the vapour space to a minimum. It is also necessary, in order to obtain equilibrium quickly, to make the distance between liquid and jelly as small as possible. The arrange-

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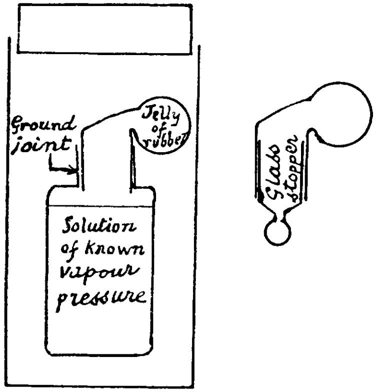
* A commercial product was used consisting of a mixture of paraffin hydrocarbons.

ment shown in Fig. 1 was used for this purpose. To minimise the effect of fluctuations in the temperature of the thermostat, the whole apparatus was enclosed in a tube which was closed with a rubber bung and immersed in water.

0·2—0·5 G. of rubber was weighed into the stoppered bulb, the stopper was removed and the bulb connected by a ground-glass joint with the vessel containing the solvent of known tension. From time to time (every 10 days) the bulb was disconnected, closed, and weighed. When no further increase of weight was noticeable, the tension of the jelly was identical with that of the liquid. From the increase of weight and the weight of rubber present initially the concentration of rubber in the jelly at a given vapour pressure can be calculated. The time necessary to obtain equilibrium was different with liquids of different tensions: When the vapour-pressure lowering in the jelly was small, 3—4 months were required, but with greater differences about 3—4 weeks sufficed.

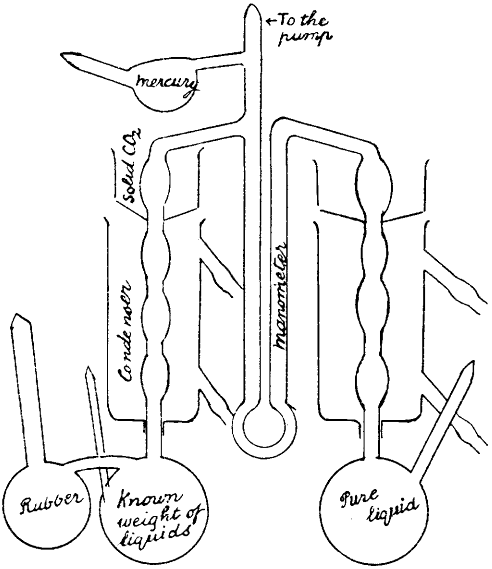
FIG. 1.



The apparatus for the direct determination of differential vapour pressure as well as for the determination of the vapour-pressure lowering of the paraffin oil solutions is shown in Fig. 2. For the latter, the pure liquid was poured through a side tube into one of the bulbs, and the solution of paraffin oil of unknown tension into the other. Both bulbs were cooled with liquid air, and the side tubes sealed. The apparatus was evacuated by means of a Langmuir high-vacuum pump (the usual precaution being taken to condense the vapour before it reached the pump). The connexion with the vacuum was then closed by a mercury trap, the condenser filled, and the liquids in the bulbs were allowed to become warm slowly. The filling in the upper part of the condenser was solid carbon dioxide, and in the lower part a freezing mixture (in the case of benzene) or acetone–carbon disulphide (in the case of chloroform or carbon disulphide).

To free the liquids completely from dissolved gases, they were kept for about 2 hours under vacuum, the whole system was then re-evacuated by a water pump, and the liquids in the bulbs were heated under reflux for 12 hours in a water-bath. It was necessary to use small amounts of liquid, about 10 c.c. in large bulbs, for otherwise when it became air-free its boiling was accompanied by violent splashing. The liquid was then cooled to about — 5° and the system was evacuated by the high-vacuum pump for an hour, the liquid being further cooled with liquid air; the connexion with the pump was closed and the liquids were allowed to attain room temperature and kept for 12 hours under vacuum. In the case of benzene, a further evacuation and 24 hours' standing were required. The necessity for the foregoing precautions may be illustrated by the fact that a liquid which had not been thus freed from dissolved gases gave a vapour pressure 15 mm. higher than after such treatment.

FIG. 2.



The air-free liquids were cooled again with liquid air, and the tube (which had naturally a capillary part) was connected with the vacuum, and gently warmed; the glass being now gas-free, the apparatus was sealed. The mercury, which had been previously boiled in a vacuum, was poured from the container connected with the manometer by gently tilting the apparatus, and the whole was put into a glass thermostat. The differential vapour pressure was read on the manometer with the aid of a cathetometer. Usually, no further change in the meniscus of the mercury was observed after 2 hours' standing in the thermostat, but if the liquids had not been completely freed from gases a small further movement of the meniscus was noticed.

Method 2. When the tension of the rubber jelly was to be determined, two bulbs instead of one were used on the one side. In the one connected with the condenser a known weight of the solvent was placed, and in the other, the dry rubber itself. The liquids were cooled and evacuated as described above, and the bulb with the dry rubber was heated to 50°. In this manner hardly any liquid condensed on the rubber even when the liquid in the first bulb was boiled. As it was impossible to make a rubber jelly air-free, it was necessary to start from the dry rubber and liquid separately.

When the liquids had been again freed from gases, as described above, the apparatus was sealed and the contents of the first bulb were poured into the second by tilting the apparatus, the contents of the third bulb being kept frozen during this operation. The apparatus was placed in a thermostat after the manometer had been filled with mercury. After 48 hours the whole of the solvent had been uniformly absorbed by the rubber, no further change in the meniscus occurred, and the differential vapour pressure could be measured. Although every precaution was taken in condensing the liquid when it was boiled, small amounts escaped and condensed in the retainers cooled with liquid air before the pumps. It was therefore necessary after every measurement to determine the concentration of the dissolved phase in the bulb directly by cutting off the second bulb, weighing it, evaporating the volatile liquid, and re-weighing the bulb.

The values given in Table II show the differences between the samples. The experimental error is estimated to be about 7%. Table III and Fig. 3 give the mean results obtained from 6—10 determinations in each case.

TABLE II.

Sol-vent.	$\frac{p_0-p_1}{p_0}$.	Concentration of rubber (% by wt.) in samples.*									
		1.		2.		3.		4.		5.	
C_6H_6	0·0241	31·4	34·2	32·5	33·0	32·3	31·0	30·8	33·0	32·6	32·0
,,	0·154	55·0	54·8	56·5	54·2	58·0	56·0	54·0	56·2	55·6	54·0
$CHCl_3$	0·014	15·9	16·4	16·2	17·4	15·2	16·4	16·5	16·7	14·9	16·8
,,	0·278	58·1	55·5	55·0	57·3	56·8	56·0	58·2	57·1	56·2	57·0

* Two determinations are given in each case.

Freundlich and Posnjak (*Koll.-Chem. Beih.*, 1912, **3**, 445; see also Katz, *loc. cit.*) derived a formula $P = -RT/MV \,.\, \log_e p_1/p_0$ for calculating the swelling pressure from the vapour-pressure lowering. Fig. 4 gives a comparison of the results thus calculated with the values determined by Posnjak.

TABLE III.

G. of solvent per 100 g. of rubber.	Conc. of rubber (g./100 g. of jelly).	G.-mols. of solvent per 100 g. of rubber.	$\frac{p_0 - p_1}{p_0}$.
Solvent : Benzene; $p^{25°} = 91$ mm.			
350	22·2	4·5	0·0042
280	26·3	3·6	0·0106
210	32·3	2·7	0·0241
190	34·5	2·4	0·0348
130	43·5	1·6	0·0617
76	56·8	0·9	0·154
55	64·5	0·7	0·220
50	66·7	0·6	0·278
Solvent : Chloroform; $p^{25°} = 200$ mm.			
850	10·5	7·5	0·0034
520	16·1	4·3	0·0146
403	19·8	3·3	0·0258
237	29·6	2·0	0·0680
174	36·5	1·4	0·105
100	50·0	0·8	0·201
75	57·0	0·6	0·278
Solvent : Carbon disulphide; $p^{25} = 480$ mm.			
525	16	6·9	0·0044
420	19·4	5·5	0·0060
310	24·4	4·1	0·0167
210	32·8	2·7	0·0366
180	35·5	2·3	0·0528
135	42·5	1·7	0·0665
126	45·5	1·58	0·0695
110	47·5	1·4	0·111
88	53·0	1·1	0·131

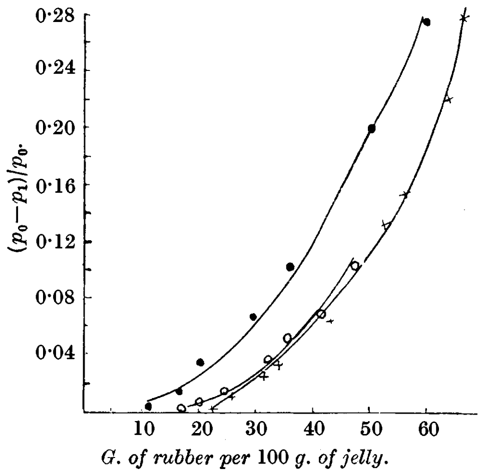
Discussion.

When the relation between vapour-pressure lowering and concentration of the rubber jellies is compared with that of molecular disperse solutions, *e.g.*, paraffin oil in benzene, or sucrose in water (Berkeley and Hartley, *Proc. Roy. Soc.*, 1906, *A*, **77**, 156), a large difference is immediately noticeable : up to a certain concentration the rubber causes no appreciable vapour-pressure lowering, but beyond this the lowering increases rapidly with concentration, whereas molecular disperse solutions give a linear relationship up to a concentration of 40—50%.

The agreement between the values obtained with *different* samples of rubber shows that they are of a very uniform nature and not mixtures of hydrocarbons of different degrees of polymerisation, thus supporting Harries's views on the existence of a definite rubber hydrocarbon, which have recently been emphasised by Pummerer, Nielsen, and Gundel (*Ber.*, 1927, **60**, 2167).

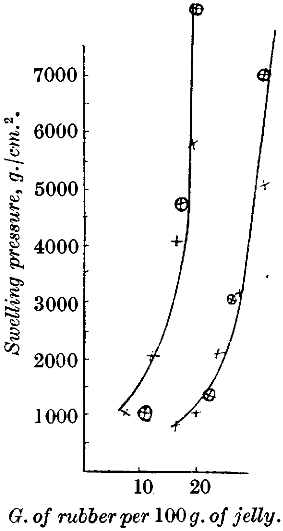
Over-masticated rubber, which combines with the solvent, giving a *viscous liquid*, behaves in exactly the same manner as the original untreated material, which in the swollen condition is an elastic solid. This behaviour makes highly improbable the explanation of the swelling phenomena by assuming *capillary forces* (Freundlich and Posnjak, *loc. cit.*, p. 454; Kruyt, "Colloids," p. 228), and supports Katz's theory, based on the similarity between the vapour-pressure isotherm of jellies and those of concentrated solutions, that swelling is mainly a process of solution. The present values obtained with much less concentrated solutions of rubber show that the behaviour is different from that of a molecular disperse solution. Freundlich (" Kapillarchemie," 2nd edtn., p. 923) thinks that a similarity to a process of adsorption exists, with the difference that, whereas in the

FIG. 3.



● $CHCl_3$. ○ CS_2. × C_6H_6.

FIG. 4.



⊗ *Calculated.*
× *Posnjak's measurements.*

case of glass, for example, only the molecules on the surface are active, in the case of jellies all the molecules combine with the solvent. This explanation is similar to that given for the process of solution when the molecules of the solute are surrounded with a solvation layer, and would hold also in the case of the " liquid " jelly of overmasticated rubber. It does not claim merely a surface adsorption or the presence of a solid wall. The incompleteness of theories explaining this part of the process of solution is discussed by Freundlich (*op. cit.*, p. 67). It seems very probable that the forces causing the imbibition of solvent in the jelly are similar.

On this basis it is possible to explain the shape of the isotherm given in Fig. 3. Only above a certain rubber concentration (about 10—20%) is appreciable vapour-pressure lowering observed: the solvent only loses its activity when it comes within the sphere of action of the molecules. The thickness of this solvated layer, in which the vapour-pressure lowering begins, can be calculated roughly. According to Sheppard, Nietz, and Keenan (*Ind. Eng. Chem.*, 1929, **21**, 126), the thickness of the rubber molecule is 4—6 Å.U., which corresponds to two carbon atoms in the isoprene molecule. Assuming that the molecules are only long chains, the width will correspond to the thickness of one carbon atom, *i.e.*, *ca.* 2 Å.U. As a rough approximation, we will consider the molecules as rectangular prisms and neglect the distance between them. The total length of rubber molecules in a given volume, *e.g.*, 1 c.c., when they are linked together in one long chain is equal to (volume)/(width × thickness), and from the above values this is $0{\cdot}125 \times 10^{16}$ cm. Further, if the thickness of the solvated layer is the same in both dimensions, for a given volume of solvent the thickness of this layer ($x/2$) can be calculated from the formula $(T + x)(W + x) = V/L$, where T is the thickness of the molecule (4 Å.U.), L the length and V the volume of 1 c.c. of rubber together with its solvated layer, and W its width (2 Å.U.). It is tacitly assumed that the solvated molecule has the same shape as the original molecule.

In the case of benzene, V is 5·25 c.c. when $(p_0 - p_1)/p_0 = 0{\cdot}0042$, whence $x/2$ is about 2·0 Å.U.; and for chloroform $x/2 = 2{\cdot}0$ Å.U., when $(p_0 - p_1)/p_0 = 0{\cdot}0034$ and $V = 8$. The thickness of the solvated layer as calculated from the smallest vapour-pressure lowerings is thus of the order of the radius of molecular attraction.

The values of swelling pressure calculated from the vapour-pressure lowering show a rough agreement with the values actually measured by Posnjak, but as his measurements were only over a very small range of concentration it is not possible to say how far the agreement will hold at higher swelling pressures.

In the case described above, it is possible to say that swelling is due to the attraction of the molecules of the jelly to those of the solvent. This results in a surrounding solvation layer. Solvent molecules show vapour-pressure lowering in this layer and naturally exhibit swelling pressure. This behaviour is similar to (or identical with) that part of the process of solution in which the *solute becomes surrounded by a solvated layer.* The other part of the process of solution, in which van 't Hoff's law holds, is different. It is remarkable that substances which show swelling are generally of high molecular weight and, according to recent investigations, long chains of unimolecular thickness (Sheppard and Keenan, *Nature*, 1928, **121**, 982; Knight and Stamberger, J., 1928, 2791; Katz and

Samwell, *Naturwiss.*, 1928, **30**, 1513). This behaviour seems to be a special property of this class of substance.

That the solvation of jellies is a molecular process and not a micellar one is most probable, because reproducible values were obtained with different samples after different treatment, and approximately the same molecular concentration causes the same relative vapour-pressure depression.

The process of swelling can be sufficiently explained by assuming that the solid molecules of the jelly *are surrounded by a solvated layer*, and there is no reason to assume the existence of a solid solution of solvent in the jelly (Katz, *loc. cit.*) : this would not hold in the case of *liquid* over-masticated rubber jellies.

Summary.

Methods and results of measurement of vapour-pressure lowering of rubber jellies are described.

From the qualitative behaviour of the jellies (consistency), from the shape of the curve given in Fig. 3, and from approximate calculations of the thickness of the solvent layer round the molecules, it is assumed that the solvent is bound by the molecules of the jelly in the form of a solvated layer.

The existence of such a layer in the sphere of action of the molecules explains sufficiently a decrease of activity of solvents, which results in vapour-pressure lowering, swelling pressure, etc., and makes the process similar to that of solution.

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