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Diffusion and Axial Ratio of Shellac and its Constituents

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DIFFUSION AND AXIAL RATIO OF SHELLAC AND ITS CONSTITUENTS

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The values of the axial ratio, as obtained by the viscometric method for shellac, hard resin and soft resin, are found to compare favourably with those obtained by diffusion measurements.

Dimensions (effective length and breadth) of shellac particles and of the constituent resins have been calculated on the assumption that these are prolate spheroids.

In a previous communication (Basu, *J. Indian Chem. Soc.*, 1947, **24**, 157) Kuhn's equation for the viscosity of solutions was applied to the case of shellac solution in determining the values of the axial ratios (a/b) for hard resin, soft resin and dewaxed shellac. Measurement of free diffusion also affords an effective method for calculating the value of axial ratios, which, besides serving as an independent check of the results deduced from viscosity studies, is somewhat to be preferred as giving a clearer insight into the dissymmetry of the particles. Accordingly diffusion measurements have been carried out on shellac and its constituents and the results reported in the present communication.

Graham was the first to recognise the effect of particle size on the diffusion constant, and attributed the low values obtained for the diffusion constant in many cases to the smallness of the size of the pores of the membrane. This viewpoint has since changed and it is now assumed that diffusibility is determined by the intensity of kinetic activity and the frictional resistance experienced by the particles. The diffusion constant (D) as deduced by Einstein theoretically (*Ann Physik*, 1905, **17**, 549) is given by the equation,

$$D = \frac{RT}{N} \cdot \frac{1}{f} \qquad \cdots \qquad \cdots \qquad (1)$$

where R is the gas constant, T, the absolute temperature, N, Avogadro number and f, the frictional coefficient. In a dilute solution, where there is little or no interaction between the dissolved particles, the frictional coefficient depends mainly on the size and shape of the particles; moreover, if the particles be spherical, then Stoke's law ($f = 6\pi\eta r$) is applicable and equation (1) becomes

$$D = \frac{RT}{N} \cdot \frac{1}{6\pi\eta r} \qquad \cdots \qquad \cdots \qquad (2)$$

where η is the viscosity of the solvent and r, the radius of the particle.

The calculation of molecular weight from the radius value obtained from equation (2) gave varying values for a protein molecule, which was construed to indicate (Neurath, *J. Amer. Chem. Soc.*, 1939, **61**, 1841 ; Polson, *Kolloid Z.*, 1939, **87**, 149 ; Swedberg, *Proc. Roy. Soc.*, 1939, **B**, **127**, 1) a high degree of dissymmetry in the dissolved molecules. For a particle of given volume the effect of shape may be expressed in terms of the diffusion constant as follows : Assuming that the particles are spherical, r can be calculated from the knowledge of the specific volume ; this, when substituted in (2), would give a theoretical value of D, termed D_0, which would be the value of the diffusion constant for spherical particles of the same size. A comparison of the observed value of D with this hypothetical value D_0 would be a measure of the dissymmetry of the particles. Thus, for a spherical particle D/D_0 will be 1 ; actually, however, for most macromolecular particles this value ranges from 1 to 100 depending on the degree of dissymmetry.

Several equations have been proposed from time to time to correct the diffusional data for molecular dissymmetry. Swedberg (*loc. cit.*) developed the equation

$$f/f_0 = \frac{RT/D}{6\pi\eta N\left(\frac{3MV}{4\pi N}\right)^{\frac{1}{3}}} \quad \ldots \quad (3)$$

where f = the experimental molar frictional constant, f_0 = the frictional constant for sphere of same mass, V = partial specific volume, other symbols having the same significance as before. The factor f/f_0 is known as Swedberg's shape factor.

Attempts have been made by Perrin (*J. Phys. Radium*, 1936, **7**, 1) and Herzog (*Z. physikal. Chem*, 1934, **A**, **167**, 329) to deduce a mathematical relation between the axial ratio and the shape factor, and the following equation has been obtained for a prolate spheroid

$$f/f_0 = \frac{\sqrt{1-b^2/a^2}}{(b/a)^{\frac{2}{3}} ln\left(\frac{1+\sqrt{1-b^2/a^2}}{b/a}\right)} \quad \ldots \quad (4)$$

where a = half-axis major and b = half-axis minor. Since, however, the frictional constant is inversely proportional to the diffusion constant, *i.e.*,

$$f/f_0 = D_0/D \quad \ldots \quad \ldots \quad (5)$$

equation (4) may be written as

$$D_0/D = \frac{\sqrt{1-b^2/a^2}}{(b/a)^{\frac{2}{3}} ln\left(\frac{1+\sqrt{1-b^2/a^2}}{b/a}\right)} \quad \ldots \quad (6)$$

Knowing D_0/D it should be theoretically possible to solve equation (6) for b/a. But instead of attempting a direct solution, the values of b/a, as obtained from viscometric measurements (Basu, *loc. cit.*), may be substituted in equation (6) and the resulting value of D_0/D compared with the observed value.

EXPERIMENTAL

Apparatus and Method.—The diffusion constants were measured by means of a diffusion cell first proposed by Northrop and Anson (*J. Gen Physiol.*, 1929, **12**, 543) and afterwards improved by McBain and co-workers (*J. Amer. Chem. Soc.*, 1931, **53**, 59). Their method consists in separating two homogeneous solutions by means of an indifferent membrane, made of sintered glass plate, the diffusion gradient being confined within this membrane. The cell is shown diagrammatically in Fig. 1.

The cell was cleansed by sucking in chromic acid through the porous disc and then expelling the acid by applying pressure, after which it was thoroughly washed with distilled water and dried. The filling up of the cell was also effected by sucking in the required solution through the porous disc till it reached the level above the stop-cock which was then closed. The cell was then placed in a beaker containing pure solvent and left for an hour in order that a uniform diffusion gradient might set up within the diaphragm. It was then removed and after the adhering solvent had been wiped off, placed in another beaker containing the same volume of solvent as the solution inside, just touching the surface of the solvent in the beaker. The whole system was placed under a bell jar in order to prevent undue evaporation of the solvent. Evaporation in the bell jar itself was reduced to a minimum by saturating the space inside with the vapour of the solvent, before placing the system under it. Actually the solvent in the beaker was found to undergo practically no change in volume after 24 hours, the period of diffusion in each experiment.

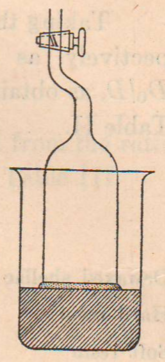

FIG. 1.

After 24 hours, the cell was taken out, wiped with filter paper (the inside of the tube above the stop-cock being also wiped), and the solution was extruded through the membrane. The concentration of the solution in the cell, as also in the beaker, was determined by means of a Dubosq colorimeter. The actual calculation of the diffusion constant from the experimental data was carried out by means of McBain's equation (applicable to the present system)

$$KD = \frac{\log_{10} c_0 - \log_{10} (c_0 - 2c)}{t} \quad \cdots \quad \cdots \quad (7)$$

where c_0=initial concentration in the cell, c=concentration in the beaker after diffusion, t=the time of diffusion in seconds and K=the cell constant. The cell constant was evaluated by measuring the diffusion constant of 0.1N-KCl, known to be 1.448 at 20° (International Critical Tables).

The methods used for separating hard and soft resins and also for preparing their alcoholic solutions were the same as described in a previous paper (Basu, *loc cit.*).

RESULTS AND DISCUSSION

The value of the cell constant, as obtained by measuring the diffusion constant of 0.1*N*-KCl, was found to 0.1267. The experimentally found diffusion constants for dewaxed shellac, hard resin and soft resin are given in Table I.

TABLE I

		t.	c_0.	*c*.	$D \times 10^7$.
Dewaxed shellac	...	24 hrs	5.010%	0.130%	20.53
Hard resin	...	24	4.989	0.110	16.90
Soft resin	...	24	3.110	0.105	28.08

Taking the molecular weights of dewaxed shellac, hard resin and soft resin respectively, as 1000, 1900 and 550, as obtained by cryoscopic method, the values of D_0/D, as obtained from Swedberg's and Herzog's equations (3 and 6), are given in Table II.

TABLE II

		V.	*a*/*b*.	*T*.	$\eta\ 10^3$ (in pois)	$(D_0/D)_S$	$(D_0/D)_H$
Dewaxed shellac	...	0.930	10.3	30°	10.1	1.49	1.55
Hard resin	...	0.934	11.7	30	10.1	1.56	1.60
Soft resin	...	0.925	7.8	30	10.1	1.37	1.42

$(D_0/D)_S$ and $(D_0/D)_H$ represent the values obtained respectively from Swedberg's and Herzog's equations.

Concordant results have been obtained in all these cases, variation between the two sets of values never exceeding 4%. Still closer agreement may not be expected considering that the exact molecular weights of the substances are not known and no method is at present available for preparing absolutely pure samples.

There may, however, be certain objections to the calculation of the axial ratio from Herzog's equation. Firstly, it assumes the particles to be rigid, whereas in actual practice they may be 'soft' or flexible. Secondly, since no method is at present available to find out the extent of solvation and hence its effect on D_0, the D_0/D value, obtained by calculating D_0 from the volume of the particles, will be inaccurate and so also the value of axial ratio deduced from it. Thus Polson (*Nature*, 1936, **137**, 740) obtained by using this equation, the values for haemoglobin and insulin as 3.8 and 3.2 respectively as against 1.5 and 0.7 obtained by the X-ray method. In the present case, however, in the range of concentration studied, which was below 5% (Basu, *J. Indian Chem. Soc.*, 1947, **24**, 159), the particles are neither solvated, nor flexible, and therefore the concordant values of *a*/*b* obtained independently by the viscometric method and the diffusion method may be accepted as more or less the true values of *a*/*b* for shellac resins in solution.

Since the equation developed for a prolate spheroid is applicable in the case of shellac and its constituent resins, the assumption that particles in the dissolved state have got an effective volume equal to that of a prolate spheroid enables us to calculate the length and breadth of the molecules. The volume of the particle in the dissolved state is given by

$$\overline{V} = \frac{VM}{N} \quad \ldots \quad \ldots \quad (8)$$

where V = partial specific volume, M = molecular weight and N = Avogadro number. Since the volume of a prolate spheroid is

$$\overline{V} = \frac{\pi SL^2}{6} \quad \ldots \quad \ldots \quad (9)$$

where S = major axis = $2a$, and L = minor axis = $2b$, we get

$$VM/N = \pi SL^2/6 \quad \ldots \quad \ldots \quad (9a)$$

$$\text{or} \quad SL^2 = 6\,MV/N\pi \quad \ldots \quad \ldots \quad (9b)$$

Thus from the value of SL^2, as obtained from ($9b$), and from the ratio S/L ($= a/b$), we can calculate the values of S and L which are given in Table III.

TABLE III

	S/L.	S.	L.
Soft resin ...	7.8	44.80 Å	5.74 Å
Hard resin ...	11 7	91.92	7.86
Dewaxed shellac ...	10.3	68.05	6.61

This type of calculation has been made in the case of polystyrene ("Second Report on Viscocity and Plasticity", 1938, p. 173) as also for cellulose acetate (Nils Gralen, Inaugural Dissertation, University of Uppsala, Sweden, 1944). For these substances, however, the particles are flexible and the results are therefore likely to be inaccurate. In the case of shellac, however, the results might be reasonably accurate since flexibility of the particles under the conditions of the experiment is negligible. But no final conclusion about these values can be drawn in absence of X-ray measurements.

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