VISCOSITY AND MOLECULAR STRUCTURE

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THE development of the molecular theory of matter has as a consequence that an increasing number of empirical constants, by which one characterizes the behaviour of a macroscopic sample, are brought into quantitative relation with the molecular structure of the material. For example, it has long been known that the *index of refraction* can be connected with the *mobility of the electric charges* in a given substance, and therefore can be used to determine the electrical polarizability of the molecules in a quantitative way. Similarly, the *dielectric constant* can be used to get quantitative information on the *distribution of the electric charges* in the molecules of a given substance, and it was P. Debye, especially, who succeeded, together with a number of collaborators, in establishing a quantitative theory which combines the macroscopic empirical constant with the molecular properties.

Recently, it seems that another quantity, which has been used for some time to characterize a given system from an empirical point of view, must be understood and evaluated from the angle of the molecular theory of matter. This is the *internal friction* or *viscosity* of solutions. This property has been accounted for in ideal gases by the kinetic theory of gases, by consideration of the masses and velocities of the individual molecules and their irregular collisions. But our knowledge of the viscosity of condensed systems had not progressed so far, although it was obvious that much valuable information would be obtained if viscosity could be interpreted kinetically.

During recent years, some special developments have been particularly favourable to the solution of this problem. The most important of them are: (1) the development of a quantitative theory of liquids; (2) the accumulation of a large amount of experimental data on high polymeric substances and their solutions, and the development of the ultracentrifuge, which enabled us to get independent information on high molecular compounds.

This progress encouraged the attempt to trace the viscosity of solutions, and especially of solutions containing high molecular substances, back to the fundamental properties of their elementary particles, namely, to the size and shape of the molecules and to their power to fix a certain amount of solvent on themselves. Such attempts were started about fifteen years ago from different

points of view. An increasing number of scientific investigators have turned to the subject since then, and we are now obtaining a first insight into the connexion between the viscosity of a solution and the fundamental properties of the dissolved material. It is not suggested that any finality has been reached in this field, but it seems that experimental conditions which are necessary to get trustworthy information have been worked out, and that the results which can be presented to-day are consistent among themselves and agree with the findings by other experimental methods.

It may therefore be appropriate to enumerate briefly the different essential steps which have led to this kinetic elucidation of viscosity and to present a few results which may be presumed to have reached a certain degree of reliability. It may be that in the future such results will have considerable interest in biochemistry, physiology and chemical industry.

EARLY FUNDAMENTAL INVESTIGATIONS

Einstein¹⁰ was the first to derive with incomparable clarity an equation showing how spherical particles which are dispersed in a liquid would raise its viscosity. He found, so early as 1905, that the increase of internal friction is proportional to the total amount of dissolved volume, but surprisingly independent of the degree of dispersion. A few large spheres produce the same viscosity increase as many small ones, provided their total volume remains constant. A few years later, Bancelin¹ and Sven Odén³⁶ confirmed experimentally Einstein's theoretical results.

Having received experimental confirmation, the Einstein equation could be used to determine the total volume of the dissolved phase, that is, the degree of swelling or solvation which the material undergoes during solution. For example, it was found that a molecule of cane sugar carries with it about five or six molecules of water tightly fixed upon its surface during the diffusion in the liquid.

But the combined theoretical and experimental results seemed to block any possibility of getting information concerning the size of the dissolved particles, because it was found that the viscosity should be independent of this quantity.

However, during the following years an increasing number of empirical facts showed that there evidently was some relation between particle size and viscosity in quite a number of cases. Measurements of Biltz³, Berl and Buttler², Hatschek²¹, Duclaux and Wollmann⁹, Ostwald³⁰, and Staudinger³⁵ gave indications that the viscosity of very dilute solutions of many typical high molecular substances decreases if one degrades the original material, and that it is increased if one raises the molecular weight. As this is apparently in disagreement with the Einstein equation, it was concluded that these substances do not behave as spherical particles.

From here on a double development became necessary: (a) to accumulate more reliable and quantitative empirical data in order to have a sound experimental background; and (b) to derive theoretical equations for non-spherical particles.

THE PROBLEM OF NON-SPHERICAL PARTICLES

Much successful work was contributed in both directions. It was especially Staudinger and his collaborators who extended viscosity measurements considerably, investigating systematically the influence of molecular weight, concentration, temperature, and solvent; and they established an empirical rule, the well-known viscosity equation of Staudinger³⁵.

This equation states that the viscosity increase due to the dissolved substance is proportional to its molecular weight, provided that the solution is sufficiently diluted. Very careful viscosity measurements by Meyer and v. d. Wijk²⁹, and by Kraemer and Lansing²⁵ showed, however, that this relation is not exact but is subject to certain deviations. But it can be safely regarded as being a valuable rule for the estimation of molecular weight, and it has proved to be very fruitful for further progress in this field.

While this experimental material was accumulating, a series of successful attempts to develop equations for non-spherical particles was made. Jeffery²³ was the first to start this development. He was followed by Eisenschitz¹³, Boeder⁵, Haller²⁰ and Kuhn²⁷. These investigators developed equations making it possible to calculate the viscosity increase due to longish particles, as the Einstein equation did for spherical particles. Obviously these relations were expected to explain theoretically the Staudinger equation, but at first sight there seemed to be a lack of agreement.

The Staudinger equation states that the viscosity increase is proportional to the molecular weight, while hydrodynamics indicate that it is proportional to the square of the molecular weight. Guth and Mark¹⁸ proposed qualitatively an

explanation for this discrepancy, but Kuhn²⁷ was the first to work out a complete and consistent theory.

If one assumes that the dissolved particles are *not stiff rods but flexible threads*, the experimental findings and the theoretical equations harmonize in a manner which shows that the idea of long flexible chains rolled or wound up to a more or less cluster-like unit is the right way out of the dilemma.

DEVELOPMENT OF THE HYDRODYNAMICAL METHOD

To get a final check on the value of this explanation, further experimental and theoretical work was undertaken. Eirich, Bunzl and Margaretha¹² studied systematically the behaviour of model suspensions with particles of exactly known size and shape. Glass, silk, rayon, mushroom spores, bacteria, microscopic crystals, etc., were used; the size varied from 1 μ to 100 μ diameter, the shape from spherical particles to rods with an axis-ratio of about 50. The viscosity of proteins was carefully investigated by Fahry and Green¹⁴ and by Polson³²; the latter giving an extensive comparison of the data obtained by viscosity measurements with the results of the Svedberg ultracentrifuge. At the same time Houwink and Klaassens²⁴, Kraemer and Lansing²⁵, Bogue⁶, Kratky and Saito²⁶, and others contributed valuable experimental material on different high polymeric substances.

The hydrodynamical treatment was pushed forward by Guth^{17,19}, Huggins²², Kuhn²⁷, and Simha³⁴, in the direction of both spherical and non-spherical suspensions, taking into account the influence of higher concentration and of the Brownian movement.

Another group of recent articles⁴ represents comprehensive work aiming at the comparison of all available data and their survey from a common point of view. Sakurada³³, and particularly Bredee and de Booy⁷, and Huggins²², have contributed in this direction.

CONCLUSIONS

As the result of the experimental and theoretical work briefly described above, some data contained in the following tables can be usefully considered. They show that although we still have to consider that we are in an early stage of the complete molecular interpretation of viscosity, a number of very interesting molecular constants can be derived from such measurements.

Table 1 shows the size and shape of some protein molecules as determined by viscosity measurements, and at the same time the corresponding values obtained with the Svedberg ultracentrifuge.

TABLE I. SIZE AND SHAPE OF PROTEIN MOLECULES IN AQUEOUS SOLUTION*

Substance	Molecular weight		Axis ratio	
	from viscosity	from ultra-centrifuge	from viscosity	from ultra-centrifuge
Ovalbumin	41,800	42,000	8.5	3.8
Hæmoglobin	70,300	68,000	5.9	3.8
Serum albumin	71,800	70,000	9.8	4.9
Homarus hæmoglobin	793,000	800,000	—	—
Tobacco mosaic virus	17.43 × 10 ⁶	—	36.9	—

* Compare refs. 4, 7, 14, 16, 28, 32.

TABLE 2. MOLECULAR WEIGHT, SOLVATION AND SHAPE OF SOME CELLULOSE DERIVATIVES*

Substance	Molecular weight	Volume of the solvated particle as multiple of the dry volume	Deviation from the spherical shape†
Nitrocellulose	500,000	345	2.5
"	150,000	121	3.7
"	40,000	40	2.6
Cellulose acetate	50,000	97.5	3.0
"	14,000	31.3	3.2
"	6,400	13.2	2.1

* Compare refs. 2, 7, 8, 9, 15, 35.

† Spherical shape is characterized by the value zero.

It can be seen that, as regards the size of the particles (molecular weight), the two methods agree fairly closely, while viscosity gives a higher axis-ratio than the ultracentrifuge.

Table 2 contains similar information on the molecular weight, solvation, and shape of some cellulose derivatives. In this case no experimental data from the ultracentrifuge were available, and therefore an experimental check of the values is not possible. However, other methods (osmotic pressure, diffusion, etc.) confirm the above values and show that they certainly reflect to a considerable extent the true conditions in these high molecular suspensions.

TABLE 3. MOLECULAR WEIGHT, SOLVATION AND SHAPE OF SOME POLYSTYRENE SAMPLES*

Molecular weight	Volume of the solvated particle as multiple of the dry volume	Deviation from the spherical shape†
280,000	205	7.3
220,000	80.5	5.7
23,000	15.4	3.1
2,400	2.65	0.4

* Compare refs. 7, 31, 33, 35.

† Spherical shape is characterized by the value zero.

TABLE 4. SOLVATION OF DISPERSED SUBSTANCES WITH APPROXIMATELY SPHERICAL PARTICLES*

Substance	Degree of solvation (per cent)
Mushroom spores	nil
Colloidal sulphur	nil
Kresol-formaldehyde-resin	10-40
Cane sugar	50
Ovalbumin	120
Gamboge	800
Gelatine	1,000-2,000

* Compare refs. 1, 4, 6, 7, 12, 14, 24, 32, 36.

Similar data concerning some samples of polystyrene are given in Table 3. They are equally supported by the results of other experimental methods.

Tables 2 and 3 show that with increasing molecular weight the solvation of the substance investigated increases, and in the case of styrene the deviation from the spherical shape also assumes higher values.

Table 4 gives the solvation of some systems the particles of which are approximately spherical, and shows that different materials behave very differently as regards their power to absorb certain amounts of solvent and to carry them about during their molecular movements.

If account is taken of the fact that it is very difficult to get any trustworthy quantitative information on size, shape, and solvation in the region of such high molecular weights, it will certainly be admitted that viscosity measurements provide a very valuable and welcome means of obtaining quantitative information on the molecular structure of such materials.

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