[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF STANFORD UNIVERSITY]

The Effect of Departure from Spherical Shape on the Viscosity Caused by Colloidal Particles and Large Molecules[1]

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The object of the following note is to point out that accepted hydrodynamic theory applicable to colloidal particles and macromolecules does not predict a very great increase in viscosity caused by extreme departure from spherical shape. Einstein[2] is responsible for the formulas commonly employed for Brownian motion, viscosity, and diffusion of colloidal particles. He obtained these by applying the ordinary formulas for hydrodynamics, assuming that the particles were spherical and large as compared with a molecule of water, that they were uncharged, that there was no slip between them and the water with which they were actually in contact (that is, the water adhered to their surface), and, finally, that turbulence was avoided. He did not hesitate to apply his calculations to molecules of sucrose in water, relating the viscosity and diffusion with the Avogadro number which he thus deduced as being equal to 6.56×10^{23}. By this procedure he obtained the well-known formula for relative viscosity $\eta_r = 1 + 2.5v$, where the viscosity, η_r, is referred to that of the solvent, $\eta_0 = 1$, and where v is the fraction of the total volume occupied by the dispersed phase.

Notoriously, the viscosity of many dilute colloidal sols is enormously greater than that so predicted by Einstein; for example, a 0.1% solution of nitrocotton may have[3] a relative viscosity equal to 1.500, that is, an increase above the solvent equal to 0.500. This increase is many hundred times greater than the value between 0.001 and 0.002 predicted from the Einstein theory for spheres (nitrocotton being much denser than acetone).

Four explanations have from time to time been put forward. First, hydration has been postulated to raise the volume to the required value. At the present time few would care to suggest solvation (additional to, or differing from, Einstein's adherent water, but not including enclosed or enmeshed solvent) to an amount greater than one weight of solvent to one of particle. Hence this explanation can account for only one or two per cent. of the observed excess. Second, the electro-viscous effect of Smoluchowski[4] is here negligible. Third, the structural viscosity advocated by many authors[5] as the method of producing the highest apparent viscosity with the least amount of material is universally accepted for many colloids such as soap. The reasoning and data to be presented indicate that here also it is the chief operative factor.

It will be noted that according to the Einstein formula mere aggregation of molecules or colloidal particles to form larger compact massive particles or micelles has no effect upon the viscosity. To produce an effect it is necessary that the aggregation should be loose and ramifying, the molecules or particles tending to stick at points where they touch, forming an incipient "brush-heap" structure such as is now ascribed to jellies, enclosing and enmeshing tracts of free solvent.

Finally, as a result of his extensive and important work upon long chain polymers or macromolecules, Staudinger has suggested that in certain cases, such as cellulose and its derivatives, as in the case here cited, enhanced viscosity may be ascribed to the extreme elongation of the molecule. In a 0.1% solution the molecules are regarded as completely independent, although of course structural viscosity is recognized in much more concentrated solutions.

Since this hypothesis did not appear to be accessible to direct experiment, the coefficient relating viscosity to molecular elongation was obtained by empirical extrapolation from substances of lower measurable molecular weight. It has been overlooked that this calculation and extrapolation must include any tendency toward association or agglomeration, a tendency which, as is most strikingly shown in the homologous series of the soaps and the sulfonates, rapidly increases with increase in molecular weight.

This note points out the maximum possible effect that can be ascribed to elongation in increas-

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[1] Read at the Pittsburgh meeting of the American Chemical Society, September, 1936.

[2] A. Einstein, *Ann. phys.*, [4] **19**, 289 (1906); **34**, 591 (1911); *Z. Elektrochem.*, **14**, 235 (1908).

[3] J. W. McBain and D. A. Scott, *Ind. Eng. Chem.*, **28**, 470 (1936).

[4] Smoluchowski, *Kolloid-Z.*, **18**, 190 (1916).

[5] For example, J. W. McBain, *J. Phys. Chem.*, **30**, 239 (1926).

ing frictional resistance to movement even when the molecule remains rigidly straight. The most extreme case so far suggested has been a long chain of glucose residues of "molecular weight" about 500,000 and with length about 5000 times the mean radius. For all other cases the effect must be less. The effect must be exhibited equally in all kinds of movement of the particles where turbulence is avoided.

The hydrodynamic formulas have been discussed by Overbeck, Lamb and Allen,[6] and are developed by Gans[7] in approximate form as follows.

The resistance to movement of a sphere is $W = 6\pi\eta\, av$. A very elongated ellipsoid is a fair model of a macromolecule or rod. For an ellipsoid of revolution, where the long semi-axis is a, the same as that of the sphere, and the other two very much smaller semi-axes, b and c, are equal, the resistance to movement is then δ times less. For the rod moving lengthwise, as when it falls in a vertical position, $\delta_a = \frac{3}{4}\left(2 \log_e \frac{2a}{c} - 1\right)$. For the rod moving broadside on, as when a horizontal fiber falls

$$\delta_c = \frac{3}{8}\left(2 \log_e \frac{2a}{c} + 1\right)$$

The terminal velocity of a falling sphere (Lamb[6]) is $\frac{2}{9} \times \frac{a^2g(s - s')}{\eta_0}$, and that of the ellipsoid $\frac{2}{9} + \frac{c^2g(s - s')}{\eta_0} \cdot \delta$, where g is the gravitational constant, $s - s'$ the difference in the density of the falling particle and the liquid, and η_0 is the viscosity of the latter. It is now easy to show that for a sphere and an ellipsoid of the same volume the ratio of their velocities is $\left(\frac{a}{c}\right)^{2/3} \times \frac{1}{\delta}$ where δ however still refers to the sphere whose diameter is equal to the length of the ellipsoid. The ratio of the two resistances to movement has this same value.

Therefore for the extreme example where $c/a = 1/2500$, and δ_a equals 12.03 and $\delta_c = 6.76$, a sphere of given weight will fall 15.3 times faster than the ellipsoid falling end on, and 27.2 times faster than the ellipsoid falling sidewise, with the intermediate positions having intermediate values. There will be no rotation of the ellipsoid as it falls,[6,7] and its deflection from the vertical fall cannot exceed 19°28′ as a maximum.[8]

Taking an average effect, for this extreme case, the frictional resistance will be only about 21-fold that of the sphere, whereas for 0.1% nitrocotton we have to explain an increase in specific viscosity of between 250- and 500-fold.

For $a/c = 100$, $\delta_a = 7.197$ and $\delta_c = 4.349$, and the sphere falls only 2.99 and 4.95 times faster than the elongated ellipsoid. For $a/c = 10$, $\delta_a = 3.744$, and $\delta_c = 2.622$, and the sphere falls 1.24 and 1.77 times faster than the elongated ellipsoid.

Hence Staudinger is correct in pointing out an influence of extreme elongation, but it is a very minor effect in comparison with viscosity increments observed. We therefore conclude that 94% or more of the total observed excess viscosity has a structural basis, whose influence is of a higher order of magnitude than that of any of the other three suggested factors.[9]

Since Lamb[6] pointed out that for purely viscous movement to be maintained, the quantity vas/η must be small compared to unity, he stated that for a silica sphere falling in water the diameter has to be small compared to 0.114 mm. Hence Stokes' law and these relations apply only to much smaller particles, which are not readily subjected to experimental study. We have attempted to overcome this difficulty by employing instead of water 60% sucrose solution, whose viscosity is 56.2-fold greater at 20°.

Our procedure was to let thin silica fibers fall through water and the sucrose solution in a vertical and in a horizontal position and also in intermediate positions. Afterward the same fibers were fused into spherical form and then time of fall was again observed. The fibers fell in water always without change in orientation, but usually failed to do so in the sucrose solution. Likewise the difference in rate between fiber and sphere was less than that calculated. Part of this was found to be due to volatilization of the silica during fusion. Also each "sphere" had a thickened tail which could not be completely removed. Hence the spheres were compared with fibers of the same

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(6) A. Overbeck, *Crelle*, **81**, 62 (1876); H. Lamb, "Hydrodynamics," Cambridge University Press, 1906, p. 554; H. S. Allen, *Phil. Mag.*, 5] **50**, 323, 519 (1900).

(7) R. Gans, *Sitzb. math. physik. Klasse Akad. München*, 191 (1911); *cf.* Guy Barr, "A Monograph of Viscometry," Oxford University Press, London 1931, p. 195.

(8) For recent discussions of the hydrodynamic equations where rotation is involved and experiments in which orientation and interference between rod-like particles (structural viscosity) occur, see for example Guth, *Kolloid-Z.*, **75**, 15 (1936); Eirich, Margaretha and Bunzl, *ibid.*, 20 (1936). See also Gans, *Ann. Phys.*, [4] **86**, 652 (1928); and Jeffrey, *Proc. Roy. Soc.* (London), **A102**, 176 (1923).

(9) In a private communication Dr. S. S. Kistler adds the information, confirmatory of the present conclusion, that owing to the difference in behavior of a sphere and of a cylinder (Lamb, *Phil. Mag.*, **21**, 112 (1911)) with regard to very low Reynolds numbers, the force acting upon a cylinder of the same volume as a sphere will not be much larger than that on the sphere.

weight, 59.7 mm. long where the ratio of length to diameter was only 1933 instead of 2500. The diameter of the fibers was 0.040 mm., that of the spheres 0.485 mm.; probably they were all still too coarse for the requirements of the formula, but the results are of interest as approximately illustrative of the general formulas.

Vertical fibers fell 17.7 cm. through sucrose solution in 901 and 949 seconds, respectively, whereas the spheres required a minimum of 84 sec. The value calculated for the sphere from Stokes' formula was 68.9 sec. The ratio between the fibers and the theoretical value for the sphere was 13.07 and 13.77, mean 13.4, whereas the theoretical ratio predicted was 13.3, and the actual ratio found was not larger than 11. In water, typical experiments gave a ratio between that observed for a vertical fiber and that calculated for a sphere the same weight equal to 14.3 as compared with the predicted value 15.3.

The effect of elongation is even less under conditions where turbulence is prominent in the observation of rate of fall. For the silica fibers and spheres falling through water the observed effect was only between 4-fold for vertical and 8-fold for horizontal fall. In dropping $^{3}/_{8}''$ (9.5 mm.) steel balls through still water and comparing them with the same weight of steel wire (0.0243″ (0.61 mm.) in diameter) whose length was again 5000 times its radius, the relative rates varied only between 1.6 for vertical and 4.5 for horizontal. Hence, in viscosity measurements the effect of elongation is even less when turbulence is not eliminated.

Summary

From observations on the actual effect on resistance to movement when a sphere is elongated to a fiber 2500 longer than its diameter, it is concluded in accordance with the hydrodynamic theory employed by Einstein for colloidal particles and large molecules that although the effect of extreme departure from sphericity is measurable it is of too low a magnitude to explain the high viscosity which 0.1% of certain colloids, such as nitrocotton, impart to solvents in which they are dissolved. It is therefore concluded that the chief factor is structural viscosity due to entanglement and local adherence of molecules and particles, effectively immobilizing a disproportionate amount of the solvent in comparison with the amount of the colloid itself.

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An X-Ray Study of Some Linear Polyesters

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By means of intermolecular polycondensation reactions Carothers and his co-workers[1] have been able to synthesize linear polyesters of high molecular weight from dihydric alcohols and dibasic aliphatic acids. Carothers and Hill[2] have pointed out the surprising fiber-like characteristics which can be obtained in certain of these polyesters when the molecular weights are sufficiently high (superpolyesters). They have also demonstrated that the polyesters in massive form are microcrystalline, furnishing sharp X-ray powder diagrams, while in the oriented state (cold-drawn fibers) they are capable of giving fiber patterns. Up to this time, however, no attempt apparently has been made to verify the chemical structures which have been proposed for these compounds by means of a study of their X-ray fiber patterns.[3] The X-ray structure of synthetic fibers of known chemical constitution is also of considerable interest since it offers a means of confirming present conceptions in regard to high polymeric substances.

In the present investigation a series of polyesters has been prepared and examined by means of X-rays. Six of these have been carried to the superpolyester state so that highly oriented fiber patterns could be obtained from them. It is the purpose of this investigation to present and discuss the results of the measurement of these fiber patterns.

Materials and Method

Since many polyesters do not crystallize, or do so very slowly, the number which is suitable for X-ray study is somewhat limited. Table I lists the materials which have been investigated together with the approximate molecular

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(1) W. H. Carothers, THIS JOURNAL, **51**, 2548 (1929), *et seq.*

(2) W. H. Carothers and J. W. Hill, *ibid.*, **54**, 1579 (1932).

(3) A. W. Kenney (ref. 2) has found that the fiber period of some polyesters approximates the length of the chemical repeating unit.