[CONTRIBUTION FROM THE EASTERN REGIONAL RESEARCH LABORATORY[1]]

Light Scattering by Sucrose Solutions at High Concentrations

BY MURRAY HALWER

The excellent agreement obtained by Debye[2] between the observed and theoretical turbidities of sucrose solutions prompted the author to investigate the application of these solutions as turbidity standards for use, along with other methods, in evaluating the performance of a photoelectric light-scattering photometer constructed in this Laboratory.[3]

In order to take advantage of the anticipated increase in turbidity with increased sucrose concentration, the measurements were extended beyond the maximum concentration of 0.4 g. per milliliter used by Debye. Contrary to expectation, however, the observed turbidity decreased instead of increasing. The calculation of theoretical turbidity from osmotic pressure data when extended to higher concentrations revealed a corresponding bending-over of the theoretical curve. The results constitute an interesting confirmation of the theory[4] which connects solute turbidity with the concentration gradient of osmotic pressure, as well as a demonstration of an anomaly, namely, a decrease in observed scattering intensity resulting from an increase in the number of scattering units.

Experimental

The highly purified sucrose supplied by the National Bureau of Standards for use in calorimetry and saccharimetry[5] was used without further purification. Solutions in water were filtered by pressure through an ultra-fine sintered glass filter (maximum pore diameter, 1.2 microns) into an optical cell. Turbidities for light of wave lengths 436 and 546 mμ were measured in the photoelectric light-scattering photometer[3] by a ratio of deflections method that involves settings at 90° for the scattered light and 0° for the transmitted light, the latter with an opal glass working standard and neutral filters in the light beam. The observed excess turbidity of a standard 0.5% polystyrene solution in toluene over that of the solvent was 0.00256 cm.$^{-1}$ for 436 mμ, as compared with a value of 0.00270 cm.$^{-1}$ obtained on the absolute turbidity camera in Debye's laboratory at Cornell University.[6]

The turbidity due to the dissolved sucrose alone was determined by subtracting the turbidity value given by the pure solvent under the same conditions.

Specific refractive increments for sucrose solutions in water were determined with a differential refractometer[7] at two levels of concentration by measuring differences in refractive index between solutions of concentration 0.1000 and 0.0900 g./ml., and 0.6000 and 0.5900 g./ml. The results are shown in Table I.

TABLE I

SPECIFIC REFRACTIVE INCREMENTS FOR WATER SOLUTIONS OF SUCROSE AT 25°

Concn. level, g./ml.	Δc, g./ml.	$\Delta n/\Delta c$ 436 mμ	546 mμ
0.1	0.01000	0.146	0.143
.6	.01000	.142	.140

Although a slight dependence on concentration is indicated for $\Delta n/\Delta c$, this is unimportant for the purpose of this study, and average values 0.144 and 0.142, respectively, are assumed for the quantity dn/dc required in the theory. Values for dn/dc calculated from published refractive index data[8] give 0.142 at the 0.1-g./ml. level and 0.141 at the 0.6-g./ml. level. These apply to the D line of sodium and 28°.

Results and Discussion

Observed and calculated turbidities are plotted in Fig. 1. The latter were calculated from osmotic pressure data, by using the equation given by Debye[2]

$$\frac{Hc}{\tau} = \frac{\partial(P/RT)}{\partial c}$$

c = concentration of solute, g./ml. of solution
τ = turbidity, cm.$^{-1}$
P = osmotic pressure, atm.
R = gas constant, cc. – atm./degree
T = absolute temperature
$H = \frac{32\pi^3 n_0^2 (dn/dc)^2}{3N\lambda^4}$
n_0 = refractive index of solvent
dn/dc = specific refractive increment
λ = wave length of light, cm.
N = Avogadro's number

Substituting the known quantities into the expression for H gives 5.60×10^{-6} and 2.20×10^{-6}, ml.^{2} g.$^{-2}$ cm.$^{-4}$ for wave lengths 436 and 546 mμ, respectively.

The osmotic pressure data are from Morse,[9] Frazer and Myrick,[10] and Lotz and Frazer.[11] All values were obtained at 30°. The slopes of the osmotic pressure *versus* concentration curve were determined by fitting the data to an empirical equation and differentiating. The equation used was

$$\frac{P}{RT} = \frac{c^2}{2.215 \times 10^{-5} + 0.03373c - 0.2831c^2} \times 10^{-4}$$

This equation fits the data with a standard error of estimate of 0.678×10^{-4}, in units of P/RT. Equations of the forms $P/RT = ac + bc^2$ and $P/RT = ac + bc^2 + dc^3$ gave less satisfactory fits.

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[1] One of the Laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, United States Department of Agriculture. Article not copyrighted.

[2] Debye, *J. Phys. and Coll. Chem.*, **51**, 18 (1947).

[3] Speiser and Brice, *J. Opt. Soc. Am.*, **36**, 364 (1946) (abstract). The improved apparatus includes use of an opal glass as a reference transmitting diffuser, a multiplier phototube, and a galvanometer. A detailed description will be published shortly.

[4] Debye, *J. Applied Phys.*, **15**, 338 (1944).

[5] U. S. Natl. Bur. Standards Circ. C398, Supplement, Dec. 11, 1946.

[6] We are indebted to A. M. Bueche for this sample and the absolute turbidity value.

[7] Brice and Speiser, *J. Optical Soc. Am.*, **36**, 363 (1946) (abstract).

[8] U. S. Natl. Bur. Standards Circ. C440, 1942.

[9] Morse, Publ. Carnegie Inst. Washington No. 198, 1914, p. 184.

[10] Frazer and Myrick, THIS JOURNAL, **38**, 1907 (1916).

[11] Lotz and Frazer, *ibid.*, **43**, 2501 (1921).

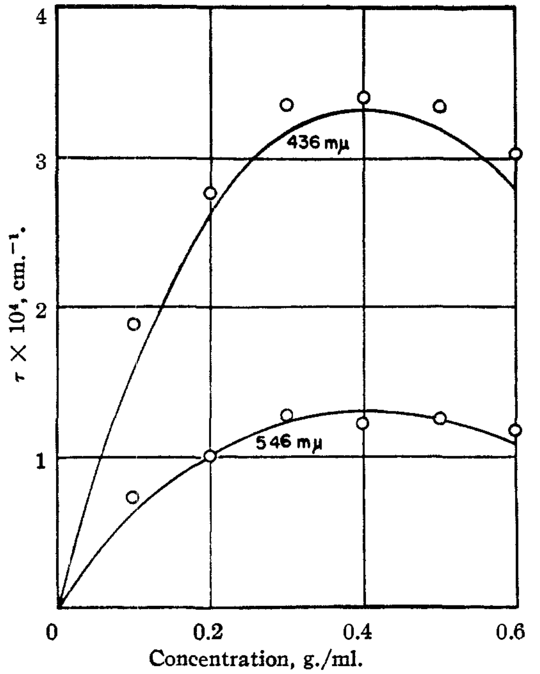

Fig. 1.—Turbidity of sucrose solutions *vs.* concentrations: the lines are the theoretical curves derived from osmotic pressure data. The points are experimentally determined turbidities.

For the former, the standard error of estimate was 2.16×10^{-4}; for the latter 0.825×10^{-4}. The cubic equation also predicts a turbidity maximum, although somewhat displaced from the correct value.

Slopes were obtained by differentiating the above empirical equation. Experimental turbidities, determined at 24–26°, were adjusted to 30° on the assumption that the turbidity is proportional to the absolute temperature.

The theoretical curve requires that the turbidity pass through a maximum at a concentration of about 0.4 g./ml. The experimental behavior conforms satisfactorily to the theory and constitutes a confirmation of it.

The decrease in turbidity when the concentration is increased beyond a certain point is most readily explained by assuming that, as the concentration increases, the randomness of the dilute solution gives way to an increasing degree of order. Increasing destructive interference of the light scattered by different molecules, with a resultant decrease in scattered light intensity, is the consequence. A point is finally reached beyond which increasing order more than balances the effect of increasing the number of scattering centers. A similar hypothesis has been advanced by Oster[12] to explain the decrease in turbidity of tobacco mosaic virus solutions with increased concentration beyond a certain point.

Summary

Absolute turbidities of solutions of pure sucrose have been determined up to a concentration of 0.6 g./ml. of solution. The turbidity increases with concentration, reaching a maximum at about 0.4 ml., then decreases. The theoretical turbidity curve derived from osmotic pressure data shows the same effect. The results confirm the validity of the theory.

[12] Oster, Doty and Zimm, This Journal, **69**, 1193 (1947).

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[Contribution from the Department of Chemistry and Chemical Engineering of the University of Washington]

Trifluoromethyl Hypofluorite

By K. B. Kellogg and George H. Cady

During the past fifty years or more, several attempts have been made to prepare hypofluorous acid and hypofluorites using methods similar to those known to be successful for the corresponding compounds of chlorine. Fluorine behaves very differently from the other halogens, however, reacting with cold water to form hydrofluoric acid, hydrogen peroxide and a small amount of oxygen fluoride. With a dilute solution of sodium hydroxide it forms fluoride ion, oxygen, peroxide ion and some oxygen fluoride.[1] In view of these facts it appears possible that a more fruitful approach to the problem of preparing hypofluorites may be found in the direct fluorination of alcohols or other organic compounds to yield hypofluorites of the type ROF in which R is a perfluoro alkyl group. To test this possibility methyl alcohol has been fluorinated by two procedures recently reported for the complete fluorination of hydrocarbons.[2,3] One of the methods actually did produce trifluoromethyl hypofluorite, CF_3OF.

While this is the first compound which should obviously be named a hypofluorite, it is not the first substance to contain an O–F bond. Others possessing this bond are the oxygen fluorides, fluorine nitrate and fluorine perchlorate.

Experimental

One of the procedures was like that of Fowler, *et al.*,[2] who employed cobalt trifluoride as the oxidizing agent.

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[1] G. H. Cady, This Journal, **56**, 1647 (1934).

[2] R. D. Fowler, W. B. Burford III, J. M. Hamilton, Jr., K. G. Sweet, C. E. Weber, J. S. Kasper and I. Litant, *Ind. Eng. Chem.*, **39**, 292 (1947).

[3] G. H. Cady, A. V. Grosse, E. J. Barber, L. L. Burger and Z. D. Sheldon, *ibid.*, **39**, 290 (1947).