Composition and Gas Phase Dissociation.—Silyldimethylamine, 17.5 cc., was treated with an excess of trimethylboron, 22.5 cc., at room temperature. The total pressure was 478 mm. and a liquid phase was observed. The system was cooled to −78° and the volatile product distilled out. The distillate, 6.0 cc., was identified as trimethylboron by its vapor pressure of 31 mm. at −78° (lit., 32.5 mm.[22]). Hence, 17.0 cc. of silyldimethylamine had combined with 16.5 cc. of trimethylboron. At 0°, the solid product had a vapor pressure of 146 mm. (138 mm. calcd. for purified sample). When completely vaporized at 24° and 72.5 mm., the volume of the gas was 33.0 cc. (calcd. for complete dissociation 34.0 cc.). It is concluded that the compound is almost completely dissociated under these conditions.

A duplicate experiment in which 15.0 cc. of silyldimethylamine and 40.0 cc. of trimethylboron were employed showed that 14.5 cc. of trimethylboron was consumed. The total volume of the sample at 26° and 62 mm. was 28.0 cc. (calcd. for complete dissociation 29.5 cc.). Minute droplets of colorless liquid were observed which did not evaporate. Since the total volume of the vessel was 378 cc., this indicates that slow decomposition was occurring.

Vapor Pressure and Melting Point.—A tensiometrically homogeneous sample of the addition compound was obtained by distillation from −50° and condensation at −78°. The saturation pressures were measured at various temperatures without observation of any irreversible decomposition. The results may be summarized by the equation $\log P = -2685/T + 11.968$ in the range −30 to −5°. The data are given in Table V with the values calculated from the equation. Assuming complete dissociation of the compound and the Clausius–Clapeyron relations, the heat of sublimation is calculated to be 24.6 kcal./mole.

TABLE V

SATURATION PRESSURES OF SILYLDIMETHYLAMINE-TRIMETHYLBORON

T, °C.	−31.4	−27.3	−18.2	−14.8	−9.1	−4.6	0
$P_{\text{mm.}}$ obsd.	7.6	11.2	27.2	37.8	63.7	93.8	...
$P_{\text{mm.}}$ calcd.	7.3	11.2	27.5	37.8	63.4	93.7	138

The melting point was 16.3–17.0° in a sealed capillary.

Acknowledgment.—This work was made possible by a Frederick Gardner Cottrell grant from the Research Corporation.

CHICAGO 16, ILLINOIS

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[22] "International Critical Tables," McGraw-Hill Book Co., Inc., New York, N. Y., 1928, Vol. III, p. 218. Same as ref. 14.

[CONTRIBUTION FROM THE POLYCHEMICALS DEPARTMENT, E. I. DU PONT DE NEMOURS AND COMPANY, INC.]

An Absorption–Extrapolation Light Scattering Method[1]

BY FRED W. BILLMEYER, JR.

RECEIVED APRIL 14, 1954

The particle size of a polystyrene dispersion has been determined by a light scattering method in which transmission measurements are made as a function of wave length. The data are extrapolated to infinite wave length, where the usual small particle light scattering treatment is valid. The results are in satisfactory agreement with the size determined by other light scattering methods.

Introduction

Three different methods of observation have been developed for measuring particle sizes and molecular weights by light scattering. All of these yield essentially equivalent information, but each of them is different from the others in its detailed application and its suitability to certain scattering systems.

The first of these techniques is the dissymmetry method developed by Debye[2] in which scattered light intensity is measured as a function of angle of observation. Scattering functions, dependent upon particle shape, are used to interpret the data in terms of particle size and molecular weight.

A second method is also based on the measurement of scattered light intensity. This is the extrapolation method of Zimm[3] in which data are obtained over as large an angular range as possible and then extrapolated to zero angle. This method is now considered to give the most accurate and precise determinations of molecular weight and size. It is less dependent upon assumptions of particle shape, but requires rather elaborate equipment and considerable skill and care in its application.

The third method, particularly suitable for use with highly scattering systems, is the transmission technique described by Doty.[4] In this method the reduction in light transmission of a colloidal solution due to scattering is measured instead of the scattered light intensity itself. The technique is complementary to the dissymmetry method, measurements being made at a series of wave lengths instead of a series of angles. Again a set of scattering functions based upon specific particle shapes and distributions is used to interpret the results.

The theory of a fourth method, which we have called the absorption-extrapolation technique, has been outlined by Cashin and Debye.[5] Like Doty's transmission method, this procedure uses a standard spectrophotometer to measure total scattering by transmission in a colloidal system. As in Zimm's extrapolation method, scattering functions dependent upon particle shape are not needed for the evaluation of molecular weight.

In the absorption–extrapolation method, the absorption[6] measurements are made at several wave lengths and extrapolated to infinite wave length. Where lack of a suitable range of wave lengths is not a limiting factor,[4] the method combines many of the advantages of other techniques. For example, it has been useful in measuring the particle sizes of dispersions of polymers. This paper describes its application to an aqueous dispersion of polystyrene.

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[1] Presented at the 124th National Meeting of the American Chemical Society, Chicago, Ill., September 9, 1953.

[2] P. Debye, *J. Phys. Colloid Chem.*, **51**, 18 (1947).

[3] B. H. Zimm, *J. Chem. Phys.*, **16**, 1099 (1948).

[4] P. Doty and R. F. Steiner, *ibid.*, **18**, 1211 (1950).

[5] W. M. Cashin and P. Debye, *Phys. Rev.*, **75**, 1307A (1949).

[6] Throughout this paper the term absorption will imply loss in transmission due to scattering only.

Theoretical

Cashin and Debye[5] have developed an extension of the conventional light scattering equations to the case where the particles in solution are no longer small compared to the wave length of the light used. In this case the small-particle equation after extrapolation to infinite dilution

$$H(c/\alpha)_0 = 1/M \tag{1}$$

where

$$H = \frac{32\pi^3}{3\mathbf{N}_0}\left(\frac{\mathrm{d}n}{\mathrm{d}c}\right)^2\frac{n^2}{\lambda^4} \tag{2}$$

does not hold. It may be replaced, to a first approximation, by

$$H(c/\alpha)_0 = f/M \tag{3}$$

In these equations α is the secondary absorption coefficient, that is, the turbidity due to scattering; $\mathbf{N}_0$ is Avogadro's number; n is the refractive index of the solution; and λ is the wave length of the light used in air. The other symbols have their usual meanings. The factor f corrects for the angular dependence of scattered light by integration over the whole angular range

$$f = \frac{\int_0^\pi (1 + \cos^2\theta)\sin\theta\,\mathrm{d}\theta}{\int_0^\pi \phi^2(1 + \cos^2\theta)\sin\theta\,\mathrm{d}\theta} \tag{4}$$

Here ϕ is one of the scattering functions given by Debye.[2] For spheres

$$\phi = (3/x^3)(\sin x - x\cos x) \tag{5}$$

$$x = 2\pi D\frac{n}{\lambda}\sin\frac{\theta}{2}$$

where D is the diameter of the sphere.

For particles not too large ϕ can be expanded in a power series in x and the integration in eq. 4 performed. The result is

$$f = 1 + \frac{2\pi^2}{5}D^2\left(\frac{n}{\lambda}\right)^2 + \ldots \tag{6}$$

or

$$H(c/\alpha)_0 = (1/M)\left[1 + AD^2\left(\frac{n}{\lambda}\right)^2\right] \tag{7}$$

where[7] $A = 2\pi^2/5 = 3.95$ for spheres of diameter D.

Similarly one can obtain the result that $A = 4.39$ for random coils, where D is replaced by the root mean square distance R between chain ends, and $A = 2.19$ for rigid rods, where D is replaced by the length L of the rod. As in Zimm's extrapolation method, the size parameter is obtained by taking the ratio of slope to intercept of the extrapolation line.

In the case of the (angular) extrapolation experiment at a fixed wave length, the function ϕ may be expanded as a power series in the angle with the result that

$$H(c/\tau)_0 = (1/M)\left[1 + 2AD^2\left(\frac{n}{\lambda}\right)^2\sin^2\left(\frac{\theta}{2}\right)\right] \tag{8}$$

for spheres of diameter D. Here τ is the turbidity of the sample.

Experimental

The polystyrene dispersion was prepared by Dr. V. E. Shashoua of the Textile Fibers Department, E. I. du Pont de Nemours and Co., Inc. The original solids content was 0.249 g./ml. The sample was diluted between 1000 and 32,000 times with distilled water to obtain dispersions for the absorption measurements. The initially diluted dispersion was filtered through a Selas 03 porous porcelain filter candle with a rated maximum pore radius of 0.6 μ. The filtered sample was further diluted with similarly filtered distilled water to give the desired concentration series.

Absorption measurements were made with a Beckman model DU spectrophotometer, using matched 10-cm. quartz cells. A cell correction was measured with distilled water in both cells and was applied to the absorption measurements, which were made with distilled water as a standard. The usual precautions in the operation of the instrument[8] were observed. The scattering error in the Beckman instrument was reduced by the addition of 4-mm. diaphragms to limit the solid angle viewed by the phototube.[9]

With water as the solvent, transmission measurements can be made between the wave lengths of 0.350 and 1.000 μ. The refractive indices for polystyrene and water were calculated[10,11] for convenient wave lengths within this region, and were used to obtain dn/dc for the polystyrene–water system by means of the Gladstone–Dale relation.[12] Some of these data, including values of the light scattering constant H, are tabulated in Table I. The wave length range actually used in the experiments was 0.400 to 0.900 μ.

Table I

Refractive Constants for the System Polystyrene–Water

λ, μ	dn/dc	$H \times 10^7$	$(n/\lambda)^2$
0.350	0.287	548	14 85
.400	.269	280	11.27
.436	.261	186	9.45
.450	.259	161	8.86
.500	.252	99.4	7.14
.546	.247	67.4	5.97
.600	.244	44.7	4.93
.700	.239	23.2	3.61
.800	.238	13.3	2.76
.900	.2365	8.24	2.17
1.000	.236	5.37	1.75

Within the error of the experiments, the quantity $H(c/\alpha)$ at a given wave length was independent of the concentration of the polystyrene dispersion. Values of $H(c/\alpha)$ were averaged for solutions having transmissions between 40 and 85% at the wave length used. The averaged values are plotted as a function of $(n/\lambda)^2$ in Fig. 1.

Angular-dependence light scattering measurements were also made on this polystyrene dispersion. An apparatus of essentially conventional design, built in this Laboratory, was used. Measurements were made at a single concentration (2.49×10^{-4} g./ml.) of the dispersion, at a wave length of 0.546 μ. An angular range of 20 to 150° was utilized. A plot of $H(c/\alpha)$ *vs.* $\sin^2(\theta/2)$ is shown in Fig. 2.

Results

Table II shows the particle diameters and molecular weights calculated from eq. 7 and 8 for the absorption-extrapolation and (angular) extrapolation methods, respectively. Particle diameters have also been calculated from the particle weights, assuming spheres having the same density as bulk polystyrene,[10] *i.e.*, 1.06. All of these results are in good agreement.

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(7) The author is grateful to Professor P. Debye and Dr. J. R. McCartney for confirming this correction of an error in Cashin and Debye's abstract.

(8) (a) K. S. Gibson and M. N. Balcom, *J. Opt. Soc. Am.*, **37**, 593 (1947); (b) L. S. Goldring, R. C. Hawes, G. H. Hare, A. O. Beckman and M. E. Stickney, *Anal. Chem.*, **25**, 869 (1953).

(9) W. F. H. M. Mommaerts, *J. Colloid Sci.*, **7**, 71 (1952).

(10) R. H. Boundy and R. F. Boyer, "Styrene," (A.C.S. Monograph No. 115), Reinhold Publ. Corp., New York, N. Y., 1952, p. 524.

(11) "International Critical Tables," McGraw-Hill Book Co., Inc., New York, N. Y., 1930, Vol. VI, p. 13.

(12) P. Outer, C. I. Carr and B. H. Zimm, *J. Chem. Phys.*, **18**, 830 (1950).

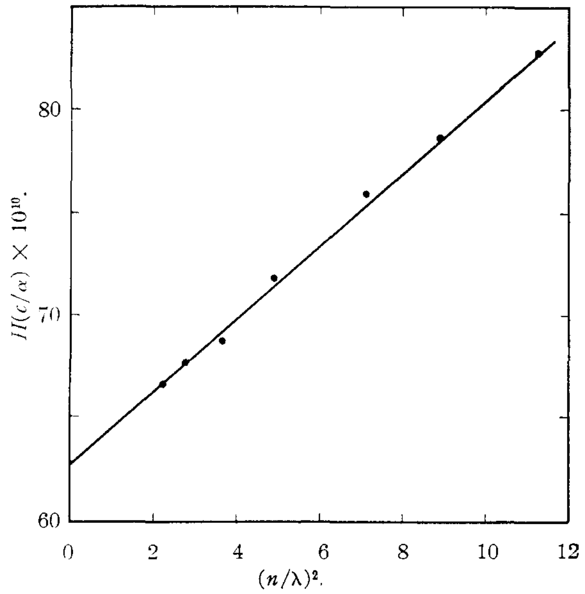

Fig. 1.—Wave length-dependence absorption data for polystyrene dispersion.

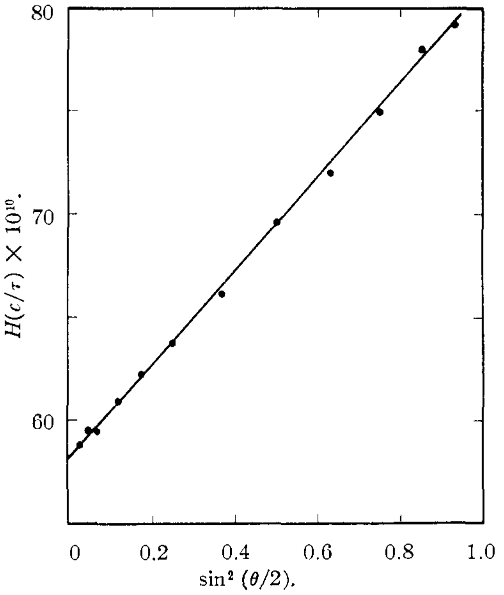

Fig. 2.—Angular-dependence light scattering data for polystyrene dispersion.

TABLE II

PARTICLE SIZE MEASUREMENTS ON A POLYSTYRENE DISPERSION

	Absorption–extrapolation (eq. 7)	Angular extrapolation, (eq. 8)
Particle mol. wt.	1.6×10^8	1.7×10^8
Particle diameter, μ		
From (slope/intercept)	0.084	0.088
From mol. wt.	0.078	0.080

McCartney[13] has carried out the complete evaluation of the integral in eq. 4. His result allows the calculation of particle diameter from the molecular weight of the sample evaluated from a single turbidity measurement at one wave length, provided that (as in this case) c/α is independent of concentration. The particle diameter of the polystyrene dispersion was calculated by this method to be 0.077 μ, in good agreement with the values in Table II.

Discussion

Range of Validity of the Method.—As for the extrapolation method, the applicability of the absorption–extrapolation method is limited to particles for which the phase shift of the incident light wave in traversing a particle is very small. For the extrapolation method this leads to the criterion[14]

$$(2\pi D/\lambda)(m - 1) < 1 \qquad (9)$$

where m is the relative refractive index for the system. A similar condition would be expected to apply to the absorption–extrapolation method. This limits the method to particle diameters smaller than about 0.1–0.2 micron for the polystyrene–water system[15] where $m = 1.2$. For the sample discussed in this paper $(2\pi D/\lambda)(m - 1)$ varies between 0.1 and 0.3. It should be noted that for larger particle sizes a misleading situation may occur[13]: values of $H(c/\alpha)_0$ calculated from the complete evaluation of eq. 4 form an apparently linear function of $(n/\lambda)^2$ over the experimentally available wave length range but curve toward a quite different intercept and initial slope at longer wave lengths.

Average Particle Sizes.—If the scattering system is heterogeneous with respect to particle size, any of the methods will give an average value for the size parameter. It is well known that light scattering methods give a weight-average molecular weight. The particle diameter derived from this molecular weight[14b] will therefore be the weight-average of D^3

$$\overline{D^3} = \frac{\sum_i N_iD_i^6}{\sum_i N_iD_i^3} = \frac{\sum_i N_iM_iD^3}{\sum_i N_iM_i} \qquad (10)$$

where N_i is the number of particles having a diameter D. The type of average obtained from the ratio of slope to intercept in the absorption-extrapolation method is a function of the particle diameter except for particles small enough that eq. 7 may be written

$$\alpha/H = \sum_i M_ic_i\,[1 - AD_i^2(n/\lambda)^2] \qquad (11)$$

In this case the average diameter obtained is the z-average of D^2

$$\overline{D^2} = \frac{\sum_i N_iD_i^8}{\sum_i N_iD_i^6} = \frac{\sum_i N_iM_i^2D_i^2}{\sum_i N_iM_i^2} \qquad (12)$$

It may easily be shown that eq. 12 is valid only for particles somewhat smaller than those for which eq. 7 begins to break down. Since this is a higher average, particle sizes calculated from the ratio of

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(13) J. R. McCartney, private communication.

(14) (a) H. C. Van de Hulst, "Optics of Spherical Particles," Duwaer and Sons, Amsterdam, 1946. (b) W. B. Dandliker, THIS JOURNAL, **72**, 5110 (1950).

(15) W. Heller (private communication) confirms this range of validity.

slope to intercept may be somewhat higher than those calculated from molecular weights. It is possible that the differences observed in our data may indicate a slight polydispersity in the sample.

Acknowledgment.—The author wishes to acknowledge helpful discussions with Professor W. Heller of Wayne University, Professor W. H. Stockmayer of the Massachusetts Institute of Technology, and Drs. J. R. McCartney, J. E. Eldridge and J. K. Beasley of the du Pont Company.

WILMINGTON, DELAWARE

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF POLYTECHNIC INSTITUTE OF BROOKLYN]

Studies on Ion Exchange Resins. XI. Activity Coefficients of Diffusible Ions in a Strong Base Anion-exchange Resin

BY MELVIN H. GOTTLIEB[1] AND HARRY P. GREGOR

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Mean activity coefficients of the diffusible electrolyte in an anion-exchange resin were calculated from the non-exchange electrolyte and water content of the resin in equilibrium with various aqueous electrolytic solutions. The calculated activity coefficients were found to decrease sharply on dilution of the solution phase, being lowest with those electrolytes whose anions appeared to form ion-pairs with the fixed exchange cations of the resin.

A previous paper in this series[2] dealt with the phase equilibria of a strong acid cation exchange resin and electrolytic solutions containing the same cationic species. This paper similarly treats the equilibria between a strong base anion-exchange resin and solutions containing the exchange anion. Mean activity coefficients of potassium chloride, hydrochloric acid, potassium acetate, potassium trichloroacetate, potassium iodide, potassium thiocyanate and sodium hydroxide in the resin are calculated using the Gibbs–Donnan relationship based upon the equilibrium resin phase composition, as in the previous paper. In these calculations, the activities of the diffusible electrolyte in the resin and solution phases are set equal to one another, and the mean activity coefficient $\gamma_{\pm}^{r}$ calculated from the expression

$$\gamma_{\pm}^{r} = (m^2\gamma_{\pm}^{2}/m_{+}^{r}m_{-}^{r})^{1/2}$$

where the molal concentrations of the diffusible cation and anion m_+ and m_- are calculated from the resin-exchange capacity, the water content and the non-exchange electrolyte content. The superscript r designates the resin phase; the solution phase is not designated.

Kraus and Moore[3] have made a similar study with a strong base resin and hydrochloric acid solutions, using essentially similar techniques.

Experimental

The anion-exchange resin was Dowex-2, a strong base resin prepared using 8% divinylbenzene as cross-linking agent. The exchange groups are of the benzyl–ethanol-dimethyl quaternary ammonium type; similar materials can be prepared by the chloromethylation of a styrene–divinylbenzene copolymer, followed by suitable treatment with the corresponding tertiary amine.

The equilibrations, elutions and analytical techniques were substantially the same as employed previously. Carbonate-free sodium hydroxide was used, and the eluate containing the non-exchange sodium hydroxide was analyzed for sodium flame photometrically. The detailed experimental values obtained are not presented here, but are available in the thesis.[1]

Discussion

The reduced mean activity coefficient $\gamma_{\pm}^{r}/\gamma_{\pm}$, hereinafter designated simply γ^r/γ, is plotted in Fig. 1 as a function of the molality of the equilibrating solution for potassium chloride, potassium acetate, potassium trichloroacetate, potassium thiocyanate and potassium iodide. In Fig. 2 the reduced activity coefficient curves are given for sodium hydroxide and hydrochloric acid.

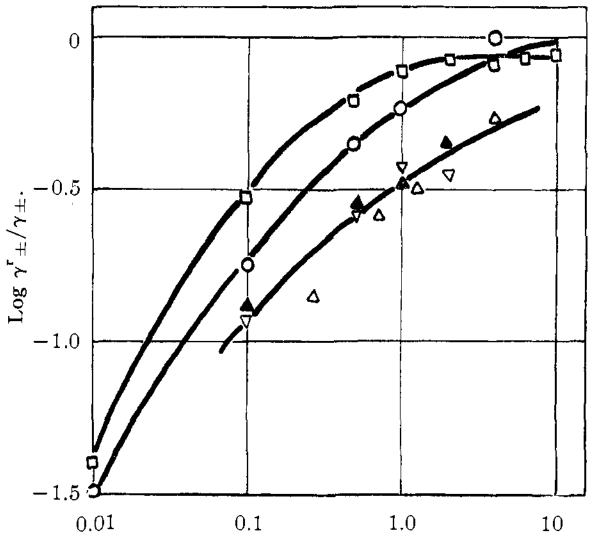

Fig. 1.—Reduced mean activity coefficient of diffusible electrolyte with DVB 8 anion-exchange resin as a function of the solution phase molality for potassium acetate (□), potassium chloride (○), potassium thiocyanate (▲), potassium iodide (▽) and potassium trichloroacetate (△).

In general, the data are similar to those obtained with cation exchange resin systems.[2] At high external concentrations $\gamma_{\pm}^{r}$ approaches $\gamma_{\pm}$; also, $\gamma_{\pm}^{r}$ decreases sharply on dilution of the equilibrating solution. Certain significant differences are, however, observed.

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[1] This paper is abstracted from the dissertation of M. H. Gottlieb, submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Chemistry, Polytechnic Institute of Brooklyn, August, 1953.

(2) H. P. Gregor and M. H. Gottlieb, THIS JOURNAL, **75**, 3539 (1953).

(3) K. A. Kraus and G. E. Moore, *ibid.*, **75**, 1457 (1953).