[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF RUTGERS UNIVERSITY]

Polyphosphates as Polyelectrolytes. I. Light Scattering and Viscosity of Sodium Polyphosphates in Electrolyte Solutions[1]

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Several samples of sodium polyphosphate, covering a molecular weight range from 7000 to 19000, were prepared by the condensation polymerization of primary sodium phosphate. The viscosity and *p*H of freshly prepared solutions decreased over the first 12-hour period, indicating the presence of a small amount of unstable branch-points in the glasses. After stability was obtained, light scattering and viscosity studies using sodium bromide solutions as solvents gave the following results: (1) The conventional Hc/τ *versus* c plots were straight lines whose slopes decreased with increasing sodium bromide concentration of the solvent. (2) For a given polymer sample, the Hc/τ intercepts were the same in all solvents. (3) The light scattering molecular weights were proportional to the intrinsic viscosities obtained in 0.035 N sodium bromide. (4) The slopes of the Hc/τ *versus* c lines in a given solvent were independent of molecular weight. (5) Measurements of a sample in several solvents yielded a simple linear relationship between light scattering slope and intrinsic viscosity. (6) The viscosimetric root-mean-square end-to-end distance of a sample in the 0.35 N sodium bromide solution, in which the light scattering slope is zero, supported the view of polyphosphate molecules as unbranched chains with very little steric hindrance to internal rotation.

If primary sodium phosphate is heated above 650°, it will polymerize with the elimination of water, and, on quenching of the melt, water-soluble glasses are obtained.[2] These products are known under various names such as *Graham's salt, sodium hexametaphosphate, sodium polymetaphosphate* and *sodium polyphosphate.* Because of their manifold usefulness, they have been extensively studied over the last hundred years,[3] but only in the last decade, mainly through the work of Lamm,[4,5] Malmgren,[5] Samuelson[6] and Van Wazer,[7] has their true nature as linear, flexible, polydisperse polyelectrolytes with average degrees of polymerization ranging up to 200 come to be recognized.

For several reasons, the polyphosphates are almost ideally suited for a study of polyelectrolyte[8] behavior. First, they are easily prepared to a degree of purity much higher than is commonly attained with organic polymers; second, they can be studied under conditions where their chains are known to be unbranched; third, their molecular weights are in a low range where the viscosity behavior is uncomplicated by velocity gradient dependence; and fourth, their molecular weight distribution function has been determined both theoretically and experimentally[7] so that results, obtained with unfractionated samples by different experimental methods can be correlated.

A study of the polyphosphates should therefore prove fruitful in obtaining a better understanding of polyelectrolyte behavior. Furthermore, information concerning the molecular dimensions of these compounds, which would result from such a study, is highly desirable. In this paper, we shall present and analyze the results of some light scattering and viscosity measurements made on sodium polyphosphate dissolved in aqueous sodium bromide solutions. Several samples were used, whose weight average molecular weights ranged roughly from 7000 to 19000.

Experimental

Sodium Polyphosphate.—Several samples were prepared by fusing sodium dihydrogen orthophosphate (Merck reagent or Fisher C.P.) in a platinum dish at constant temperature in the range between 700 and 1000° and subsequent rapid chilling of the melt between cold iron plates.[9] Clear, colorless glasses were obtained in this manner which were powdered and stored over phosphorus pentoxide. Their molecular weights depended on the temperature and time of fusion, in line with the findings of others.[6,10,11] Two of the samples were analyzed for phosphorus content by potentiometric titration with sodium hydroxide between the first and second neutralization points of the ortho-pyrophosphate solutions formed by boiling the polyphosphate in dilute nitric acid.[7] Results for sample no. 134 were 9.81, 9.80 and 9.78 meq. phosphorus per gram, for sample no. 169, 9.84 and 9.83 meq. per gram were obtained.[12] The theoretical value for a glass of the metaphosphate composition, $NaPO_3$ is 9.81. These results which agree within 1 part in 300, the maximum accuracy attainable with the analytical technique, are sufficient to indicate the reliability of the method of preparation for producing compounds of the desired composition, and no need for similar analyses of the other samples was seen.

Solvents.—Solutions of sodium bromide (Merck and Co., reagent) in distilled water were prepared by weight. The exact normality of each sodium bromide solution was determined by potentiometric titration with silver nitrate.

Light Scattering.—Light scattered at 90° to the incident beam, which was monochromatized to 4358 Å., was measured at 22° by means of a light scattering microphotometer purchased from the American Instrument Co. A paper by Dr. Gerald Oster of the Brooklyn Polytechnic Institute, containing a description of this instrument and instructions for its use, is in preparation.[13]

All solutions were freed of optical impurities by filtration through sintered glass filters of "fine" porosity before their light scattering was determined.

The instrument was calibrated with a standard polystyrene sample, kindly supplied by Professor P. Debye of Cornell University. A 0.5% solution of this sample in toluene has an apparent excess turbidity of 0.0035 cm.$^{-1}$

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[2] T. Graham, *Phil. Trans. Roy. Soc.*, **123**, 253 (1833).

[3] For a review of the early literature, see, for instance, K. Karbe and G. Jander, *Kolloid Beih.*, **54**, 1 (1943).

[4] O. Lamm, *Arkiv Kemi Mineral Geol.*, **17A**, 25 (1944).

[5] O. Lamm and H. Malmgren, *Z. anorg. allgem. Chem.*, **245**, 103 (1940).

[6] O. Samuelson, *Svensk. Kem. Tid.*, **56**, 343 (1944); *ibid.*, **61**, 76 (1949).

[7] J. R. Van Wazer, *et al.*, THIS JOURNAL, **72**, 639, 644, 647, 655, 906 (1950).

[8] For reviews of the literature on synthetic polyelectrolytes see R. M. Fuoss, *Faraday Soc. Disc.*, **11**, 125 (1952), or U. P. Strauss and R. M. Fuoss, "Polyelectrolytes" in "Physik der Hochpolymeren," Vol. II. ed. H. A. Stuart, Springer Verlag, Berlin, 1953.

[9] L. F. Audrieth and R. N. Bell, in "Inorganic Syntheses," Vol. III, McGraw-Hill Book Co., New York, N. Y., 1950, p. 105.

[10] E. L. Weinberg, Thesis, Univ. of Illinois, 1947.

[11] H. J. Weiser, Jr., Thesis, Univ. of Cincinnati, 1951.

[12] We are indebted to Mr. Theodore L. Treitler for these analyses.

[13] G. Oster, private communication.

over that of the solvent. The calibration constant obtained in this manner was multiplied by the appropriate refractive index correction factor[14] and used to calculate the turbidities of the aqueous solutions from the instrumental readings.

Refractive index differences between solutions and solvents were measured at 22°, with light of 4358 Å. wave length, in a Brice–Phoenix Differential Refractometer[15] which was calibrated by means of sucrose solutions.[16]

The entire light scattering procedure was tested on a sample of "crystallized" bovine serum albumin[17] dissolved in 0.1 *N* sodium chloride solution. The specific refractive index increment was found to be 0.196 and the molecular weight 73000. These values agree closely with those found by Edsall and co-workers,[18] namely, 0.195 and 77000, respectively, and those by Halwer, Nutting and Brice,[19] namely, 0.1924 and 73000, respectively.

Viscosity.—A Bingham viscometer[20] operating at driving pressures ranging from 30 to 200 g./cm.^{2} was used to measure viscosities at 25.00°. The viscometer was calibrated with sucrose solutions according to the method of Fuoss and Cathers.[21] The viscometer constant for water was 8047 g. sec./cm.^{2}. Viscosities were measured with an accuracy of 1 part per 1000.

Results and Discussion

Stability.—When viscosity measurements of an aqueous sodium polyphosphate solution were begun soon after dissolution was complete, which required approximately 30 minutes, a decrease lasting about 12 hours was observed, after which the viscosity remained constant for several days.[22] This behavior is illustrated by curve 1 of Fig. 1 where the reduced viscosity η_{sp}/C[23] of a 1.082% solution of sample 312 in water is shown as a function of time.

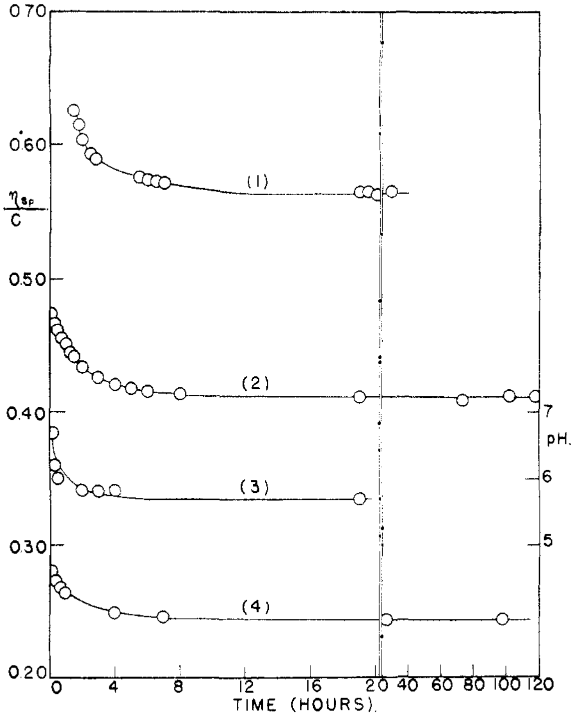

Fig. 1.—Initial changes of reduced viscosity and *p*H: curve 1, sample 312 in water, C = 1.08; curves 2 and 3, sample 270 in water, C = 1.59; curve 4, sample 270 in 0.035 *N* NaBr, C = 1.20. Curves 1, 2 and 4, read left ordinate; curve 3, read right ordinate.

In all cases, the total decrease of the reduced viscosity amounted to about 10 to 15% of its initial value. This also held true when the solutions were prepared in such a way that viscosity measurements could be started within ten minutes after the sample had come into contact with water. This was accomplished by exposing a large polymer sample to water for two minutes and immediately afterwards filtering the solution into the viscometer. The concentration of the solution was determined later from its refractive index. A typical run is illustrated by curve 2 in Fig. 1, while curve 4 shows similar behavior when the solvent was a 0.035 *N* sodium bromide solution instead of pure water.

Some light is thrown on the cause of this effect by curve 3 which represents the change in *p*H of the same solution whose viscosity change is illustrated by curve 2. The *p*H is seen to decrease initially, and to become constant after about the same period of time required for the reduced viscosity to reach constancy. This correlation between the viscosity and the *p*H can be explained if one assumes a partial hydrolytic degradation of the polymer molecules. Such a degradation would result in a decrease of the molecular weight and hence in a decrease of the viscosity, and also in an increase of the hydrogen ion concentration since two acidic groups are created for each P–O bond ruptured by hydrolysis. The halt in the degradation indicates the presence of some specially weak bonds in the glassy samples. This is exactly what would be expected if the glasses were to contain some branched polymer molecules, since for theoretical reasons branch-points should be unstable.[7] Evidence for the presence of branched molecules in polyphosphates derived from starting materials whose Na:P ratio is 1:1 has also been obtained by purely analytical methods.[11] An experimental study aimed at correlating the degree of branching with the exact Na:P ratio is in progress.

The light scattering and viscosity results described below were all obtained more than 12 hours after dissolution so that, if the views just stated are correct, all the branch-points will have disappeared, and one may assume the observed behavior to be caused by linear, unbranched polyelectrolyte molecules.

Since, by following this procedure, the samples were investigated in a state different from that obtaining in the solid glass, it was necessary to show that the final states

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(14) C. I. Carr and B. H. Zimm, *J. Chem. Phys.*, **18**, 1616 (1950).

(15) Purchased from the Phoenix Precision Instrument Co., Philadelphia, Pennsylvania.

(16) C. A. Browne and F. W. Zerban, "Physical and Chemical Methods of Sugar Analysis," Third Edition, John Wiley and Sons, Inc., New York, 1941, p. 1206.

(17) Purchased from Armour and Co., Chicago, Ill.

(18) J. T. Edsall, H. Edelhoch, R. Lontie and P. R. Morison, THIS JOURNAL, **72**, 4641 (1950).

(19) M. Halwer, G. C. Nutting and B. A. Brice, *ibid.*, **73**, 2786 (1951).

(20) E. C. Bingham, "Fluidity and Plasticity," McGraw-Hill Book Co., New York, N. Y., 1922.

(21) R. M. Fuoss and G. I. Cathers, *J. Polymer Sci.*, **4**, 97 (1949).

(22) To be perfectly correct, one should say that the viscosity decreases further, but at such a slow rate that about a week is required before any change can be observed. The faster rates of decrease which have been reported by some other investigators[5] were obtained under conditions different from ours. Thus, the rate increases rapidly with decreasing *p*H or with increasing temperature or molecular weight. See R. Pfanstiel and R. K. Iler, THIS JOURNAL, **74**, 6059 (1952).

(23) C is the polymer concentration in g./100 ml. of solution, and $\eta_{sp} = (\eta - \eta_0)/\eta_0$, η_0 and η being the viscosities of solvent and solution, respectively.

attained were the same, whether the initial hydrolysis occurred in water or in a sodium bromide solution. To this end the following two experiments were performed: (1) A solution of sample 312 in water (C = 0.943) was allowed to stand at 25° until its reduced viscosity had become constant at 0.598. Enough 0.35 N sodium bromide solution was then added to bring the sodium bromide normality to 0.035. Owing to this dilution, the polymer concentration, C, became 0.86, and the reduced viscosity, measured immediately after mixing, 0.319. (2) A portion of sample 312 was dissolved in enough 0.035 N sodium bromide solution to bring C to 0.86. The solution was allowed to stand until the reduced viscosity reached constancy at 0.314.

The final reduced viscosity values, 0.319 and 0.314, agree closely within the precision attainable in such experiments, which indicates that the final chemical state obtained is independent of the sodium bromide concentration of the solvent in which the viscosity decrease takes place. It should be noted that this conclusion is based entirely on experimental evidence, and in no way depends on any theory concerning the cause for the initial viscosity decrease.

Molecular Weights and Intrinsic Viscosities.—For ordinary non-ionic polymers whose molecules are isotropic and small compared to the wave length of the light, the light scattering results can be expressed by the equation[24,25]

$$Hc/\tau = 1/M + 2Bc \qquad (1)$$

Here τ is the excess turbidity of the solution over that of the solvent, c is the concentration of polymer in g./ml. of solution, and $H = (32\pi^3 n_0^2/3N_0\lambda^4)\cdot[(n - n_0)/c]^2$ where N_0 is Avogadro's number, λ is the wave length of the light, and n_0 and n are the refractive indices of solvent and solution, respectively. M is the molecular weight, and B is a constant[26] which depends on the interactions of the polymer molecules with the solvent and with one another.

While equation (1) is not applicable to polyelectrolytes under all conditions,[27,28] our results show that it is applicable to sodium polyphosphate in sodium bromide solutions. This is illustrated in Fig. 2 where Hc/τ against c plots for solutions of sample 242 in sodium bromide solutions ranging from 0.10 to 0.35 N are seen to be straight lines. While their slopes differ, they have, in accordance with equation (1), a common intercept which is the reciprocal of the molecular weight of the sample.

The molecular weights of seven other samples were determined similarly, although for most of them only one or two sodium bromide solutions were used as solvents. In Table I, the results are compared with the intrinsic viscosities obtained in a 0.035 N sodium bromide solution. This normality of sodium bromide was chosen because, as is illustrated in Fig. 3, it is high enough to produce linear η_{sp}/C against C plots and yet low enough for the attainment of specific viscosity values which are sufficiently large to be determined with good precision.

TABLE I

MOLECULAR WEIGHTS AND INTRINSIC VISCOSITIES

Sample	M	$[\eta]$ in 0.035 N NaBr	$([\eta]/M) \times 10^5$
134	7400	0.134	1.81
169	9800	.169	1.73
181	9900	.181	1.83
242	14000	.242	1.73
270	15800	.270	1.71
305	17100	.305	1.78
309	17400	.309	1.78
312	18200	.312	1.71

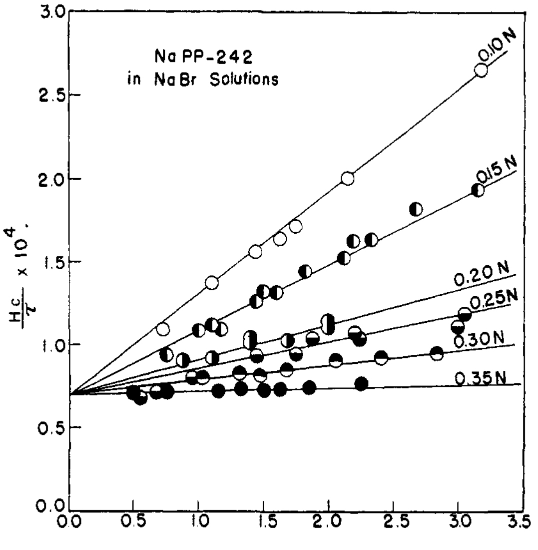

Fig. 2.—Effect of solvent on light scattering curve.

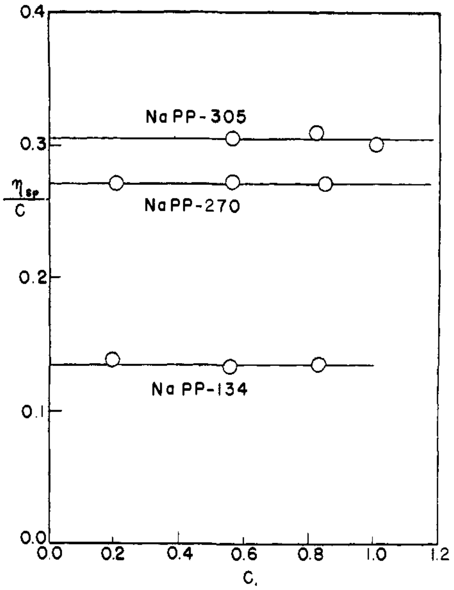

Fig. 3.—Reduced viscosity in 0.035 N NaBr.

The last column in Table I shows that the intrinsic viscosity to molecular weight ratio is constant within the experimental precision limits. On averaging, this relationship can be expressed in the form of Staudinger's law

$$[\eta](\text{in } 0.035\ N\ \text{NaBr}) = 1.76 \times 10^{-5} M \qquad (2)$$

This equation is of theoretical importance because it indicates that the polymer molecules are

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[24] P. Debye, *J. Applied Phys.*, **15**, 338 (1944); *J. Phys. Colloid Chem.*, **51**, 18 (1947).

[25] P. M. Doty, B. H. Zimm and H. Mark, *J. Chem. Phys.*, **12**. 144 (1944); *ibid.*, **13**, 159 (1945).

[26] B is related to the osmotic pressure, P, by the expression $P/cRT = 1/M + Bc$.

[27] P. Doty and R. F. Steiner, *J. Chem. Phys.*, **17**, 743 (1949); *ibid.*, **20**, 85 (1952).

[28] A. Oth and P. Doty, *J. Phys. Chem.*, **56**, 43 (1952).

hydrodynamically free-draining.[29] It also has practical value in that its use will make it possible henceforth to determine molecular weights of sodium polyphosphate samples directly from viscosity measurements.[30] It is of interest that the validity of equation (2) should be independent of molecular weight distribution, since both the light scattering molecular weight and the intrinsic viscosity in sodium bromide solution are weight average values.

Light Scattering Slopes and Intrinsic Viscosities.—The specific refractive increments, $(n - n_0)/c$, which enter into the constant H, were found to be independent of both the polymer concentration and of the molecular weights of the samples. They did, however, depend somewhat on the nature of the solvent as is shown in Table II. The small decrease of the refractive increment with increasing sodium bromide normality may indicate that the polarizability of the polyelectrolyte decreases slightly with decreasing ionization.

TABLE II

EFFECT OF SOLVENT ON SODIUM POLYPHOSPHATE

[NaBr]	$(n - n_0)/c$	$2B \times 10^4$	$[\eta]$ of NaPP-242	$2B \times 10^4/[\eta]$
0.10	0.109	6.1	0.158	39
.15	.108	4.0	.135	30
.20	.108	2.0	.114	18
.25	.107	1.5	.103	15
.30	.106	0.8	.094	8
.35	.104	0.0	.086	0

The slopes of the Hc/τ against c lines were found to be independent of the molecular weight. This is illustrated in Fig. 4 by the light scattering behavior of two samples of different molecular weight, each measured in three different solvents. It is apparent that the lines corresponding to a common solvent are parallel. Therefore, the slopes depend only on the solvent. Their values are given in the third column of Table II. The vanishing of the slope in 0.35 N sodium bromide solution makes the latter a very convenient solvent for molecular weight determinations. No extrapolation to infinite dilution is necessary, but the molecular weight can be calculated from one light scattering measurement at a finite concentration. Moreover, in such a "van't Hoff solvent" the net thermodynamic interactions between polymer segments vanish,[31,32] and the intrinsic configurational character of the polymer chains can be determined. Thus, the intrinsic viscosity of sample 242 in 0.35 N sodium bromide solution is 0.086. Using Debye's formula[29] for free-draining polymer

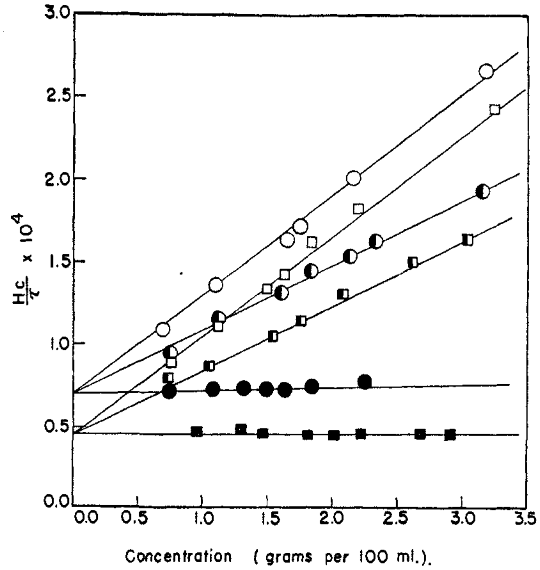

Fig. 4.—Effect of molecular weight on light scattering curves. Circles refer to sample 242, squares to sample 349. Open circles or squares refer to 0.10 N NaBr, half-shaded to 0.15 N NaBr, shaded to 0.35 N NaBr.

$$[\eta] = (\pi/600)(\rho R^2/m) \qquad (3)$$

molecules, and setting ρ, the radius of an effective monomer sphere, equal to 1.5 Å., and m, the mass of a monomer unit, equal to $102/N_0$, one obtains the value of 43 Å. for R, the root-mean-square distance between the ends of the polymer chain. On the other hand, the theoretical root-mean-square distance of an unbranched polymer molecule of n links, each of length l, with a fixed valence angle α between successive bonds, and free internal rotation about each bond, is given by the expression[33]

$$R = ln^{1/2}[(1 + \cos \alpha)/(1 - \cos \alpha)]^{1/2} \qquad (4)$$

For polyphosphates, l = 1.56 Å.,[7] $\cos \alpha = 1/3$, and since the molecular weight of sample 242 is 14,000, its degree of polymerization is 137 and n = 274. With these values, the theoretical root-mean-square end-to-end distance becomes 37 Å. The agreement between the experimental and theoretical values is quite close, supporting the conception of polyphosphate molecules as unbranched chains with very little steric hindrance to free internal rotation.

The theory of light scattering by multi-component systems has been treated by several authors[34-36] and applied to polyelectrolytes in electrolyte solutions by Edsall and co-workers.[18] Their results for the light scattering slopes can be summarized by the expression

$$2B = \frac{100Z^2}{M^2}\frac{1}{2s} + 2B' \qquad (5)$$

The first term on the right hand side, in which Z is the effective valence of the polyelectrolyte and s is the simple electrolyte molality, is called the Donnan term since it is related to the Donnan effect. The second term contains several parameters depending on the interactions between the various components of the solutions. If the polyelectrolyte were completely ionized, the value

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[29] P. Debye, *J. Chem. Phys.*, **14**, 636 (1946).

[30] Equation (2) can, of course, be used safely only for the molecular weight range for which it has been shown to hold, *i.e.*, up to molecular weights of about 20000. Further investigations are necessary to show the intrinsic viscosity–molecular weight relationship in the higher molecular weight range.

[31] P. J. Flory and T. G Fox, Jr., THIS JOURNAL, **73**, 1904 (1951).

[32] P. J. Flory, *J. Chem. Phys.*, **21**, 162 (1953).

[33] H. Eyring, *Phys. Rev.*, **39**, 746 (1932).

[34] H. C. Brinkman and J. J. Hermans, *J. Chem. Phys.*, **17**, 574 (1949).

[35] J. G. Kirkwood and R. J. Goldberg, *ibid.*, **18**, 54 (1950).

[36] W. H. Stockmayer, *ibid.*, **18**, 58 (1950).

of the Donnan term would be $0.05/s$, or about 0.5 in the 0.1 N sodium bromide solution. Actually, as can be seen in Table II, the experimental slope is two orders of magnitude smaller than this value. Moreover, the slopes are linear in $s^{-1/2}$ and not in s^{-1}, as were the osmotic pressure slopes of sodium pectinate and sodium carboxymethylcellulose, where the Donnan term was the controlling factor.[37] Apparently, the sodium polyphosphate is so slightly ionized in the sodium bromide solutions that the Donnan term becomes unimportant. This is in line with results by Van Wazer[7] which show that sodium ions tend to form weak complexes with polyphosphate ions.

A more fruitful approach is based on the exact correspondence between the osmotic pressure equation (and hence the light scattering equation), of a solute, and the virial equation of a real gas.[38,39] As a consequence of this correspondence, the product of B and M^2 is equivalent to the second virial coefficient of a gas, and may therefore be considered a measure of the excluded volume of the polymer molecules,[40,41] *i.e.*, the extent to which two polymer chains resist interpenetration. The excluded volume depends on the shape and extension of the polymer molecules, and since the intrinsic viscosity does also, a correlation between these two quantities is expected. Actually, a theoretical relationship between the osmotic pressure slope and the reduced viscosity was developed and experimentally verified by Flory.[42] A somewhat simpler approach, which is sufficient for a qualitative interpretation, is to consider the two limiting cases of a flexible chain, namely, the stiff rod and the hard sphere. For each of these, the osmotic pressure slope and the intrinsic viscosity have the same theoretical dependence on the respective geometrical parameters. For a stiff rod, both B and $[\eta]$ are proportional to its diameter and the square of its length,[43,44] while for a hard sphere, both are proportional to its volume.[43,45] Using formula (24) of reference (43) for B (Zimm's A_2) and equation (IX. 37) of reference (44) for $[\eta]$, one obtains for a stiff rod

$$B/[\eta] = 300\ N_0m/M^2 \qquad (6)$$

Using formula (21) of reference (43) for B and setting $[\eta]/0.025$ equal to the specific volume,[45] one obtains for a hard sphere

$$B/[\eta] = 160/M \qquad (7)$$

For sample 242, $M = 14000$ and $N_0m = 102$. With these values the ratio $2B \times 10^3/[\eta]$ should be 0.31 if the molecules were stiff rods and 23 if the molecules were hard spheres. Since the molecules are flexible chains, the ratio should lie between these limits. The experimental values which are given in Table II are of the right order of magnitude, but exceed the theoretical limits on both sides of the range. These discrepancies are due to intermolecular forces which were not included in the purely geometrical considerations discussed above. Since such forces between two polymer segments should be similar whether the segments belong to the same or to different chains, one would expect their influence on $[\eta]$ and B to be in the same direction. However, they have a much greater effect on B than on $[\eta]$, partly because of the differences inherent in the definitions of these quantities, partly because *intramolecular* geometrical restraints limit the effect of long-range repulsive forces upon $[\eta]$, whereas no such limitations are encountered in the case of B which depends on *intermolecular* interactions.

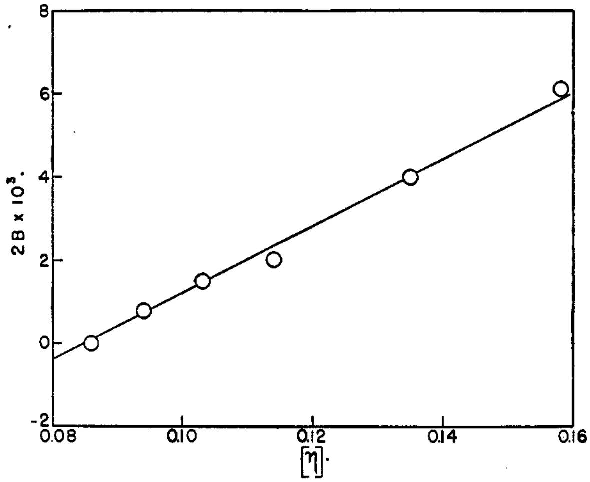

Fig. 5.—Correlation between light scattering slope and intrinsic viscosity of sample 242 in sodium bromide solutions.

A surprisingly simple empirical linear relationship between B and $[\eta]$ is shown in Fig. 5. This relationship is represented by the equation

$$2B \times 10^3 = 82[\eta] - 7.05 \qquad (8)$$

The form of this equation resembles the expression for the second virial coefficient of a real gas as it appears in the virial expansion of van der Waals equation. With this in mind one may consider the positive term on the right hand side to represent the repulsive forces, and the negative term the attractive forces between two polymer molecules. Pursuing the analogy a step further, the repulsive forces may be represented by an imaginary sphere around the center of each polymer molecule. This effective sphere of repulsion is then 82/23 times as large as the effective sphere measured by the intrinsic viscosity,[46] which implies a ratio of 1.5 for the corresponding diameters. This is a quite reasonable value, if one pictures the effective geometrical sphere as surrounded by a Debye–Hückel type ionic atmosphere which increases its effective collision diameter without having much

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[37] D. T. F. Pals and J. J. Hermans, *Rec. trav. chim.*, **71**, 458 (1952).

[38] W. G. McMillan and J. E. Mayer, *J. Chem. Phys.*, **13**, 276 (1945).

[39] P. J. Flory, *ibid.*, **17**, 1347 (1949).

[40] P. M. Doty and R. F. Steiner, *J. Polymer Sci.*, **5**, 383 (1950).

[41] P. Doty and J. T. Edsall, "Light Scattering in Protein Solutions" in "Advances in Protein Chemistry," Vol. VI, Academic Press, Inc., New York, N. Y., 1951, p. 44.

[42] P. J. Flory, *J. Chem. Phys.*, **13**, 453 (1945).

[43] B. H. Zimm, *ibid.*, **14**, 164 (1946).

[44] H. Mark and A. V. Tobolsky, "Physical Chemistry of High Polymeric Systems," Interscience Publishers, Inc., New York, N. Y., 1950, p. 294.

[45] A. Einstein, *Ann. Phys.*, **19**, 289 (1906); *ibid.*, **34**, 591 (1911).

[46] It has been shown above that the relation between B and $[\eta]$ should be $2B \times 10^3 = 23[\eta]$ if the polymer molecules are assumed to be hard spheres and if no forces are acting between them.

effect on the intrinsic viscosity. The attraction term should be due to short-range van der Waals and dipole interactions of the polymer molecules with one another (relative to those between polymer and solvent). Since the changes in the solvent and polymer over the range investigated are relatively small as far as their effect on these non-ionic forces is concerned, the constancy of this term is not unreasonable. However, further experimental work, especially studies of the effect of temperature on the parameters in equation (8), is needed to confirm the validity of this interpretation.

Acknowledgment.—Grateful acknowledgment is made to Dr. Edward R. Allen for bringing this problem to the authors' attention and for his generous helpfulness during the course of this work.

NEW BRUNSWICK, N. J.

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Observations on the Rare Earths. LXII.[1] Some Observations on Solutions of Certain Rare Earth Metal Salts in Basic Solvents

BY THERALD MOELLER AND PAUL A. ZIMMERMAN

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In investigations preliminary to the study of the electrolysis of rare earth metal salts in anhydrous basic solvents, it was found that certain of these anhydrous salts are moderately soluble in both ethylenediamine and monoethanolamine but only slightly soluble in morpholine. General solubility decreases were found in the order acetates, nitrates, iodides, bromides. Monoethanolamine was found by conductance studies to be superior to ethylenediamine as an ionizing solvent for weak electrolytes, but for stronger electrolytes, particularly in dilute solution, ethylenediamine was found to be superior. Morpholine was shown to be a poor electrolytic solvent for all compounds studied. In general, rare earth metal acetates were found to be weak electrolytes, whereas nitrates, bromides and iodides were fairly strong electrolytes.

Introduction

The electrodeposition of the rare earth metals is successfully effected by use of fused salts, *e.g.*, chloride mixtures, but the possibilities of lower temperature depositions from electrolytic solutions are intriguing. Inasmuch as electrolytic deposition from aqueous solution is precluded by preferential hydrogen discharge, except possibly when mercury cathodes are employed, such procedures must of necessity involve non-aqueous systems. Reported studies on such non-aqueous systems have been singularly unproductive, except for the preparation of amalgams.

Thus, comprehensive investigations carried out a number of years ago in this Laboratory gave negative results for a variety of solvents with all cathodes except mercury.[2,3] With mercury cathodes, contrary to the earlier observations of Kettembeil,[4] amalgams were obtained upon electrolyses of solutions of the anhydrous chlorides in absolute ethanol.[3,5–7] These were then decomposed thermally to the metals. Deposition of thorium and lanthanum as carbonaceous complexes from a variety of alcohols and pyridine has been reported,[8] as has both the deposition of comparable cerium compounds from certain alcohols and the deposition of elemental cerium from isoamyl alcohol.[9] These reports lack confirmation. Other scattered literature reports are equally negative.

The highly electropositive natures of the rare earth metals and the consequent difficulty of complete reduction of their derived cations suggest that if the metals are to be electrodeposited at all, the greatest success should be achieved using highly basic solvents. Such solvents, because of their strong donor characters, provide media in which solvated electrons can readily exist and in which lower oxidation states are strongly stabilized. This is particularly well exemplified by liquid ammonia, where the stabilities of active metals such as sodium, potassium, barium, *etc.*, have been long recognized, and it should be noted among a variety of amines.

It seems reasonable, therefore, that given a strongly basic solvent of suitably high dielectric constant and sufficiently low viscosity in which ionic rare earth metal compounds dissolve without excessive solvolysis, one might successfully electrodeposit these metals. Although ammonia seems a logical choice, its reactivity with anhydrous rare earth metal compounds to give solvolysis products of limited solubilities[3] precludes its use. Certain of the amines offer possibilities. Of the amines, ethylenediamine was suggested by Putnam and Kobe[10] as combining best the properties desired of a good solvent for a variety of inorganic salts, but it also functioned as a medium from which active metals such as sodium[10,11] could be deposited. It is of interest also that anhydrous monoethanolamine also has been reported as an electrolytic solvent from which metals such as magnesium and aluminum could be deposited.[12]

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[1] For the preceding communication in this series, see T. Moeller and N. Fogel, THIS JOURNAL, **73**, 4481 (1951).

[2] L. F. Audrieth and H. W. Nelson, *Chem. Revs.*, **8**, 335 (1931).

[3] B. S. Hopkins and L. F. Audrieth, *Trans. Electrochem. Soc.*, **66**, 135 (1934).

[4] W. Kettembeil, *Z. anorg. Chem.*, **38**, 213 (1904).

[5] L. F. Audrieth, E. E. Jukkola and R. E. Meints with B. S. Hopkins, THIS JOURNAL, **53**, 1805 (1931).

[6] R. E. Meints, B. S. Hopkins and L. F. Audrieth, *Z. anorg. allgem. Chem.*, **211**, 238 (1933).

[7] E. E. Jukkola with L. F. Audrieth and B. S. Hopkins, THIS JOURNAL, **56**, 303 (1934).

[8] I. A. Ananasiu and M. Babor, *Bul. chim. Soc. Romani chim.*, **38**, 83 (1935–36).

[9] I. A. Ananasiu and M. Babor, *ibid.*, **37**, 67 (1934).

[10] G. L. Putnam and K. A. Kobe, *Trans. Electrochem. Soc.*, **74**, 609 (1938).

[11] N. P. Fedot'ev and R. N. Kinkul'skaya, "Proc. 1st All-Union (U.S.S.R) Conf. Non-Aqueous Solns.," 1935, 114.

[12] T. P. Dirske and H. T. Briscoe, *Metal Ind.*, **36**, 284 (1938).