[CONTRIBUTION FROM THE OAK RIDGE NATIONAL LABORATORY, CHEMISTRY DIVISION]

Hydrolytic Behavior of Metal Ions. VIII. Ultracentrifugation of Bismuth(III) in Perchlorate Solution[1,2]

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Equilibrium ultracentrifugations of bismuth(III) perchlorate solutions were carried out as a function of acidity, of supporting electrolyte ($NaClO_4$) concentration and of bismuth concentration. Over a range of acidity (*ca.* 0.01 to 0.1 M H_3O^+) where bismuth is considerably hydrolyzed (hydroxyl number n = *ca.* 2) a monodisperse hydrolytic polymer of degree of polymerization N = 5 or 6 was found. This polymer appears to be appreciably complexed by perchlorate ions.

Early investigators[3] of the hydrolysis of bismuth in aqueous solutions tended to describe their results in terms of the monomeric ions $Bi(OH)^{++}$ and BiO^+. More recently evidence has been proposed for the existence of hydrolytic polymers[4,5] even in the early stages of hydrolysis.

Granér and Sillén[6] investigated the hydrolytic equilibria in bismuth–perchlorate solutions by potentiometric methods in which both the hydrogen and bismuth ion concentrations were measured. They found reproducible and steady potentials, which indicated that the system is reversible and amenable to interpretation by equilibrium considerations. Their results showed that the unhydrolyzed ion Bi^{+3} is predominant in solutions of acidity greater than *ca.* 0.5 M. Below this acidity, hydrolysis dependent upon bismuth concentration was found. They interpreted their results in terms of the successive formation of polymeric particles of the general formula $Bi_NO_{N-1}^{+N+2}$, with the average degree of polymerization N (the number of bismuth atoms per polymer particle) rapidly increasing with Bi(III) concentration and *p*H.[7]

Souchay and Peschanski[8] investigated bismuth–perchlorate solutions by a photographic ultraviolet light absorption technique under conditions similar to those of Granér and Sillén. They interpreted their data using only the equilibrium

$$NBi^{+3} + NH_2O \rightleftharpoons (BiO)_N^{+N} + 2NH^+ \quad (1)$$

They stated they could not experimentally distinguish between the degrees of polymerization N of 4, 5 or 6, but preferred $N = 4$.

Swinehart and Garrett[9] described the solubility of $BiONO_3$ in dilute HNO_3 solutions on the basis of an equilibrium between solid $BiONO_3$ and unhydrolyzed Bi^{+3} even at acidities where other investigators found appreciable hydrolysis of the ions in solution. This interpretation is not necessarily inconsistent with that of the other workers, since Swinehart and Garrett worked in a different medium and at lower Bi(III) concentrations.

Procedures have been outlined recently for the determination of molecular weights in charged systems by equilibrium ultracentrifugation.[2a,10,11] This technique has been applied here in an attempt to resolve the divergent opinions regarding Bi(III) hydrolysis.

Experimental

Equilibrium ultracentrifugations were carried out, as previously described,[12] in a Specialized Instrument Corporation Model E ultracentrifuge using a Philpot–Svensson optical system. A quantity Z proportional to the gradient of the refractive index with radius of rotation x is measured for two runs: a "polymer run" containing both bismuth and supporting electrolyte and a "background run" containing only supporting electrolyte. The difference between these values of Z is designated by Z^* and measured in cm. This quantity forms the basis of the interpretations.

Bismuth oxyperchlorate solutions of known acidity were prepared by dissolving bismuth oxide in a known amount of perchloric acid (*ca.* 6 M).[3a] The dissolution, often slow, was usually complete after overnight digestion at *ca.* 100°.

Sodium perchlorate was prepared by neutralizing sodium hydroxide with perchloric acid and then filtering to remove insoluble impurities. All chemicals were reagent grade and were used without further purification.

Densities of solutions containing bismuth oxyperchlorate dissolved in sodium perchlorate–perchloric acid mixtures were measured pycnometrically at 25.0° in the Bi(III) and acid concentration ranges of interest (M Bi(III) $\leqslant$ 0.1, M $HClO_4$ $\leqslant$ 0.15). Apparent molal volumes ϕ_v for the component $BiOClO_4$ were computed. It was found that ϕ_v was sufficiently independent of bismuth concentration to equate ϕ_v with the partial molal volume $\bar{V}$ with negligible error to the ultracentrifugation results. The change of $\bar{V}_{BiOClO_4}$ with $HClO_4$ concentration was similarly small. Acidities were determined (25.0°) potentiometrically using a glass-calomel electrode assembly with a vibrating reed electrometer.[13]

Results and Discussion

Granér and Sillén[6] showed that for 0.05 M Bi(III) in 3 M perchlorate, hydrolysis begins near 0.5 M H^+. The hydroxyl number n[14] rises with decreasing acidity but near 0.1 M H^+ tends to level at n = *ca.* 2. Their data were extended in this Laboratory to lower acidities with the following results for 0.05 M Bi(III) in 3 M $NaClO_4$: 0.025 M H^+, $n = 2.01 \pm 0.02$; 0.050 M H^+, n =

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[1] This document is based on work performed for the U. S. Atomic Energy Commission at the Oak Ridge National Laboratory.

[2] Previous papers: (a) VI, J. S. Johnson and K. A. Kraus, THIS JOURNAL, **78**, 3937 (1956); (b) VII, K. A. Kraus, "Hydrolytic Behavior of the Heavy Elements," Proceedings of the International Conference on the Peaceful Uses of Atomic Energy, Vol. 7, p. 245, Session 10B.1, P/731, United Nations (1956).

[3] See, for example, (a) D. F. Smith, THIS JOURNAL, **45**, 360 (1923); (b) E. H. Swift, *ibid.*, **45**, 371 (1923).

[4] A. Holmqvist, *Svensk Kem. Tidskr.*, **48**, 106 (1936).

[5] M. Prytz and P. Nagel, *Z. anorg. allgem. Chem.*, **227**, 65 (1936).

[6] F. Granér and L. G. Sillén, *Acta Chem. Scand.*, **1**, 631 (1947).

[7] See also (a) L. G. Sillén, *ibid.*, **8**, 299, 318 (1954); (b) S. Hietanen and L. G. Sillén, *ibid.*, **8**, 1607 (1954).

[8] P. Souchay and D. Peschanski, *Bull. soc. chim. France*, **15**, 439 (1948).

[9] D. F. Swinehart and A. B. Garrett, THIS JOURNAL, **73**, 507 (1951).

[10] J. S. Johnson, K. A. Kraus and G. Scatchard, *J. Phys. Chem.*, **58**, 1034 (1954).

[11] J. S. Johnson, K. A. Kraus and R. W. Holmberg, THIS JOURNAL, **78**, 26 (1956).

[12] J. S. Johnson, K. A. Kraus and T. F. Young, *ibid.*, **76**, 1436 (1954).

[13] K. A. Kraus, R. W. Holmberg and C. J. Borkowski, *Anal. Chem.*, **22**, 341 (1950).

[14] n is defined as the average number of hydroxides per metal ion. For its computation from measured acidities, see *e.g.*, K. A. Kraus and R. W. Holmberg, *J. Phys. Chem.*, **58**, 325 (1954).

1.99; 0.101 M H^+, $n = 1.95$. For 0.05 M Bi(III) in 1 M $NaClO_4$: 0.025 M H^+, $n = 2.00$. The lack of dependence of n on acidity over a considerable acid range strongly suggests the existence of hydrolytic species of the general formula $(BiO)_N^{+N}$ at low acidities, though the formula $Bi_NO_{N-1}^{+N+2}$—with N large—as proposed by Granér and Sillén[6] is also consistent.

Ultracentrifugations were carried out under a variety of conditions of bismuth concentration, supporting electrolyte concentration and acidity (see Table I). In most experiments the acidity was such as to correspond to hydroxyl numbers n of *ca.* 2.0; the main exception was expt. 16 where n was *ca.* 1.6. One run was made at low temperature (0.8°); all others were near room temperature. Although centrifugation equilibrium was attained in approximately 3 days, the centrifugations usually were continued for 2 or 3 days longer.

TABLE I

ULTRACENTRIFUGATION OF BISMUTH(III) IN PERCHLORATE SOLUTION

Expt. no. and conditions[a]		Initial molarities					
		$BiOClO_4$	$NaClO_4$	$HClO_4$[b]	S_e[c]	α_e	Temp., °C.
1[d]	C-3	0.020	1.00	0.010	0.101	8.6	30.4
2[d]	C-3	.050	1.00	.025	.092	7.9	30.4
3	B-2	.050	1.00	.100	.093	7.9	26.9
4a	B-2	.050	1.00	.100	.091	7.7	26.5
4b	B-2	.050	1.00	.100	.096	7.5	0.8
5[d]	E-1	.070	1.00	.036	.080	7.6	26.7
6	B-3	.100	1.00	.050	.085	7.3	31.4
7	A-4	.0063[e]	3.00	.006[e]	.145	7.5	29.9
8	A-4	.026	2.97	.013	.157	8.1	30.1
9	B-2	.025	2.99	.050	.086	7.3	28.4
10[d]	E-1	.050	2.99	.025	.081	7.7	26.7
11	B-4	.050	3.00	.025	.144	7.4	28.7
12[d]	D-1	.050	3.00	.067	.082	7.9	28.1
13	B-2	.048	2.97	.083	.088	7.4	27.9
14	B-2	.050	3.00	.087	.090	7.6	26.4
15[d]	D-1	.050	3.00	.140	.076	7.3	28.1
16	B-4	.050	2.77	.180	.130	6.8	33.2

[a] Bar Angle: A, 35°; B, 45°; C, 50°; D, 55°; E, 60°. Approximate speed of rotation (r.p.m.): 1, 16,930; 2, 17,960; 3, 18,030; 4, 23,130. [b] Molarity of $HClO_4$ in excess of the component $BiOClO_4$. For all solutions n = *ca.* 2; hence the stoichiometric $HClO_4$ concentration is approximately equal to the hydrogen ion concentration. [c] The listed values of S_e were used to compute Fig. 1. [d] Experiments carried out in cells with 30 mm. light path; all others in 12 mm. cells. [e] Initial Bi(III) concentration 0.025 M. Most of Bi(III) precipitated during run. It is assumed that the $HClO_4$ concentration did not change as a result of the precipitation. Remaining Bi(III) concentration determined polarographically.

Graphs of log Z^*/x *vs.* x^2 were made for all experiments. In all cases, approximately straight lines were obtained; *i.e.*, $S_e = d \ln (Z^*/x)/d(x^2)$ is nearly independent of x^2, suggesting that the systems are monodisperse.[15] This behavior is demonstrated in Fig. 1 in which the experimental data are presented as deviation functions (log (Z^*/x) − $S_e x^2/2.303$) plotted against x^2. The average slopes S_e listed in Table I were used to compute these functions.

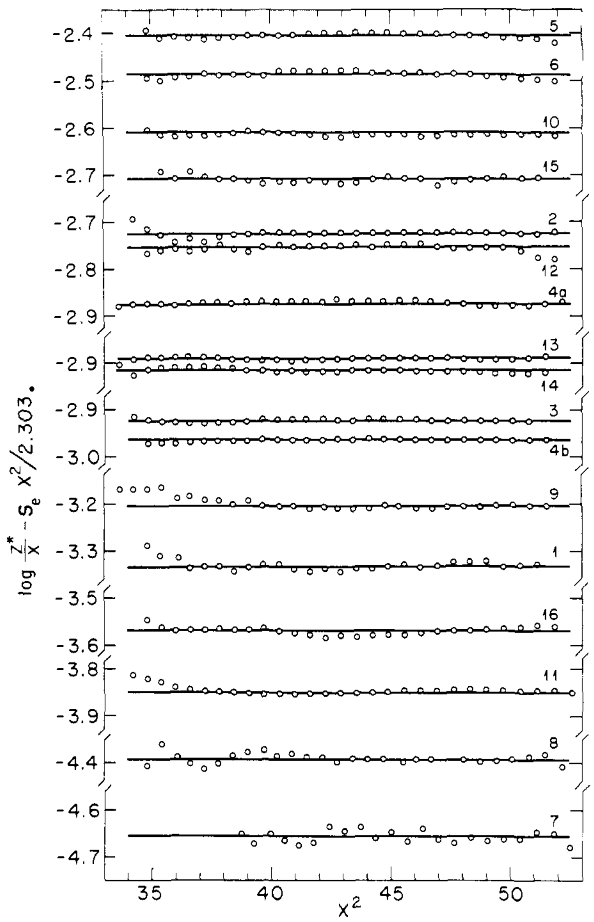

Fig. 1.—Test of constancy of S_e (experiment numbers indicated refer to conditions listed in Table I).

Table I also includes values of $\alpha_e = 10^6 S_eT/\omega^2$; *i.e.*, values of the slope S_e adjusted so that experiments performed at different angular velocities ω and temperatures T are comparable. Over the entire range of conditions investigated α_e averaged 7.6 with a maximum deviation of 13%. Such constancy suggests monodispersity. At constant $NaClO_4$ concentration, α_e decreases somewhat with Bi(III) concentration (expt. 1–6), but this is expected for a charged monodisperse system (see eq. 2). An increase in α_e would be expected for a polydisperse system with concentration dependent degree of polymerization.[11] No appreciable dependence of α_e on temperature (expt. 4a and 4b) or angular velocity (expt. 10 and 11) was found. Experiments 10 to 16 were carried out at the same bismuth and sodium perchlorate concentrations but at different acidities (M $HClO_4$ from 0.025 to 0.18). With the exception of expt. 16, the values of α_e fall in a narrow range and show no trend with acidity. In expt. 16 the acidity was highest of the series and for it the hydroxyl number $n = 1.6$ (interpolated from the data of Granér and Sillén)[6] is significantly below the value of *ca.* 2.0 applicable to the others. Hence, for this experiment, a lower degree of polymerization might

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[15] The term "monodisperse" will be used here to imply that the polymeric component occurs principally in the form of a species with a definite degree of polymerization. In general, however, the method is not sufficiently sensitive to permit unambiguous exclusion of small concentrations of other polymeric aggregates, particularly with similar degrees of polymerization.

reasonably be expected. In expt. 7, most of the bismuth precipitated during centrifugation. It is interesting to note that α_e was about the same for this experiment as for the others, though the final concentration of Bi(III) was much lower.

The distribution of a polymeric electrolyte PX_z in a centrifugal field depends upon the charge of its ions as well as its molecular weight. These quantities may be determined from centrifugations in the presence of a supporting electrolyte BX for systems for which species activity coefficients, specific refractive index increments, partial specific volumes $\bar{v}$, solution density ρ, weight average degree of polymerization N or N_w and charge of the polymeric ion z may be assumed constant.[2a,10,11] For purposes of computation the polymer component (component 2) is defined as $PX_z - (z/2)$ BX and is considered to be made up of N or N_w monomer units, each containing one metal atom (N_w is a weight average for a polydisperse system).

We have assigned the formula $BiOClO_4-(z'/2)NaClO_4$ to the monomer unit where z' is the charge per monomer unit. This is equivalent to the assumption that the polymeric ion, except for complexing by ClO_4^- ions, has the formula $(BiO)_N^{+N}$. Since most of the experiments were carried out at a hydroxyl number n = *ca.* 2, such an assignment appears justified. Small deviations in the degree of hydrolysis would not significantly affect the calculated values of N.[11]

The values of α_e may be used to estimate the degree of polymerization N and the charge per monomer unit $z' = z/N$ with the equation[11]

$$\frac{1}{\sqrt{\alpha_e}} = \frac{1}{\sqrt{\alpha_{e0}}} + \frac{Nz'^2}{2\sqrt{\alpha_{e0}}}\frac{c_2'}{c_3} \qquad (2)$$

where c_2' is the concentration of component 2 expressed as monomer ($c_2' = c_{Bi(III)}$), c_3 is the concentration of the supporting electrolyte BX (component 3) and $\sqrt{\alpha_{e0}}$ is the limit of $\sqrt{\alpha_e}$ at $c_2'/c_3 = 0$. Initial concentrations c_2 and c_3 were used together with the tabulated values of α_e (Table I) since these concentrations occur at equilibrium near the center of the cells where $\mathbf{S}_e$ and hence α_e apply.

In the derivation of eq. 2 the sedimentation of the supporting electrolyte is assumed negligible compared to that of the polymer. In the present work $\sigma = d \ln c_3/d(x^2)$[16] was *ca.* 3% of $S = d \ln c_2'/d(x^2)$ which is always larger than $\mathbf{S}_e$ (see eq. 6), and hence this assumption appears justified here. A plot of $1/\sqrt{\alpha_e}$ *vs.* c_2'/c_3 should give a straight line of positive slope for a charged monodisperse polymeric system. From the slope $(Nz'^2/2\sqrt{\alpha_{e0}})$ and intercept $(1/\sqrt{\alpha_{e0}})$ of such a plot, N and z' may be evaluated by a short iteration using the relations

$$N = \frac{\alpha_{e0}\omega^2}{10^6 A_2' T} \qquad (3)$$

and

$$A_2' = \frac{M_2'(1 - \bar{v}_2\rho)\omega^2}{2RT} \qquad (4)$$

M_2' is the formula weight of the monomer unit, R the gas constant and $\bar{v}_2$ the partial specific volume of the monomer unit (here $\bar{v}_2 = (\bar{V}_{BiOClO_4} - (z'/2)\bar{V}_{NaClO_4})/M_2'$). The value $\bar{V}_{BiOClO_4} = 50$ was determined in 1 M $NaClO_4$ and was assumed to hold in 3 M $NaClO_4$. Values of $\bar{V}_{NaClO_4} = 45.6$ and 48.4 for 1 M $NaClO_4$ and 3 M $NaClO_4$ solutions were taken from the literature.[17] The average values of the solution densities $\rho = 1.09$ (observed for 0.05 M $BiOClO_4$–1 M $NaClO_4$) and 1.23 (observed for 0.05 M $BiOClO_4$ – 3 M $NaClO_4$) were used for 1 M and 3 M $NaClO_4$ solutions irrespective of the bismuth concentration.

Plots of $1/\sqrt{\alpha_e}$ *vs.* c_2'/c_3 are shown in Fig. 2. The points for the 1 M $NaClO_4$ experiments fall approximately on a straight line. From the slope 0.46 and the intercept 0.33, values $N = 6.2$ and $z' = 0.67$ are obtained.

The small range of the data for the 3 M $NaClO_4$ solutions precludes an unambiguous evaluation of N and z'. A line with a slope that corresponds to the $z' = 0.67$ found for the 1 M $NaClO_4$ series has been arbitrarily drawn through the points for the experiments in 3 M $NaClO_4$. Since as much or more perchlorate complexing would be expected in 3 M $NaClO_4$, this line represents an upper limit to the expected slope. From the slope and intercept of this line $N = 5.4$ is obtained. If a lower value for z' is chosen, a lower value of N results (*e.g.*, for $z' = 0$, $N = 4.8$). The points for the 3 M $NaClO_4$ solutions are significantly higher than those for the 1 M series. The reason for this divergence is not clear, although it was also found in another system.[11] Presumably, some of the restrictions on which this method is based do not apply strictly. The assumption that species activity coefficients are constant is the most suspect.

Another method of estimating N and z' makes use of the equations (eq. 1 and 11 of reference 11)

$$N = \frac{S/A_2'}{1 - \frac{z'^2c_2'}{2A_2'c_3}(S - \sigma)} \qquad (5)$$

and

$$S - \mathbf{S}_e = \frac{\frac{z'^2c_2'}{2A_2'c_3}(S - \sigma)^2}{1 + \frac{z'^2c_2'}{2A_2'c_3}\sigma} \qquad (6)$$

These equations do not involve the assumption that σ is negligible in comparison to $S = d \ln c_2'/d(x^2)$. To evaluate N and z', S is computed from $\mathbf{S}_e$ and the other experimental quantities by eq. 6 for a series of assumed values of z'. The values of S are then substituted into eq. 5 and apparent degrees of polymerization $N_{z'}$ determined. Ideally the various curves of $N_{z'}$ *vs.* z' should cross at a point which gives both the degree of polymerization N and the charge z'. Figure 3 is such a plot, prepared for the 1 M $NaClO_4$ series. The curves cross in a rather narrow range near $N = 5.5$ and $z' = 0.6$, in good agreement with the values obtained by the method described by Fig. 2.

In the preceding paragraphs values of N and z' were obtained by computational processes in which each ultracentrifugation contributed one piece of information (*i.e.*, one average value of $\mathbf{S}_e$ per experiment). Several experiments were compared graphically (Figs. 2 and 3) to arrive at a simultaneous solution for N and z'. In principle,

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(16) Values of σ were estimated using eq. 18, reference 10.

(17) H. E. Wirth and F. N. Collier, THIS JOURNAL, **72**, 5292 (1950).

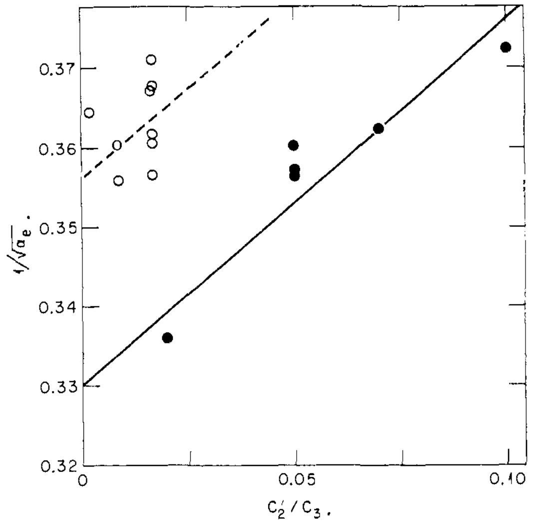

Fig. 2.—Effect of concentration variables on sedimentation: ●, 1.0 M $NaClO_4$; ○, 3.0 M $NaClO_4$.

it is possible to calculate both N and z' from a single experiment. If eq. 2 is expanded and integrated, the following equation is obtained

$$\ln c_2' = NA_2'\left(x^2 - \frac{z'^2c_2'}{2A_2'c_3}\right) + I \qquad (7)$$

where I is an integration constant. If $\ln c_2'$ is plotted against the variable $(x^2 - z'^2c_2'/2A_2'c_3)$, a straight line will be obtained if the proper charge has been chosen. The concentration c_2' can be computed as a function of the radius of rotation x by the equation[18]

$$Z^*/x\ (1 + Nz'^2/c_2'/2c_3) = kc_2' \qquad (8)$$

The constant k depends on refractive index increments in the solution and the optical constants of the ultracentrifuge. These need not be specifically evaluated, however, since the values of c_2' as a function of radius x are related to the initial concentration of that component, c_{02}' in the cell by the relation $\int c_2'x\,dx = c_{02}'\int x\,dx$.[19]

As can be seen from eq. 7 and 8, this procedure is most sensitive to the charge z' if c_2'/c_3 is large. It has been applied to the data of expt. 6 which has the highest ratio c_2'/c_3 of this investigation. The results are summarized in Fig. 4 as graphs of the deviation function $(\ln c_2' - NA_2'\ (x^2 - z'^2\ c_2'/2A_2'\ c_3))$ plotted *vs.* x^2. The deviation function has been computed for $z' = 0.0$, 0.5, 0.6 and 0.75. Least curvature remains for $z' = 0.6$, for which $N = 5.8$. The agreement with the previous methods is satisfactory.

The equilibrium ultracentrifugation results have thus established the existence of a hydrolytic polymer of Bi(III) of degree of polymerization $N = 5$ or 6, which is stable over a wide range of acidities (*ca.* 0.01 to *ca.* 0.1 M $HClO_4$) and $BiOClO_4$ concentrations (*ca.* 0.01 to *ca.* 0.1 M). The charge $z' =$ *ca.* 0.6 observed is significantly below the $z' = 1.0$ predicted from the observed degree of hydrolysis $n = 2$. Thus, this polymer appears to be appreciably complexed by ClO_4^- ions.

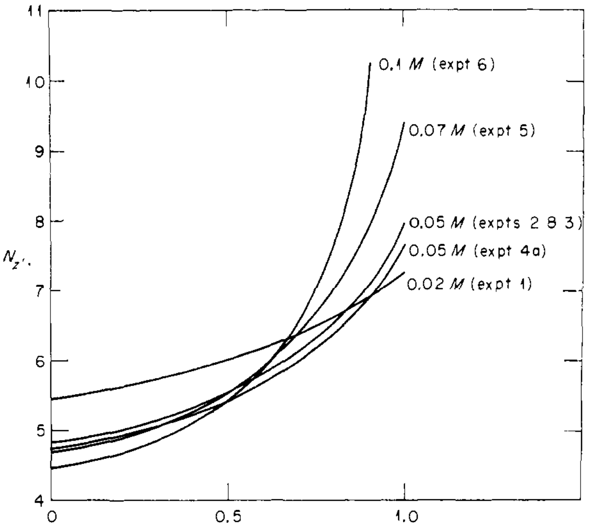

Fig. 3.—Degree of polymerization of Bi(III) computed as function of change (all solutions 1 M in $NaClO_4$; Bi(III) concentrations as indicated).

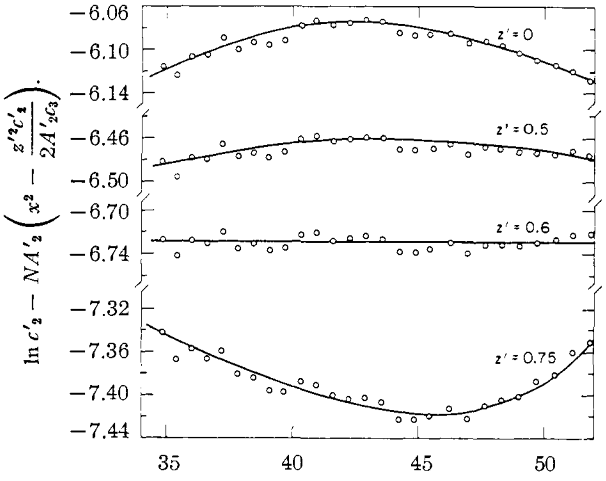

Fig. 4.—Determination of charge from a single experiment (expt 6, Table I: 1 M $NaClO_4$–0.1 M Bi(III)).

Granér and Sillén proposed that the polymers which exist in Bi(III)-perchlorate solutions are fragments of Bi–O sheets commonly found in a large number of bismuth oxy-salts, including BiOCl. This hypothesis presumably was introduced to account for the polydisperse distribution of bismuth species which they believed to exist. We have been informed recently by Professor Sillén[20] that a re-examination of the hydrolytic properties of bismuth is under way at his laboratory by the same techniques used previously. Their present work covers a much broader range of acidity and bismuth concentration than the work of Granér and Sillén and, according to Professor Sillén, the existence of a hexamer is now indicated, in substantial agreement with our ultracentrifugation results.

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(18) This equation is derived from eq. 20, reference 10, by replacing molalities (m) with molarities (c) and by assuming that dc_2'/xdx is proportional to Z^*/x.

(19) T. Svedberg and K. O. Peterson, "The Ultracentrifuge," The Oxford University Press, Oxford, England, 1940, p. 312.

(20) L. G. Sillén, private communication.

Thus, the postulate that the bismuth polymer is a fragment of the bismuth–oxygen sheets no longer seems tenable, since it does not offer an easy mechanism by which a discrete polymer could be stabilized. The stability of a "hexamer" (or pentamer) over a wide range of conditions implies that it has a unique, presumably closed, structure and further aggregation cannot occur without a large change in free energy. It is unfortunate that the structure of bismuth oxyperchlorate is not known. One might expect the structure of this salt to be related to the structure of the polymeric ion in perchlorate solutions. These structures presumably would differ from the layer lattices found for the bismuth oxyhalides.

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[CONTRIBUTION FROM THE GRASSELLI CHEMICALS DEPARTMENT, E. I. DU PONT DE NEMOURS & CO., INC.]

Magnesium Polymetaphosphate

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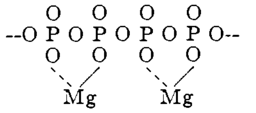
Hydrated magnesium polymetaphosphate prepared from non-cross-linked potassium polymetaphosphate is a viscous water-immiscible liquid which appears to be a coacervate. Since the hydrated polymer is a fluid rather than a gel, it is presumably not cross-linked; the divalent magnesium ions may therefore be chelated along the metaphosphate chain rather than bridged between chains. Upon being dried at 110° to the composition $[Mg(PO_3)_2 \cdot 2H_2O]_n$, the composition reverted to a brittle, white, opaque solid which is probably crosslinked by coördination of magnesium ions with the oxygen ions of adjacent polymetaphosphate chains.

It is the purpose of this paper to call attention to the unusual behavior of hydrated magnesium polymetaphosphate. When formed in aqueous solution, this inorganic polymer separates as a heavy viscous water-immiscible liquid containing about 60% water and 40% $[(Mg(PO_3)_2)_n]$. This liquid phase appears to be a coacervate. H. G. Bungenberg de Jong[1] has pointed out that coacervation, or the precipitation of a second liquid phase, is a behavior which is typical of linear macromolecular colloids of the highly viscous type.

It is postulated that the magnesium ions are firmly bound to the polymetaphosphate chains by chelation



$$\begin{array}{ccccccccc} & O & & O & & O & & O & \\ \text{--}O & P & O & P & O & P & O & P & O\text{--} \\ & O & & O & & O & & O & \\ & & Mg & & & & Mg & & \end{array}$$

thus producing an essentially non-ionic linear polymer. Such molecules probably tend to coil up and also to associate with each other and, as stated by Bungenberg de Jong, "in the coacervate there are mutually associated macromolecules which penetrate each other at any rate with their peripheral loops." The amount of water in the coacervate, 15 molecules per $Mg(PO_3)_2$ unit, is probably about sufficient to complete the coördination sphere of the magnesium and to form a single hydrogen-bonded layer of water molecules about the polymer chain. The tendency of a hydrophilic colloid particle to bind water at least to the extent of a monomolecular layer has been pointed out recently by Dalton and Iler.[2] The coacervate phase of magnesium polymetaphosphate may therefore be pictured as a tangled skein of thread-like hydrated magnesium polymetaphosphate molecules.

Pure hydrated magnesium polymetaphosphate has not been described previously in the literature. The fact that alkali metal polymetaphosphates are precipitated when calcium or barium salts are added in sufficient quantity to be equivalent to about two-thirds of the alkali metal ion content, has been pointed out by Karbe and Jander.[3] Precipitation of alkali metal polymetaphosphate by magnesium and other divalent ions as gummy or oily precipitates is described by Thilo, Schulz and Wichmann.[4]

Experimental

Magnesium chloride will precipitate the corresponding polymetaphosphate from a solution of KPO_3 when a stoichiometric quantity of the salt is added. When a non-cross-linked KPO_3[5] is used, this initial rubbery precipitate, which still contains some alkali metal ions, can be dissolved by stirring in cold water. Since more than half of the cations in this product are divalent, yet the polymer is not cross-linked since it is still water soluble, it is concluded that the divalent ions must be chelated to the polymer chains. The introduction of a small amount of a trivalent cation such as aluminum, gives a rubbery, insoluble, obviously cross-linked product. An insoluble product also is obtained from KPO_3 which is cross-linked through a deficiency of K in the melt.

If the above redissolved magnesium–sodium–potassium polymetaphosphate is again precipitated with an excess of magnesium salt, the product is at first a rubbery mass, having the mechanical characteristics of a partially cross-linked gel. It is possible that as the last of the sodium and potassium ions are removed, adjacent metaphosphate units may not be available for chelation, so that the magnesium ions then cause cross-linking. However, the fresh precipitate, which resembles art gum, becomes less rigid after a few hours and is transformed into a very viscous taffy-like mass which can be pulled out into thin threads and is thus apparently no longer cross-linked. It is postulated that there is a rearranging of the chelate groups to permit the magnesium ions, which are initially present as cross-links between adjacent chains, to migrate to suitable positions for chelation. This seems reasonable, since it might be expected that the chelate structure would be the more stable arrangement. The stability of the magnesium

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