nitrile. Current investigation[18] in this Laboratory shows that when cations are added to these two nitriles new C≡N peaks appear in the 2240–2275 cm.$^{-1}$ infrared region. The $\Delta\nu$ values of the new C≡N peaks from that for the pure nitriles are larger for benzonitrile than acetonitrile which indicates that benzonitrile interacts more strongly with cations than does acetonitrile. Therefore, benzonitrile must be more basic than acetonitrile. The work of French and Roe[19] on the ionization of picric acid in acetonitrile and benzonitrile also indicates a greater availability of electrons (basicity) in benzonitrile. One can only conclude then that metal ions are more strongly solvated by benzonitrile than acetonitrile. The less negative values of the half-wave potentials for the reduction of metal ions in benzonitrile as compared to acetonitrile cannot, therefore, be explained on the basis of lower solvation energies arising from the less basic character of benzonitrile.

A plausible explanation for the ease of reduction of cations in benzonitrile consistent with the foregoing information is that the electrode process involves benzonitrile molecules constituting the solvation sphere serving as bridges for electron transfer.[20,21] Since acetonitrile and benzonitrile contain the C≡N group, the difference obviously is due to the contribution of the delocalized electrons of the phenyl ring in benzonitrile. The ease of reduction may also be in part the result of the fact that the dielectric constant of benzonitrile (25) is lower than that of acetonitrile (36).

Benzonitrile containing tetraethylammonium perchlorate does not exhibit a new C≡N peak in the infrared—an indication that the weak charge density around this large ion is insufficient to bring about an interaction with the benzonitrile molecule. The more negative half-wave potentials of metal ions with lithium, sodium, or magnesium perchlorate as supporting electrolyte are probably the result of these ions interacting with benzonitrile or acetonitrile and thereby decreasing the ability of the nitrile to function as an electron sink in the bridge mechanism.

It appears from the results of this investigation that the less negative values of the half-wave potentials of metal ions in acetonitrile and benzonitrile as compared to those in water are not the result solely of the lower solvation energies arising from the less basic character of the nitriles but also of a bridge mechanism involving the nitriles.

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[18] Unpublished results.

[19] C. M. French and I. G. Roe, *Trans. Faraday Soc.*, **49**, 314 (1953); *ibid.*, **49**, 791 (1953).

[20] E. H. Lyons, Jr., *J. Electrochem. Soc.*, **101**, 376 (1954).

[21] J. T. Funkhouser, Ph.D. Thesis, Massachusetts Institute of Technology, 1953.

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Studies on Hydrolyzed Bismuth(III) Solutions. II. Light Scattering[1]

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The polymerization of the aquo-bismuth(III) ion has been investigated by light scattering measurements at 25°. In solutions where *ca.* 2 hydroxide ions are bound, on the average, per bismuth atom, the degree of polymerization was found to be 5.6. $NaClO_4$ was used as a supporting electrolyte to give $[Na^+] + [H^+] = 1.000\ M$. The value of the charge on the complex, *ca.* 4, indicates that some binding of gegenions from the solution occurs; the predominant complex, therefore, has the approximate formula $Bi_6O_6(ClO_4)_2{}^{+4}$. Measurements of the apparent molar refraction and apparent molar volumes of hydrolyzed and unhydrolyzed bismuth solutions show that both the molar refraction and molar volume of the bismuth-containing cation increase slightly as a result of the hydrolysis. The absence of depolarization suggests that the complex has a symmetrical rather than a chain structure.

Introduction

In a previous communication,[3] equations were derived relating the turbidity of solutions containing polynuclear complexes and supporting electrolyte to the charge and degree of polymerization of the complexes. These relations were tested with certain idealized systems similar to those used by Johnson, Kraus and Scatchard[4] in testing equations derived for the interpretation of sedimentation equilibrium experiments in an ultracentrifuge with a Schlieren optical system. These idealized systems were chosen to represent conditions found in systems with polymerized aquo-acids and bases.

In order to test further the relations describing the scattering of highly charged, low molecular weight species in the presence of supporting electrolyte, it was decided to study the light scattering of highly hydrolyzed bismuth(III) solutions. This system has been investigated by Holmberg, Kraus and Johnson[5] using sedimentation equilibrium measurements in the centrifuge with Schlieren optics. These experiments indicated that there were 5 or 6 bismuth atoms in the predominant complex present in solutions with *ca.* 2 hydroxide ions bound per bismuth atom. Some complexing

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[3] R. S. Tobias and S. Y. Tyree, Jr., THIS JOURNAL, **81**, 6385 (1959).

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

[5] R. W. Holmberg, K. A. Kraus and J. S. Johnson, THIS JOURNAL, **78**, 5506 (1956).

of the polymeric cation by ClO_4^- was indicated, resulting in about a 30% reduction in its charge from the maximum value. Olin,[6] using an e.m.f. titration technique, has proposed that the predominant complex in these solutions is $Bi_6O_6^{+6}$. Particularly careful measurements were made using bismuth amalgam electrodes, since it is generally difficult to determine the complexes formed at such high degrees of polymerization using e.m.f. methods. The equilibrium constant was determined in the constant ionic medium with $[ClO_4^-] = 3\ M$, and therefore no determination could be made of the degree of hydration or of complexing of the polynuclear species by perchlorate ion. The data for the hydrolysis of Bi^{+3} in solutions with $[ClO_4^-] = 1\ M$ in the range with $0 \leqslant \bar{Z} \leqslant 2.00$, where $\bar{Z}$ is the average number of hydroxide ions bound per bismuth atom, could also be fitted by assuming the single complex $Bi_6O_6^{+6}$ to be present.[7,8] Earlier studies on the hydrolysis of Bi^{+3} have been reviewed in the previous communication in this series.[7]

At the completion of this research, a new report on the equilibrium ultracentrifugation of hydrolyzed Bi(III) solutions was published.[9] In this work, the centrifuge was fitted with an interference optical system in place of the Schlieren scanning system, and the precision of the measurements was considerably improved. The results indicated that there are 6 bismuth atoms in the complex and that the complex appears to bind about 2 ClO_4^-. It should be noted that the treatment of light scattering and sedimentation equilibrium data is rather closely related, since both experiments share a common thermodynamic basis and both involve the simultaneous determination of the charge and degree of aggregation of the complex.

Since the turbidity of hydrolyzed bismuth(III) solutions with approximately 2 OH^- bound per bismuth atom should be similar to the values assumed in the calculations with idealized systems,[3] the bismuth system seemed to be an ideal one with which to test the scattering relations.

Maximum Charge and Distribution of the Polymeric Species.—The assumptions of constant charge of the polymeric species and constant composition of the system are inherent in the relations derived for the determination of the charge and the degree of polymerization. The maximum average charge per mole of monomer (per monomole) may be determined in the usual way by e.m.f. titrations. When $\bar{Z} = (h - H)/B$[10] = the number of protons lost per bismuth atom, the hydrolyzed solute has the general formula $[Bi(OH)_{\bar{Z}}(ClO_4)_{\bar{\nu}}^{(3-\bar{Z}-\bar{\nu})} + (ClO_4)_{(3-\bar{Z}-\bar{\nu})}]_N$. The average maximum charge per monomer unit, $(3 - \bar{Z})$, will in general be somewhat larger than the actual charge per monomer unit because of the binding of $\bar{\nu}$ ClO_4^-. So long as the gegenion concentration remains constant, the degree of complexing will be constant at constant $\bar{Z}$.

The problem of maintaining the system with a constant distribution of the total acid, B, among all species is somewhat less simply achieved. In the case of a species which undergoes no polymerization or depolymerization over a wide range of concentrations (*e.g.*, silicotungstic acid, a tetrabasic acid) measurements at constant *p*H correspond to measurements at constant average ligand number $\bar{n}$.[11] Since the degree of formation of the n^{th} species $\alpha_n = [AH_n]/B$ is a function of *p*H alone, measurements at constant *p*H and hence $\bar{n}$ correspond to measurements at a constant distribution of the total acid irrespective of the total acid concentration *B*. The light scattering of silicotungstic acid has been studied under these conditions.[12]

With an aquo-acid like $Bi(OH_2)_n^{+3}$, the case is further complicated by the polymerization which the hydrolyzed Bi(III) monomer undergoes. For this system, $\bar{Z}$ has been observed to be a function of both the *p*H and the total bismuth concentration *B*.[7] Dilution of a polymerized Bi(III) solution at constant *p*H could, therefore, result in a slow depolymerization. It has been observed for the hydrolysis of bismuth,[7] that $\bar{Z}$ can be described in terms of a single variable $X = \log B - t \log h$.[13] Since the bismuth system appears to consist of one polymeric species, the degree of formation is $\alpha_n = \bar{Z}(n + 1)/nt$ so that measurements at constant $\bar{Z}$ and X correspond to a constant distribution of bismuth between Bi^{+3} and polymer. For this system, t has the value 2.4.

In the Bi(III) system, the curves $\bar{Z}(\log h)_B$ all approach the value $Z = 2$ asymptotically at high *p*H.[7] If measurements could be made at sufficiently high *p*H, *i.e.*, where $Z = 2.00$ for the most dilute solution employed, α_n would be independent of B and h; however, the low solubility of the hydrolyzed bismuth species at high *p*H requires that the measurements be made at slightly lower values of Z when $B > 25$ m*M*. Since the light scattering measurements involve the determination of the turbidity of solutions over a fairly wide range of bismuth concentrations, the solutions should be prepared to have constant X rather than constant *p*H to avoid any depolymerization in the dilute solutions on standing. Since sedimentation equilibrium in an ultracentrifuge is attained only after several days, it was felt that the light scattering study would afford a check on the significance of any depolymerization occurring during the attainment of equilibrium.

Experimental

Bismuth and $NaClO_4$ Solutions.—The preparation and analysis of the reagents used to prepare the Bi(III) solutions

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[6] Å. Olin, *Acta Chem. Scand.*, **11**, 1445 (1957).

[7] R. S. Tobias, THIS JOURNAL, **82**, 1070 (1960), Part I.

[8] Throughout this paper, the bismuth hexamer with $\bar{Z} = 2$ will be written in the anhydrous form, $Bi_6O_6^{+6}$, since no information exists as to the degree of hydration of the complex.

[9] J. S. Johnson, G. Scatchard and K. A. Kraus, *J. Phys. Chem.*, **63**, 787 (1959).

[10] $\bar{Z}$ is the average ligand number, h is the equilibrium $[H^+]$, H is the analytical hydrogen ion concentration and B is the total bismuth concentration. See ref. 7 for a discussion of the determination of the function $\bar{Z}(\log h)_B$. $\bar{Z}$ is used here in place of the more common Z to avoid confusion with the charge Z' determined by light scattering.

[11] $\bar{n}$ is used for the average ligand number in systems with only mononuclear complexes, since this function has somewhat different properties from $\bar{Z}$.

[12] M. J. Kronman and S. N. Timasheff, *J. Phys. Chem.*, **63**, 629 (1959).

[13] Experimentally t is given by $(d \log B/d \log h)_{\bar{Z}}$ and is related to the number of OH^- in the polymeric species $M[M(OH)_t]_n$ by the relationship OH^- bound $= nt$.

have been described earlier.[7] The solutions for the light scattering measurements were prepared by the addition of the calculated amounts of $NaHCO_3$, a Bi(III) stock solution which contained about 0.9 *M* $HClO_4$, and $NaClO_4$ solution. A strong stream of N_2 was used to dispel CO_2 from the solutions. The *p*H was adjusted to give $X = 1.500$ which corresponds to $\bar{Z} = 1.85$. For $B > 50$ millimoles/l., the e.m.f. data[7] were extrapolated to give the *p*H corresponding to $X = 1.5$. The $[Na^+] + [H^+]$ was adjusted to 1.000 *M*. At values of $X > 1.5$ a dense white precipitate was formed in the more concentrated solutions. The densities were determined pycnometrically at 25°.

Light Scattering Measurements.—Measurements of the turbidity were made with unpolarized 4358 Å. light using a modified Brice photometer.[14] The turbidity of the supporting electrolyte was approximated by the turbidity of 1.000 *M* $NaClO_4$. This was subtracted from the turbidity of the solutions to give the turbidity τ^* due to the hydrolyzed bismuth species.

The solutions were clarified by filtration through 0.45 μ Millipore filters directly into the scattering cells. A special pressure filtration apparatus was constructed entirely from glass with no ground surfaces in contact with the solutions. Each value of the turbidity represents the average of 15–20 separate determinations made on several different lots of solution. The solutions were passed from 5 to 10 times through the filters and were discarded if any trend was observed in the turbidities from filtration to filtration. The use of sintered glass filters tended to cause precipitation of very small amounts of a colloidal bismuth salt giving erratic values of the turbidity.

Measurements normally were made with matched 3 cm. cells. These were orientated with the same face normal to the light beam at all times. A cylindrical cell was used to check for any dissymmetry of scattering between 45° and 135°. The solutions were filtered until the dissymmetry was less than 1.05. The normalized scattering envelope obtained by multiplying the experimental values of the turbidity by $\sin \theta/(1 + \cos^2 \theta)$ corresponded to that of an isotropic scatterer.

The absence of fluorescence was demonstrated by the method described by Brice, Nutting and Halwer.[15] Depolarizations were determined by the method of Maron and Lou[16] and found to be negligibly small.

The photometer was calibrated using purified reagent grade benzene. Since the corrections for the change in the volume seen by the phototube and for the refraction of the scattered radiation at the solution–air interface are rather large in going from benzene to aqueous solutions, the calibration was checked using Ludox solutions. These solutions varied from 2 to 8% by weight SiO_2, and the calibration followed the method of Maron and Lou.[17] These two standards gave values of the turbidity agreeing within 2%. All measurements were made in a room maintained at 25 ± 2°.

Refractive index increments were determined at 4358 Å. with a Brice–Phoenix differential refractometer which was calibrated with sucrose solutions.

Spectrophotometric Measurements.—Measurements of the ultraviolet absorption spectra of the bismuth solutions were made at 25° using a Beckman DU spectrophotometer.

Results and Discussion

The scattering of light by ionized solutes depends on the charge as well as the molecular weight. The effect of the charge varies with the concentration of the solute and of the supporting electrolyte. For a monodisperse polymer PX_z which ionizes in solution to give P^{z+} and zX^-, two supporting electrolytes HX and BX, and a solvent, the turbidity due to PX_z is given by[3]

$$\tau^* = \frac{\varphi H''\psi_2^2}{1/m_2 + Z_2^2/2(m_3 + m_5)} \qquad (1)$$

In this equation, φ is the volume fraction of solvent, $H'' = 8000\pi^3(n + n_0)^2/3N\lambda^4$, m_2 is the molarity of the polymeric electrolyte component 2, Z_2 is its charge, m_3 and m_5 are the molarities of components 3 and 5 and $\simeq$ [HX] and [BX] and ψ_2, the refractive index increment of component, 2 is given by $dn/dm_{PX_z} - Z_2m_3/2(m_3 + m_5)\, dn/dm_3 - Z_2m_5/2(m_3 + m_5)\, dn/dm_5$. This expression for the refractive index increment of the polymeric component follows from the definition of component 2 as $PX_z - Z_2m_3/2(m_3 + m_5)\ HX - Z_2m_5/2(m_3 + m_5)\ BX$.

It is convenient to express the polymeric solute in terms of the monomer unit, *i.e.*, $[Bi(OH)_2(ClO_4)_{\bar{\nu}}{}^{(1 - \bar{\nu})+}(ClO_4)_{(1 - \bar{\nu})}]_N$, where N is the degree of polymerization, and to introduce the relations $Z' = Z_2/N = (1 - \bar{\nu})$, $M' = M_2/N$, $m' = m_2N$ and $\psi' = \psi_2/N$. Substituting these quantities into equation 1, and rearranging, we obtain

$$\frac{1}{N_{Z'}} = \frac{\varphi H''\psi'^2{}_{m'}}{\tau^*} - \frac{Z'^2m'}{2(m_3 + m_5)} \qquad (2)$$

Using equation 2, values of $1/N_{Z'}$ may be computed from the experimental data with Z' as a parameter. When the correct value of Z' is taken, $1/N$ will be independent of m'. This treatment is subject to the restrictions that Z', the component activity coefficients, and the refractive index increments are constant.

Volume, Refractive Index Increments and Extinction Coefficients.—The refractive index increment for the bismuth species was obtained by measurements on solutions with $m_{H^+} + m_{Na^+} = 1.000$ *M*. Since the concentrations of both $HClO_4$ and $NaClO_4$ were known accurately, the contribution of these species to the gross Δn values could be determined accurately. The subtraction of these contributions from the gross Δn gives the Δn due to the hydrolyzed bismuth *species*.

The refractive index increments of $NaClO_4$ were determined in the range 0.1 to 1.0 *M*. These data were fitted by the method of least squares and are described by the equation $\Delta n = 8.178 \times 10^{-3}m - 5.95 \times 10^{-4}m^{3/2}$; m = moles/liter. The refractive index increments of $HClO_4$ were independent of concentration within the experimental error in the concentration range 0.1 to 1.0 *M* and given by the expression $\Delta n = 6.339 \times 10^{-3}\ m$. The values for $dn/dm_{BiOClO_4} = 1/N\ dn/dm_{PX_z}$ are given in Table I. The values of dn/dm_{BiOClO_4} are almost independent of concentration, and an average value was used in all calculations. Thus, $\Delta n = 3.22 \times 10^{-2}m'$; the concentrations are in monomoles/liter.

The apparent molar volume of the hydrolyzed bismuth species computed as monomer, Φ_{BiOClO_4}, was determined by measurements of the density of the solutions. Corrections were applied for the contribution of the $NaClO_4$ and the $HClO_4$ using the apparent molar volumes of 1*M* $NaClO_4$ and dilute $HClO_4$ in 1 *M* $NaClO_4$ given by Wirth and Collier.[18] An average value of $\Phi_{BiOClO_4} = 34 \pm 4$ was obtained. This is considerably lower than the value reported in the literature of *ca.* 50.[5,9] This quantity cannot be obtained with great accuracy, since slight errors in the concentration of the $NaClO_4$ or $HClO_4$ greatly affect the value obtained for Φ_{BiOClO_4}.

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[14] B. A. Brice, M. Halwer and R. Speiser, *J. Opt. Soc. Am.*, **40**, 768 (1950).

[15] B. A. Brice, G. C. Nutting and M. Halwer, THIS JOURNAL, **75**, 824 (1953).

[16] S. H. Maron and R. H. L. Lou, *J. Phys. Chem.*, **59**, 231 (1955).

[17] S. H. Maron and R. H. L. Lou, *J. Polymer Sci.*, **14**, 29 (1954).

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

The volume fraction of the solvent φ was computed using the literature values of the partial molar volumes of 1.0 M $NaClO_4$ and dilute $HClO_4$ in 1 M $NaClO_4$.[18] The effect of the polymeric species on the volume fraction was negligible. In the equations derived earlier,[3] φ was assumed to be unity for all solutions. This would cause an error of *ca.* 5% in this work because of the rather high concentration of supporting electrolyte.

Since it was of interest to compare the molar refraction of the aquobismuth(III) ion with that of the hydrolyzed species, the refractive index increment of $Bi(ClO_4)_3$ in 1 M $HClO_4$ was determined, using this expression for the concentration range 0.0250 to 0.1000 M: $\Delta n = 5.504 \times 10^{-2}m - 5.59 \times 10^{-3}m^{3/2}$. The apparent molar volume of $Bi(ClO_4)_3$ was determined for the same concentration range and found to be 98 ± 1 cc. The literature[18] value for the apparent molar volume of 1.00 M $HClO_4$ was used for the calculations.

Using the data for the refractive index increments of solutions of $Bi(ClO_4)_3$ and the hydrolyzed species together with values for the refractive index of water at 25° measured at 4358 Å.[19] and the apparent molar volumes of $Bi(ClO_4)_3$ and $BiOClO_4$, the apparent molar refractions were calculated for the solvents 1M $HClO_4$ and 1M $NaClO_4$, respectively. Under these conditions, the screening effect of ClO_4^- will be constant. These were independent of concentration within the experimental error and hence equal to the molar refraction, and these values were obtained: $R_{Bi(ClO_4)_3} = 51.0$ cc./mole, $R_{BiOClO_4} = 25.2$ cc./mole. Using the value for the ionic refraction of ClO_4^- given in the literature,[20] 13.24 cc., the following ionic refractions were obtained: $R_{Bi(OH_2)_n}{}^{+3} = 11.4$ cc., $R_{Bi(OH_2)_m}{}^{+} = 12.0$ cc. Using 44.5 ml. as the apparent volume of the aqueous perchlorate ion,[21] the apparent volume of the trivalent bismuth ion is −36 cc. while the volume of the hydrolyzed species computed as monomer is −10 cc. The increases in the molar refraction and volume of the bismuth ion upon hydrolysis are primarily a result of the decrease in the strong constrictive forces exerted by Bi^{+3} on the water molecules. The increase in the molar refraction is slight because of the increase in strength of the bond between Bi^{+3} and the oxygen atoms in the two OH^-.

Values of the average molar extinction, e/B, where e is the extinction coefficient and B the total bismuth in the solutions, were determined at 2850 Å. At this wave length the molar extinction coefficient of the hydrolyzed species is *ca.* 18 times greater than that of the unhydrolyzed bismuth species. These data are listed in Table I. The constancy of e/B over a ten-fold range of concentration is indicative of a constant system composition, since depolymerization would result in a decrease in this quantity.

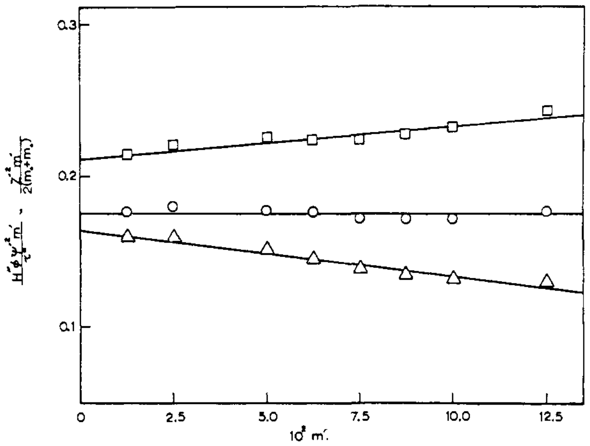

Fig. 1.—$\dfrac{H''\varphi\psi'^2m'}{\tau^*} - \dfrac{Z'^2m'}{2(m_3 + m_5)}$ as a function of m' with Z' as a parameter; concentrations in monomoles/l. The symbols refer to the values of Z': △, 1.0; ○, 0.7; □, 0.0.

Calculation of Z' and N for the Polymer.—Fig. 1 shows the deviation plot $\dfrac{H''\varphi\psi'^2m'}{\tau^*} - \dfrac{Z'^2m'}{2(m_3 + m_5)} = 1/N_{Z'}$ *versus* m', for Z' = 1.0, 0.7 and 0.0. The correct value of Z' should lead to a straight line with 0 slope. The average deviation of the points from the mean value can be used to estimate the best straight line. The deviation decreases rapidly from *ca.* ± 0.010 at Z' = 1.0 to a minimum of ±0.003 from Z' = 0.7 to 0.5 and gradually increases at lower values of Z' to ± 0.006 at Z' = 0. Since the deviation of the calculated values of $1/N_{Z'}$ from equation 2 is not symmetrical with respect to values of Z' which are greater and less than the correct value by a given amount but varies as the difference between the squares of the correct and assumed charges, it appears to be most satisfactory to select the maximum charge which is consistent with the minimum deviation in $1/N_{Z'}$. The best value of the charge is Z' = 0.65 and $N_{Z'}$ = 5.6 ± 0.1.

TABLE I

TURBIDITY, REFRACTIVE INDEX AND SPECTROPHOTOMETRIC DATA

Component 2, monomole/l.	h, M/l.	ψ' for Z' = 0 (4358 Å.)	$10^5\ \tau^*$, cm.$^{-1}$	10 e/B
0.0125	0.03819	0.0316	1.59	0.98
.0250	.05102	0322	3 06	1.00
.0500	.06806	.0325	6.00	1.03
.0625	.07469	.0329	7.52	1.14
.0750	.08060	.0320	9.08	1.00
.0870	.08572	.0324	10.4	1.01
.1000	.09084	.0318	11.8	1.05
.1250	.09970	.0319	13.9	1.01
		.0322[a]		

[a] Used in the computations.

In Fig. 2, $1/N_{Z'}$ is plotted as a function of Z' for the different values of m'. The curves should all intersect at the correct value of Z'. They appear to approach one another at about Z' = 0.65, N = 5.6.

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(19) L. W. Tilton and J. K. Taylor, *J. Research Natl. Bur. Standards*, **20**, 419 (1938).

(20) K. Fajans and R. Luhdeman, *Z. physik. Chem.*, **B29**, 150 (1935). This value was determined at the Na "D" line, and hence the dispersion is assumed to be negligible. This will not cause any appreciable error, since the molar refraction of $NaClO_4$ determined at the Na "D" line and the apparent molar refraction of 1 M $NaClO_4$ determined at 4358 Å. differ only by about 1%.

(21) K. Fajans and O. Johnson, THIS JOURNAL, **64**, 668 (1942).

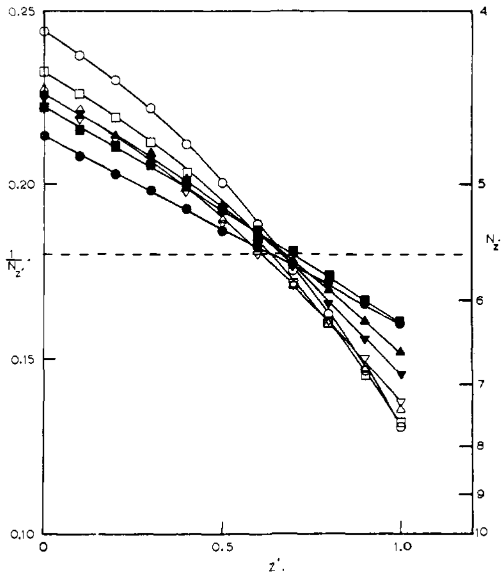

Fig. 2.—$N_{z'}$ of BiOClO$_4$ as a function of charge Z' with the concentration in monomoles/l., m' as a parameter. The symbols refer to the values of m': ●, 0.0125; ■, 0.0250; ▲, 0.0500; ▼, 0.0625; ▽, 0.0750; △, 0.0870; □, 0.1000; ○, 0.1250.

Since the measurements were performed on solutions with $\bar{Z} = 1.85$, this corresponds to *ca.* 93% conversion to a hexameric bismuth complex. Under these conditions, the weight average degree of polymerization would be 5.65. Considering the uncertainty in the effect of the small monomer concentration on the turbidity, the agreement is perhaps fortuitous; N should, at any rate, be slightly less than 6 if only a hexamer is formed. Considering the binding of gegenions, the complex has the formula $Bi_6O_6(ClO_4)_2^{+4}$.

In the calculations, the value $H'' = 8000\pi^3\cdot(n + n_0)^2/3N\lambda^4$, where n is the solution refractive index and n_0 that of the solvent, was used instead of introducing the usual approximation that $(n + n_0)^2 \simeq 4n_0^2$. The value of ψ' was computed from the relation $\psi' \simeq dn/dm_{BiOClO_4} - (Z'/2)\, dn/dm_{NaClO_4}$. The neglect of component 3, the HClO$_4$, causes at most an error of about 0.2% in ψ', since $m_3 << m_5$ and the refractive index increments of these components are about the same. The value of the sum $(m_3 + m_5)$ as a function of Z' was calculated by solution of the simultaneous equations $m_H = m_3(1 - Z'm'/2(m_3 + m_5))$ and $m_{Na} = m_5(1 - Z'm'/2\ (m_3 + m_5))$ which gives $(m_3 + m_5) = m_H + m_{Na} + Z'm'/2$.

The results obtained are in good agreement with those determined from e.m.f. measurements[6,7] which indicate that the complex $Bi_6O_6^{+6}$ (or some more hydrated form) exists in perchlorate solutions. The values of the charge and degree of aggregation $Z' = 0.65$ and $N = 5.6$ are in good agreement with the values obtained by centrifugation.[5,9]

The absence of any measurable depolarization suggests that the bismuth polymer is not a chain of bismuth atoms joined by diol bridges but some more symmetrical structure. The existence of a compact structure of high symmetry has been proposed by Holmberg, Kraus and Johnson[5] and also by Olin[6] to explain the preferred stability of the hexamer over other possible species. It should be noted, however, that some non-isotropic particles still show negligible depolarization because of the presence of negative birefringence.

General Discussion.—The determination of the degree of aggregation of low molecular weight polyelectrolytes necessitates the simultaneous determination of the charge on the species. This effect vanishes for high polymers where dn/dm_{PX_Z} is much greater than the increment of the supporting electrolyte, and hence $dn/dm_{PX_Z} \simeq dn/dm_2$. The use of a supporting electrolyte with a smaller molar refraction than NaClO$_4$, *e.g.*, LiCl or NaCl, would reduce the effect of Z' on N shown in Fig. 1. In the case of the bismuth polymer, the use of salts containing Cl^- would result in precipitation because of the low solubility of basic bismuth chlorides. The use of perchlorates is generally preferable because of the absence of strong complexing tendencies which would tend to stabilize the unhydrolyzed monomer.

The determination of the charge is rather difficult since it essentially depends on the invariance of $1/N$ over a fairly large range of m' values. This in turn requires that the values of $\beta_{22} = (\partial \ln \gamma_2/\partial m_2)$, $\beta_{23} = (\partial \ln \gamma_2/\partial m_3)$ and $\beta_{25} = (\partial \ln \gamma_2/\partial m_5)$ be negligibly small. γ_2 is the activity coefficient for the polymeric *component.* The slopes of the deviation functions in Fig. 1 could be increased by performing measurements on solutions with a higher $m'/(m_3 + m_5)$ ratio; however, this would make the assumption of the constancy of activity coefficients even less tenable. If the correct value of the charge, Z', were known *a priori*, extrapolation of the plot of $H''\varphi\psi'^2m'/\tau^*$ *versus* m' to zero concentration would insure that $\beta_{22} = 0$, since in the presence of a constant concentration of supporting electrolyte $\lim_{m' \to 0} \gamma_2 =$ a constant. It is also true, however, that at concentrations of about 0.1 M and less in a supporting electrolyte the activity coefficients of electrolytes of low valence types are essentially independent of concentration.[22,23] The charge density of the hydrolyzed bismuth cation will be rather low, so that large variations in β_{22} from zero would not be expected over the range of concentrations studied.

It was shown earlier[3] that the ideal solutes PX_Z and BX scatter independently of one another in solutions with constant [BX] up to rather high concentrations of the polymer, so that equation 2 is valid if β_{23} and β_{25} are negligibly small. These quantities are rather difficult to estimate and are essentially functions of the ionic strength for a given supporting electrolyte. The conditions of this experiment, *i.e.*, a solute with a low charge density in the presence of the 1:1 electrolyte NaClO$_4$, would be expected to reduce them to a minimum. In addition the change of activity coefficients tends to be at a minimum in NaClO$_4$ solutions of 1 to 3 M concentration.

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[22] H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," 3rd Ed., Reinhold Publishing Corp., New York, N. Y., 1958, p. 598.

[23] (a) J. N. Brønsted, *Medd. Vetenskapsakad. Nobelinst.*, **5**, No. 25 (1919); (b) J. N. Brønsted, *Trans. Faraday Soc.*, **23**, 429 (1927).

Considering the experimental errors and the uncertainties in the activity coefficients, the values for the degree of aggregation probably can be considered accurate to about ±10%. This appears to be about comparable to that obtained by measurements on sedimentation equilibria in the centrifuge with Schlieren optics.[5]

Note added in proof.—Since the completion of this work, H. A. Levy, M. D. Danford and P. A. Agron, *J. Chem. Phys.*, **31**, 1458 (1959), have published results of an X-ray diffraction study of hydrolyzed 5.81 monomolar Bi(III) solutions. The data can be explained by assuming one aggregate containing six bismuth ions which has cubic symmetry. This would explain the absence of depolarization which was noted in this work.

[Contribution from Laboratory of Photochemistry and Spectroscopy, The Weizmann Institute of Science, Rehovoth, Israel]

Temperature Dependence of Photoisomerization Equilibria. Part I. Azobenzene and the Azonaphthalenes

By Ernst Fischer

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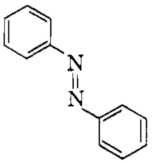
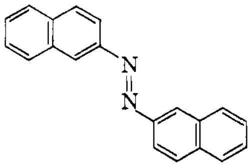
On irradiation of solutions of azobenzene or the azonaphthalenes with light at specific wave lengths, a photoequilibrium between the respective *cis* and *trans* isomers is established. It is found that, in the absence of *thermal* isomerization, cooling shifts the photoequilibrium toward the *trans* isomer to an extent depending on the nature of the compound, the solvent, and the wave length of the photoactive light. Thus photoequilibration at 365 mμ of 2,2′-azonaphthalene results in 20% *trans* at −20° and in 82% at −125°. The results indicate that the quantum yields of photoisomerization strongly depend on temperature.

Previous reports from this Laboratory[1,2] and from Zimmerman and co-workers[3] described the dependence of the *cis-trans* photoisomerization equilibria of azocompounds on the wave length of the light used in photoequilibration, at one temperature.

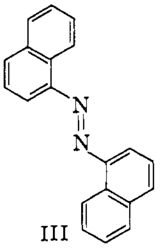
The present paper shows how the photoequilibrium, reached by irradiation at certain wave lengths, changes with the temperature at which the irradiation is carried out. All irradiations were performed at temperatures sufficiently low to stop any *thermal* isomerization, *i.e.* below 0° for azobenzene (I) and 2,2′-azonaphthalene (II) and below minus 20° for 1,1′-azonaphthalene (III).



I



II



III

Experimental

Reagents. Azobenzene.—Eastman Kodak white label azobenzene was recrystallized from ethanol and from hexane.

1,1′-Azonaphthalene and 2,2′-azonaphthalene were prepared as described previously.[4] No *cis* isomers were separated for the purpose of the current investigation.

Solvents.—Methylcyclohexane, methylcyclopentane and isononane were purified by passage through columns of activated silica and activated alumina (Woelm, basic, activity I).[5] In the experiments with azonaphthalenes these solvents were distilled from a potassium–sodium alloy, in a high vacuum, into the optical cell containing the solute. The cell was then fused-off under vacuum.[6] The same procedure was used with tetrahydrofuran and 2-methyl-tetrahydrofuran. A 1:1 mixture of the two served as solvent in some cases. 1-Propanol was freshly distilled from potassium hydroxide.

Photochemistry and Spectrophotometry.—Irradiations and spectrophotometric measurements in a wide range of temperatures were carried out in a Cary Model 14 spectrophotometer, as described previously.[6] Photoisomerization was investigated for each compound in a temperature range limited upwards by the required absence of *thermal cis* → *trans* isomerization and downwards by the freezing points of the solvents used. Each experiment started with a solution of the respective *trans* isomer. Absorption spectra were recorded at the various required temperatures. This was followed by irradiation, at each temperature, with light from an a.c. operated Philips Spectral lamp No. 93110 mercury arc, at several wave lengths corresponding to the mercury emission "lines." These were isolated by the usual Corning filter combinations[3] (for the 578, 546, 436 and 365 mμ bands), a Balzer interference filter (for the 405 mμ band) and a combination of a solution of nickel chloride and Corning filters 9863 and 0620 (for the 313 mμ band).[7] The light beam filled practically 100% of the cell windows. The number of light quanta at 365 mμ incident on the solution in the cell was determined by iron oxalate actinometry in the same cells, at room temperature, as approximately 4 × 10^{17} quanta/minute. The solutions had a volume of three ml. and were not stirred. Unless stated otherwise, cells had a cross section of 10 × 10 mm.

The position of the photoequilibrium reached on irradiation of any solution with light at any particular wave length was found to be independent of the isomeric composition before irradiation (*cf.* Fig. 2), the intensity of the light incident on the solution (down to $^1/_4$ of the value given above), the concentration of the solutions (*cf.* caption to Fig. 3 E) and the absorbance of the solutions (up to 1.2). These points are important since, in the absence of stirring and rapid diffusion, light which is strongly absorbed may not even reach the deeper layers of the solution, making it impossible to attain true photoequilibrium.

The present investigation aimed primarily at the determination of photoequilibria, and only crude measurements of the rates of photoequilibration were made in some cases. The results of these kinetic experiments are expressed as half-life times, *i.e.*, the time required to achieve one half of the total change in isomeric composition resulting from irradiation with light at a particular wave length.

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[1] E. Fischer, M. Frankel and R. Wolovsky, *J. Chem. Phys.*, **23**, 1367 (1955).

[2] E. Fischer and Y. Frei, *ibid.*, **27**, 328 (1957).

[3] G. Zimmerman, This Journal, **80**, 3528 (1958), and earlier literature listed there.

[4] M. Frankel, R. Wolovsky and E. Fischer, *J. Chem. Soc.*, 3441 (1955).

[5] G. Hesse and H. Schildknecht, *Angew. Chem.*, **67**, 737 (1955).

[6] Y. Hirshberg and E. Fischer, *Rev. Sci. Irst.*, **30**, 197 (1959).

[7] R. E. Hunt and W. Davis, This Journal, **69**, 1415 (1947).