From both F12 and F13 q and k_q are determined when the proper value of q is assumed.

Possibility of Determining Additional Constants

Under highly favorable conditions, two more constants can be determined. It is believed that the data will never be sufficiently accurate to determine more than six extinction coefficients.

Starting from the central atom we can determine the first two formation constants in the manner already indicated. Under highly favorable conditions the approach of Kingery and Hume[6] permits the determination of the next formation constant. The method employs the utilization of the calculated constants and extinction coefficients to determine the absorbance of a solution for a particular ligand and central atom concentration. The difference between the calculated and the observed absorbance is attributed to the formation of a fourth species which has to be assumed not to absorb at the wave length selected. A log plot similar to that of eq. D13b is made for the equilibrium between the third and fourth species. The change in ligand ratio and another constant can be determined.

It has also been seen that starting with the central atom in its highest complexed state, the two highest formation constants can be determined. Once again, the method of Kingery and Hume can be employed whereby the third highest formation constant can be calculated. Therefore, under highly favorable conditions, as many as six formation constants can be determined.

The utilization of many of the equations for the mixed similar ligands and for one-ligand systems will be demonstrated in subsequent papers.

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CAMBRIDGE, MASS.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND LABORATORY FOR NUCLEAR SCIENCE OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

A Spectrophotometric Study of the Bismuth–Chloride Complexes[1]

BY LEONARD NEWMAN AND DAVID N. HUME

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By application of spectrophotometric methods developed in a previous paper, the following constants were determined for the bismuth–chloride system: $270 \pm 5 = [BiCl^{++}]/[Bi^{+++}][Cl^-]$, $900 \pm 100 = [BiCl_2^+]/[BiCl^{++}][Cl^-]$, $20 \pm 10 = [BiCl_3]/[BiCl_2^+][Cl^-]$, $60 \pm 5.0 = [BiCl_4^-]/[BiCl_2^+][Cl^-]^2$, $2.7 \pm 1.0 = [BiCl_4^-]/[BiCl_3][Cl^-]$, and $3.0 \pm 0.5 = [BiCl_5^{--}]/[BiCl_4^-][Cl^-]$. All were determined in 1 M perchloric acid and the last three in a salt concentration of 4.0 M. The absorption spectra for all the species except $BiCl_2^+$ were resolved.

Introduction

Although the existence of complex formation between bismuth(III) and chloride ions is well known, comparatively little information is available concerning the nature or stability of the species formed. None of the earlier workers[2,3] undertook extensive studies on the system and the more recent work[4,5] has not taken fully into consideration the effects of variable ionic strength. The observation by Merritt, Hershenson and Rogers[6] that the ultraviolet absorption of bismuth in acid solution was influenced profoundly by chloride concentration has prompted us to investigate the system spectrophotometrically using the methods developed and described in a previous paper.[7]

Exerimental

Materials and Apparatus.—Solutions of bismuth perchlorate were prepared by dissolving Baker and Adamson reagent bismuth oxide in a stoichiometric concentration of warm Mallinckrodt 60% perchloric acid analytical reagent and then diluting to the proper concentration. A 5 M stock solution of sodium perchlorate was prepared by dissolving and then filtering Fisher Scientific Company purified sodium perchlorate. Stock solutions of 5 M sodium chloride were prepared by dissolving and filtering Mallinckrodt analytical reagent material.

Two spectrophotometers were used: A Beckman model DU quartz spectrophotometer equipped with a photomultiplier attachment, and a Cary recording spectrophotomer model 11 MS. Unless otherwise specified, 1.000 cm. cells were used and cell corrections applied if necessary. For each experiment the spectrophotometer used is specified.

General Characteristics of the Absorption Curves.—The absorption spectra of solutions containing 15 p.p.m. bismuth, 1 M perchloric acid, and varying ratios of sodium chloride to sodium perchlorate to maintain a salt concentration of 4.0 M were measured against a blank containing 1 M perchloric acid on the Cary. It can be seen in Fig. 1 that at 4 M sodium chloride, there is an absorption peak at 327 mμ for a bismuth complex of the form $BiCl_n^{3-n}$. There is a gradual shift of the peak as the chloride concentration is decreased, indicating that chloride complexes lower than n must also be formed. Since the blank contained only 1 M perchloric acid the curves include the absorption due to sodium perchlorate and sodium chloride. The absorption due to sodium perchlorate can be neglected throughout the wave length covered. Although the absorbance of 4 M sodium chloride becomes significant at wave lengths less than 260 mμ, it does not affect the spectra around the absorption peaks for the high chloride concentrations. When the peaks are shifted to the region of 260 mμ (*e.g.*, expt. 15, Fig. 1) the chloride concentration is so low that its contribution to the spectra is negligible.

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[1] Taken in part from the Doctoral Thesis of Leonard Newman, Massachusetts Institute of Technology, May, 1956.

[2] A. A. Noyes, F. W. Hall and J. A. Beattie, THIS JOURNAL, **39**, 2526 (1917).

[3] T. DeVries and E. M. Mattox, *Proc. Indiana Acad. Sci.*, **44**, 138 (1934).

[4] A. K. Babko and A. M. Golub, *Sbornik Statei Obschchei Khim., Akad. Nauk, S.S.S.R.*, **1**, 64 (1953).

[5] K. B. Yatsimirskii, *ibid.*, **1**, 97 (1953).

[6] C. Merritt, H. M. Hershenson and L. B. Rogers, *Anal. Chem.*, **25**, 572 (1953).

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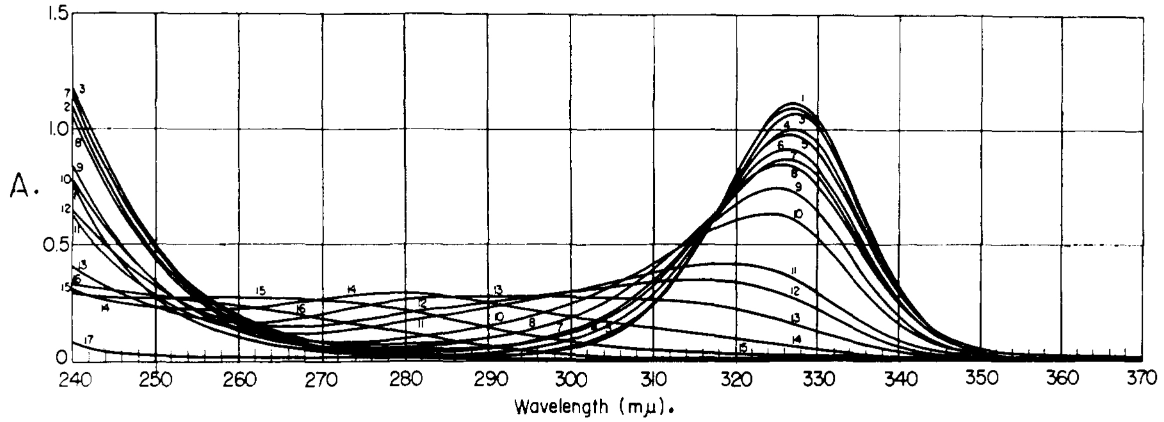

Fig. 1.—Absorption spectra of 15 p.p.m. (7.18×10^{-5} *M*) solutions of bismuth perchlorate in 1 *M* perchloric acid and various mixtures of sodium chloride and sodium perchlorate giving a total ionic strength of 5.0 *M*. The sodium chloride concentrations were for the curves as numbered: (1) 4.0 *M*, (2) 3.0 *M*, (3) 2.0 *M*, (4) 1.0 *M*, (5) 0.8 *M*, (6) 0.6 *M*, (7) 0.5 *M*, (8) 0.4 *M*, (9) 0.3 *M*, (10) 0.2 *M*, (11) 0.1 *M*, (12) 0.08 *M*, (13) 0.05 *M*, (14) 0.025 *M*, (15) 0.01 *M*, (16) 0.005 *M*, (17) 0.000 *M*. The reference solution for absorption measurements was in each instance 1.0 *M* perchloric acid.

Continuous Variations.—Although the method of continuous variations is widely used for the determination of combining ratios of metal ions and complexing ligands, it is not generally realized that erroneous conclusions may be drawn when more than one complex is formed. Katzin and Gebert[8] derived general relationships for the case of as many as three complexes present simultaneously and showed that even though only one complex species absorbs, the position of the maximum is dependent upon the formation constants and may or may not appear at the position corresponding to its stoichiometric composition.

A discussion of the various shapes and positions that the maxima in a continuous variations plot might attain, dependent upon the number of species formed and the number absorbing, is given in the article of Katzin and Gebert.[8] Woldbye[9] presents a detailed analysis of the characteristics of the plots for the method of continuous variations when more than one complex is present and/or more than one species is absorbing. From both papers it is readily apparent that when more than one complex is formed, the method becomes very limited in its application. Woldbye also points out some of the erroneous conclusions and results obtained by previous workers.

With these limitations in mind, continuous variations experiments for the bismuth chloride system were attempted under a variety of conditions most favorable for ascertaining the maximum ligand number. The results are shown in Fig. 2. The acidities chosen were the minimum necessary to prevent the precipitation of bismuthyl chloride. Since the position of the maximum is variable, the complex formed might be anything from $BiCl_5^{-2}$ to $BiCl_8^{-5}$. The results obtained appear to be a clear example of the unreliability of the method of continuous variations when more than two species are present.

Katzin and Gebert point out that the position of the maximum for the highest complex would appear above its formal composition when three species are formed. This, coupled with the fact that a coördination for bismuth greater than six is highly improbable, suggests that the highest complex formed is certainly less than $BiCl_8^{-5}$.

Noyes, Hall and Beattie[2] observed in a solubility study of BiOCl that there is at least a tetrachloro and probably a pentachloro complex. It will be seen that the spectrophotometric data also lead to the conclusion that the maximum coördination is at least five.

Highest Complexes.—For a discussion of the over-all method of application reference should be made to the previous paper.[7] In order to determine the formation constant for the highest complex, wave lengths were first selected where it could be assumed that only the highest complex was absorbing. From Fig. 1 it is obvious that the higher the wave length, the greater the likelihood of this occurrence. Measurements of absorbance at 345, 347 and 349 mμ were made with a Beckman spectrophotometer on solutions containing 100 p.p.m. of bismuth, 1 *M* perchloric acid and varying ratios of sodium chloride to sodium perchlorate maintaining the salt concentration at 4.0 *M*, against a blank containing 1 *M* perchloric acid. The results are summarized in Fig. 3.

From Fig. 3 it is obvious that at 4 *M* sodium chloride, the absorbance has not levelled off indicating that the highest complex is still partially ionized. The extrapolated values of A_0 were the minimum absorbance necessary to give a straight line plot for eq. C13. Reference to the previous paper should be made for all equations.

A plot of eq. C13 assuming two species with only the highest absorbing is shown in Fig. 4. All three wave lengths used are seen to lead to the same result. Since the slope, *m*, is unity, the following equilibrium must exist

$$BiCl_{n-1}{}^{4-n} + Cl^- = BiCl_n{}^{3-n}$$

$$k_n = \frac{[BiCl_n{}^{3-n}]}{[BiCl_{n-1}{}^{4-n}][Cl^-]]}$$

From the intercept, k_n was calculated as 3.0 ± 0.5. The curves drawn in Fig. 3 are the theoretical curves calculated from the extrapolated values of A_0 and the observed k_n. The fit with the data is remarkably good.

In order to verify that only the highest cómplex was absorbing at the wave lengths selected, eq. C12 was applied to the data. This equation assumes two species present with both absorbing. A single straight line was obtained with an intercept at zero (see Fig. 5). Since the intercept represents the extinction coefficient for the lower complex, it is evident that the assumption is correct that only one species absorbs in this region. The value of k_n obtained from this plot is 3.1 ± 0.5 which is in excellent agreement with the previous plot.

At the same three wave lengths, the absorbance of various solutions containing lower concentrations of sodium chloride also was measured. The absorbances are plotted in Fig. 6. Since it was shown in Fig. 1 that as the complexation decreased the absorption peak shifted to lower wave lengths, and in Fig. 5 that $BiCl_{n-1}{}^{4-n}$ does not absorb, eq. C12 (which assumes three species present, but only the highest absorbing) could be applied.

The results are plotted in Fig. 7. From the slope, *p* equal to two, which was attained for the three wave lengths, the following equilibrium can be written

$$BiCl_{n-3}{}^{6-n} + 2Cl^- = BiCl_{n-1}{}^{4-n}$$

$$(k_{n-1})\ (k_{n-2}) = \frac{[BiCl_{n-1}{}^{4-n}]}{[BiCl_{n-3}{}^{6-n}][Cl^-]^2}$$

The value of $k_{n-m} = (k_{n-1})(k_{n-2})$ obtained from the intercept is 60 ± 5. The deviations at the lower values of chloride concentration were due to the formation of a fourth species.

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[8] I. I. Katzin and E. Gebert, THIS JOURNAL, **72**, 5455 (1950).

[9] F. Woldbye, *Acta Chem. Scand.*, **9**, 299 (1955).

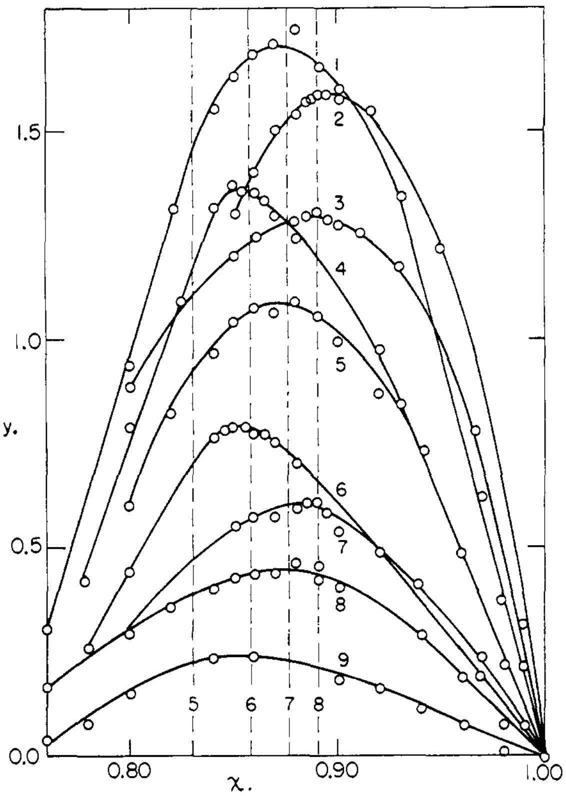

Fig. 2.—Continuous variations plots for bismuth-chloride mixtures.

No.	λ (mμ)	a[1] (*M*)	HClO$_4$ (*M*)	NaClO$_4$[2] (*M*)	μ (*M*)	Cell (cm.)
1	366	0.20	8.0	1.0	9.2	10
2	348	.10	7.0	0.5	7.6	1
3	330	.04	4.0	.2	4.2	1
4	363	.50	9.0	.0	9.5–10	1
5	369	.20	8.0	1.0	9.2	10
6	366	.50	9.0	0.0	9.5-10	1
7	360	.20	8.0	1.0	9.2	1
8	375	.20	8.0	1.0	9.2	10
9	380	.30	*	0.0	9.3	10

Blanks contained corresponding perchloric acid concentrations plus sodium perchlorate to give proper ionic strength. (1) Concentration of bismuth and chloride solutions. (2) Sodium perchlorate added in chloride solution to maintain a constant ionic strength. * 7.5 *M* in the bismuth solutions and 9.0 *M* in the chloride.

Utilization of eq. C12, C10 and C11 for 2 species-2 absorbing, 3 species-2 absorbing, and 3 species-3 absorbing, permitted the establishment of the spectra for the species involved. The absorbances obtained from the Cary and plotted in Fig. 1 were employed. Data from the Cary are not as accurate as from the Beckman and there was a more random distribution of points in the associated plots than previously observed.

In the utilization of these data at those wave lengths where $BiCl_n^{3-n}$ and $BiCl_{n-1}^{4-n}$ had low absorbances, it became obvious that the transition was not $BiCl_n^{3-n}$ to $BiCl_{n-1}^{4-n}$ to $BiCl_{n-3}^{6-n}$ but rather $BiCl_n^{3-n}$ to $BiCl_{m-1}^{4-n}$ to $BiCl_{n-2}^{5-n}$ to $BiCl_{n-3}^{6-n}$.

Figure 8 which depends upon the utilization of eq. C9 for 3 species-3 absorbing at 290 mμ gave for the equilibrium

$$BiCl_{n-2}^{5-n} + Cl^- = BiCl_{n-1}^{4-n}$$

$$k_{n-1} = \frac{[BiCl_{n-1}^{4-n}]}{[BiCl_{n-2}^{5-n}][Cl^-]}$$

a value of $k_{n-m} = k_{n-1} = 2.7 \pm 1.0$ where p is now equal to 1. The value of k_{n-1} could not be too well established

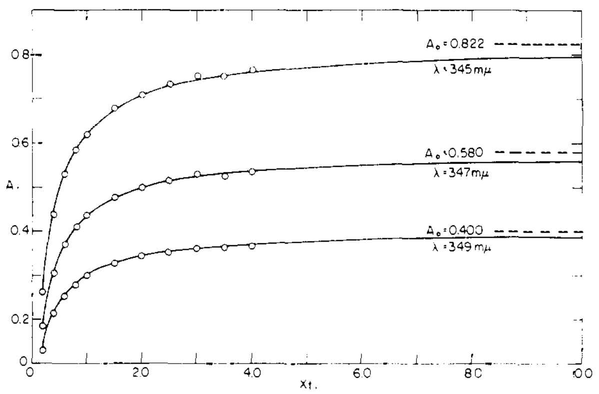

Fig. 3.—Absorbance as a function of chloride concentration for 100 p.p.m. (1.44 × 10^{-4} *M*) bismuth perchlorate solutions 1 *M* in perchloric acid and at an ionic strength of 5.0 *M*. The reference blank was 1.0 *M* perchloric acid.

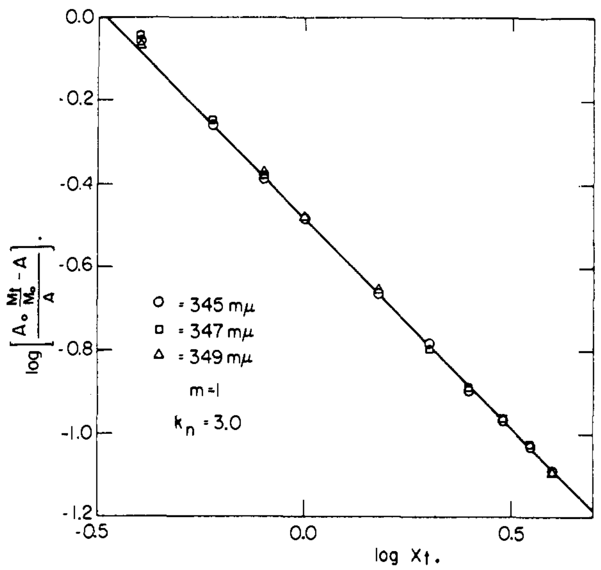

Fig. 4.—Determination of highest formation constant with two species present and one absorbing: 100 p.p.m. bismuth in 1 *M* perchloric acid and ionic strength 5.0 *M*.

since there was some variation with wave length. Since the value of k_{n-1} is so small, the presence of $BiCl_{n-2}^{5-n}$ could not be detected unless it were the species with the greatest extinction coefficient. The best value for this constant was obtained when the differences in extinction coefficients were at a maximum. At the wave lengths where the second ionization appeared as a two-chloride transition, it did so because both the concentration and the extinction coefficient of $BiCl_{n-2}^{5-n}$ were so small that the differences taken for the log plots involved were not appreciably affected. The constant obtained was therefore a reliable value for the two chloride transition. The spectra of the various species, which, as will be seen later, can be attributed to $BiCl_5^{--}$, $BiCl_4^-$ and $BiCl_3$, were obtained from the appropriate equations. The results are given in Fig. 9.

Some care had to be employed in the application of the equations. For example, if the extinction coefficients were too similar, the changes in the absorbance would not be great enough to permit accurate calculations. Another source of difficulty was observed when the absorbance went through a maximum or minimum as the chloride concentration was decreased (*e.g.*, at 315 mμ). Here again, the taking of differences accounts for large errors.

Lowest Complex.—Since bismuth was found to absorb in the same region as the lowest chloride complexes it was necessary, before attempting to determine the formation constant of the lowest complex, to ascertain that the ab-

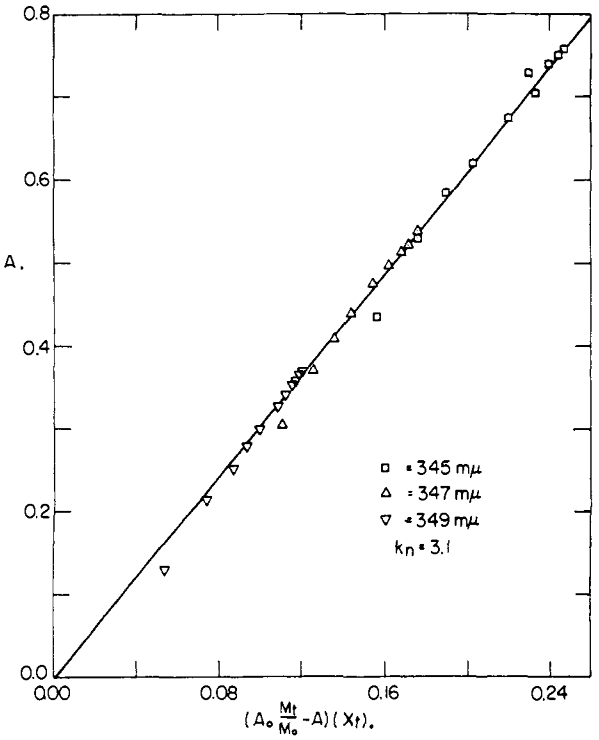

Fig. 5.—Determination of highest formation constant with two complex species present, both absorbing: 100 p.p.m. bismuth, perchloric acid 1 *M* and ionic strength 5.0 *M*.

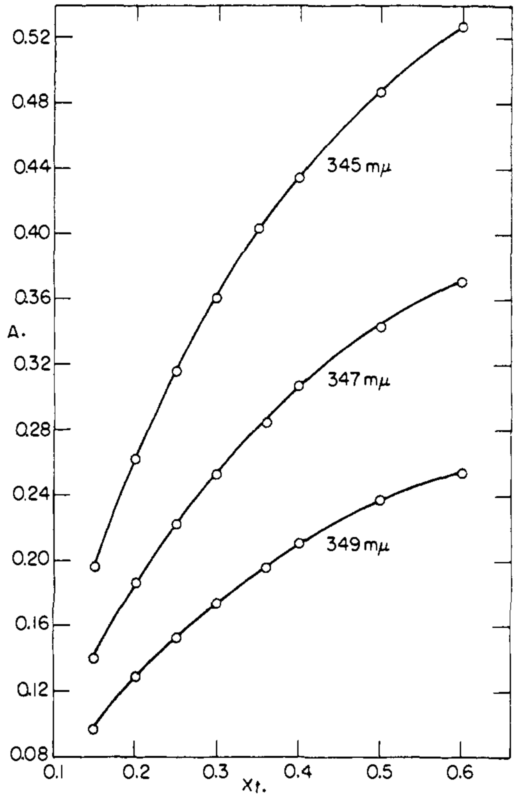

Fig. 6.—Absorbance of 100 p.p.m. bismuth in 1 *M* perchloric acid as a function of chloride concentration at an ionic strength of 5.0 *M*.

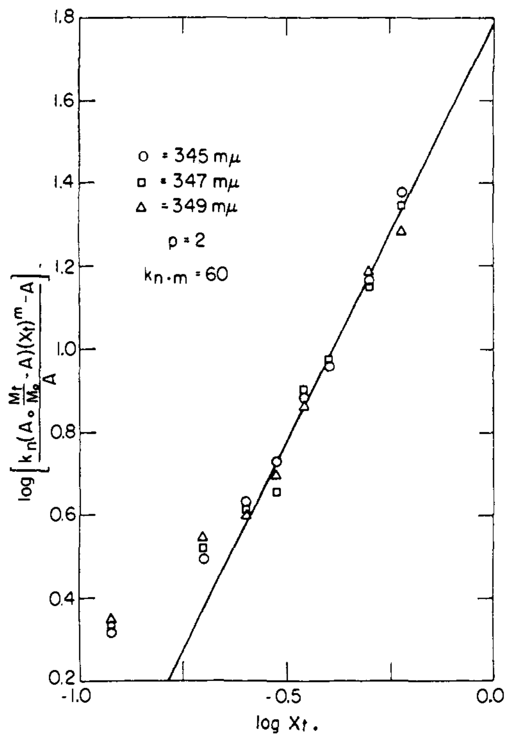

Fig. 7.—Determination of constant for the reaction $BiCl_2^+ + 2Cl^- \rightarrow BiCl_4^-$: three species present, one absorbing.

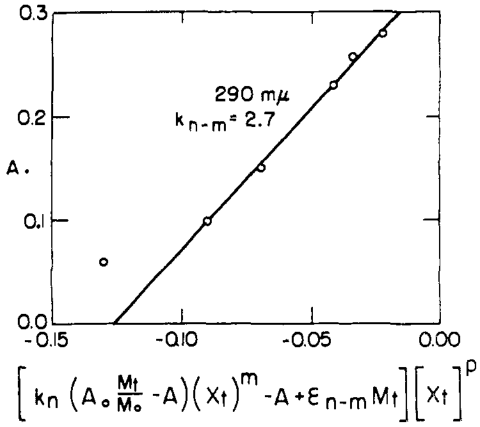

Fig. 8.—Determination of stepwise formation constant of the $BiCl_4^-$ ion: three species present, one absorbing.

sorbance of bismuth followed Beer's law. The absorbances of samples containing 1 *M* perchloric acid and varying amounts of bismuth were measured on the Beckman spectrophotometer against a blank 1 *M* perchloric acid at six different wave lengths. Straight line plots were obtained as evidence that bismuth obeys Beer's law.

To obtain an accurate measure of the extinction coefficient for the complex, a blank was prepared containing the largest amount of bismuth which would still permit the zeroing of the Beckman spectrophotometer. A reasonable blank was found to contain 6 × 10^{-3} *M* bismuth and 1 *M* perchloric acid. Samples were then made to contain this concentration plus sodium chloride varying from 3 × 10^{-5} to 20 × 10^{-5} *M*. The measured absorbance was, as a first approximation, attributed solely to the formation of the lowest complex. From the plot of absorbance *vs.* assumed $BiCl^{++}$ concentration a first approximation of the extinction coefficient of the $BiCl^{++}$ ion was estimated.

The measure of the formation constant for the lowest complex could then be obtained when a reasonable amount of it was ionized. It was necessary to take measurements when the concentration of X_t was comparable with that of M_t. The absorbance was measured on the Beckman spectrophotometer at 244 mμ, for samples containing 1.5 × 10^{-4} *M* sodium chloride, 1 *M* perchloric acid and 2.0 × 10^{-4}

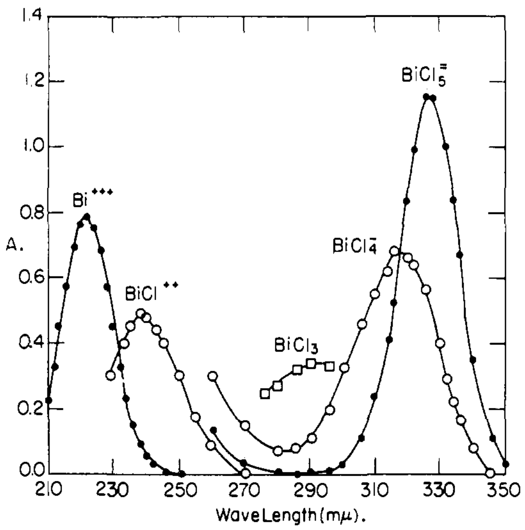

Fig. 9.—Resolved spectra of bismuth chloride complexes. All apply to 7.18 × 10^{-5} *M* bismuth in 1 *M* perchloric acid and ionic strength 5.0 *M* except $BiCl^{++}$ which was studied at unit ionic strength.

to 14 × 10^{-4} *M* bismuth against a blank containing everything but the bismuth.

Equation E12 for the two species both absorbing with X_t comparable to M_t becomes applicable. As a first approximation the extinction coefficient for the complex at 244 mμ was assumed equal to 3.25 × 10^3 M^{-1} cm.$^{-1}$ (see Table I). The extinction coefficient of bismuth at 244 mμ was obtained as 0.28 × 10^3 M^{-1} cm.$^{-1}$.

TABLE I

DETERMINATION OF CONSTANTS BY SUCCESSIVE APPROXIMATIONS

Bi^{+++} = (2.0 to 14) × 10^{-4} *M*, Cl^- = 1.5 × 10^{-4} *M*, $HClO_4$ = 1.0 *M*, μ = 1.0 *M*, λ = 244 mμ

Approximation	$E_1 \times 10^{-3}$	$k_1 \times 10^{-2}$
1	3.25	6.00
2	4.40	3.69
3	4.93	3.17
4	5.25	2.90
5	5.41	2.77
6	5.48	2.72
Extrapolated	5.50 ± 0.05	2.70 ± 0.05

If the lowest complex is assumed to be $BiCl^{++}$ then *q* becomes one. In order to obtain the greatest changes in the ordinates, eq. E12 was rearranged and plotted as indicated in Fig. 10. If the proper choice of *q* was made, the slope should still be unity. A line with such a slope was drawn and found to agree quite well with the data. The following equilibrium can therefore be written

$$Bi^{+++} + Cl^- = BiCl^{++}$$

$$k_1 = \frac{[BiCl^{++}]}{[Bi^{+++}][Cl^-]}$$

where, as a first approximation, k_1 equals 6.00 × 10^2. The deviations at the lower end of the curve are due to the formation of a second complex.

From this value of *k*, a second approximation to the actual concentrations of the species in solution was calculated for the data used in the determination of the extinction coefficient of $BiCl^{++}$. It should be remembered that the same concentration of bismuth was added to the blank and sample; therefore, the absorbance had to be corrected for any bismuth used up in the formation of the complex.

As a second approximation, the concentration of $BiCl^{++}$ formed, and its absorbance, was calculated. From a plot of the absorbance *vs.* $BiCl^{++}$ concentration the extinction coefficient was calculated and is included in Table II. Again using eq. E12, a new value of k_1 was obtained. This procedure was repeated six times. The plot for the sixth approximation of k_1 is included in Fig. 10. The results summarized in Table I could be extrapolated to an E_1 = (5.50 ± 0.05) × 10^3 at 244 mμ and a k_1 = (2.70 ± 0.05) × 10^2.

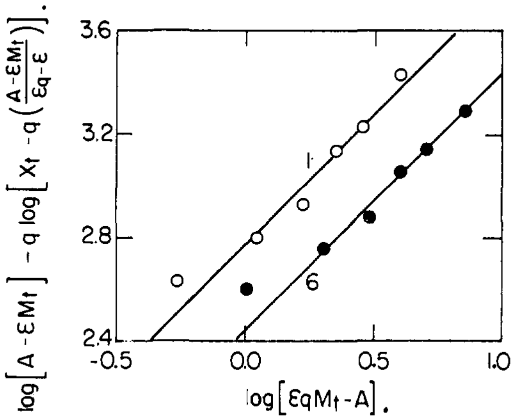

Fig. 10.—First and sixth approximations for the determination of the formation constant of $BiCl^{++}$ at 244 mμ.

Spectra.—The spectrum of 15 p.p.m. bismuth in 1 *M* perchloric acid and 4 *M* sodium perchlorate was measured on the Cary against a blank containing everything except the bismuth. This, together with the derived spectra of the complex ions, is plotted on Fig. 9.

For the spectrum of $BiCl^{++}$, the absorbance of a sample containing 10^{-3} *M* bismuth, 10^{-4} *M* sodium chloride and 1 *M* perchloric acid was measured against a blank containing 5 × 10^{-4} *M* bismuth and 1 *M* perchloric acid. Another sample containing 10^{-3} *M* bismuth and 1 *M* perchloric acid also was measured against the blank. This gave the absorbance of 5 × 10^{-4} *M* bismuth. The high concentration of bismuth in the sample was necessary, in order to complex most of the chloride as $BiCl^{++}$. The bismuth was added to the blank to keep the absorbance readings less than 1.2 and, for most of the wave lengths, between 0.2 and 0.6. If both the bismuth and chloride concentrations were decreased, the concentration of the complex formed and its absorbance would have been too low to give a good measure of the spectrum of $BiCl^{++}$.

From the value of k_1 in Table I, the concentrations of bismuth, $BiCl^{++}$, and chloride in the sample were calculated as 9.79 × 10^{-4} *M*, 2.09 × 10^{-5} *M* and 7.91 × 10^{-5} *M*. The sample absorbance, therefore, was due to the presence of both Bi^{+++}, 4.79 × 10^{-4} *M*, and $BiCl^{++}$, 2.09 × 10^{-5} *M* (the blank contained 5 × 10^{-4} *M* Bi^{+++}). When the absorbance of 5 × 10^{-4} *M* bismuth was multiplied by the ratio 4.79/5.00 and subtracted from the sample, the absorbance due to 2.09 × 10^{-4} *M* $BiCl^{++}$ remained. The absorbance of 7.17 × 10^{-5} *M* $BiCl^{++}$, corresponding to 15 p.p.m. bismuth in the form of the complex, was calculated and plotted in Fig. 9.

Second Complex.—In attempting to work out the spectrum and formation constant of $BiCl_2^+$ two major difficulties were encountered. In order to prevent the formation of appreciable amounts of higher complexes and yet form enough $BiCl_2^+$ the experiment had to be conducted with X_t comparable to M_t. Since the concentrations of X_t and M_t were both changing, the equations necessary for three species being present become extremely cumbersome. The only alternative was to assume X_t greater than M_t and use the equations developed for this condition. The actual concentration for X_t could be solved for by a series of approximations. This would have worked, if it were not for the fact that the absorbance of $BiCl_3$, $BiCl_4^-$ and $BiCl_5^{--}$ becomes very large at the wave lengths where $BiCl_2^+$ absorbs (see Fig. 1 and 9). It was found that as soon as appreciable quantities of $BiCl_2^+$ were formed, small amounts of higher complexes also were formed. Therefore, the absorbance attributable to $BiCl_2^+$ could not be obtained with any degree of accuracy. However, from the deviations observed in the determination of k_1, it could be ascertained that the absorption peak of $BiCl_2^+$ appears between 245 and 265 mμ with a peak absorbance of 0.2 to 0.4 for a 7.17 ×

10^{-5} *M* solution. The determination of k_2 was little more than a rough estimate due to these difficulties, and it was found that any value between 100 and 1000 could be made to fit the data.

Discussion

The above analysis of the spectrophotometric data shows clearly the existence of at least five chloro complexes of bismuth. The data can be interpreted satisfactorily on the assumption that there are only five present and that the highest complex, $BiCl_n^{3-n}$, is $BiCl_5^{--}$. From these data alone it cannot be proved that another species in the middle of the series, present only in small concentrations and having a relatively low extinction coefficient, was not overlooked but this possibility is a very unlikely one. As will be seen in a later publication, quantitative studies of the replacement of chloride ions with bromide ions in the highest chloro complex agree very well with the assumption of a maximum ligand number of five. Accordingly, the most reasonable value to assume for the maximum ligand number of bismuth in chloride medium is five with the sixth coördination position occupied by water. Dr. Sten Åhrland at the University of Lund has kindly made available to us[10] results from a potentiometric study he has been carrying out on the bismuth–chloride system at ionic strength of 2 *M* which also shows five fairly stable complexes together with indications of a very weak sixth. Dr. Åhrland's value for the over-all formation constant of the ion $BiCl_5^{=}$, which he estimates as $(4.5 \pm 0.5) \times 10^7$, can be used together with our data to give 900 for k_2 which is a much more reliable value than that obtained directly. With the aid of this datum we calculate from our results

$$270 \pm 5 = \frac{[BiCl^{++}]}{[Bi^{+++}][Cl^-]}$$

$$900 \pm 100 = \frac{[BiCl_2^+]}{[BiCl^{++}][Cl^-]}$$

$$20 \pm 10 = \frac{[BiCl_3]}{[BiCl_2^+][Cl^-]}$$

$$60 \pm 5 = \frac{[BiCl_4^-]}{[BiCl_2^+][Cl^-]^2}$$

$$2.7 \pm 1.0 = \frac{[BiCl_4^-]}{[BiCl_3][Cl^-]}$$

and

$$3.0 \pm 0.5 = \frac{[BiCl_5^{--}]}{[BiCl_4^-][Cl^-]}$$

The wave lengths and extinction coefficients of the peaks were determined as

$BiCl_5^{--} = 327 \pm 1$ mμ; $(1.61 \pm 0.01) \times 10^4$
$BiCl_4^- = 317 \pm 2$ mμ; $(0.95 \pm 0.03) \times 10^4$
$BiCl_3 = 300 \pm 10$ mμ; $(0.49 \pm 0.03) \times 10^4$
$BiCl_2^+ = \sim 255 \pm 10$ mμ; $\sim(0.4 \pm 0.1) \times 10^4$
$BiCl^{++} = 238 \pm 2$ mμ; $(0.68 \pm 0.01) \times 10^4$
$Bi^{+++} = 222 \pm 1$ mμ; $(1.10 \pm 0.01) \times 10^4$

The first two formation constants and the absorbance characteristics of $BiCl^{++}$ and $BiCl_2^+$ were determined at an ionic strength of 1.0 obtained with perchloric acid. All other constants were also obtained in 1.0 *M* perchloric acid but with a salt concentration of 4.0 *M* yielded an ionic strength of 5.0.

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[10] S. Århland, private communication.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND LABORATORY FOR NUCLEAR SCIENCE OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

A Spectrophotometric Study of the Mixed Ligand Complexes of Bismuth with Chloride and Bromide[1]

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By application of spectrophotometric methods for the study of mixed ligand complexes, developed in a previous paper, the following constants were determined for the bismuth–chloride–bromide system at an ionic strength of 5.00 *M*: $0.55 \pm 0.05 = [BiBr_5^{--}][Cl^-]/[BiBr_4Cl^{--}][Br^-]$, $3.3 \pm 0.05 = [BiBr_4Cl^{--}][Cl^-]^2/[BiBr_2Cl_3^{--}][Br^-]^2$, $\sim 0.3 \pm 0.2 = [BiBr_4Cl^{--}][Cl^-]/[BiBr_3Cl_2^{--}][Br^-]$, $5.9 \pm 0.9 = [BiBr_2Cl_3^{--}][Cl^-]/[BiBrCl_4^{--}][Br^-]$ and $17 \pm 2 = [BiBrCl_4^{--}][Cl^-]/[BiCl_5^{--}][Br^-]$. All were determined in 1.0 *M* perchloric acid and 4.0 *M* halide ion concentration.

Introduction

Quantitative studies in which formation constants are determined for a series of consecutive mixed ligand complex systems appear to be essentially non-existent. The spectrophotometric methods derived in a preceding paper[2] offer an attractive approach to this difficult problem when the absorption spectra of the various complexes involved differ appreciably. Previous workers[2] had noted a 50 mμ difference in the positions of the absorption peak of bismuth when in 4 *M* chloride and in 4 *M* bromide medium. Accordingly, we have studied the spectra of bismuth in chloride–bromide mixtures in which the total halide concentration was maintained at 4 *M*, which according to previous workers was sufficient to maintain practically all the bismuth in its most complexed state.

From Fig. 1, it can be seen that there is no way of apportioning the spectra of the individual bismuth halide absorption curves to arrive at the spectra observed when both halides are present. Therefore, the spectra observed can only be accounted for by the formation of new complexes.

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[1] Taken in part from the Doctoral Thesis of Leonard Newman, Massachusetts Institute of Technology, May, 1956.

[2] L. Newman and D. N. Hume, THIS JOURNAL, **79**, 4576 (1957).

[3] C. Merritt, H. M. Hershenson and L. B. Rogers, *Anal. Chem.*, **5**, 572 (1953).