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A Spectrophotometric Investigation of Bismuth Iodide Complexes[1]

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A spectrophotometric study has been made of the formation of bismuth iodide complexes. It has been established that with decreasing iodide concentration the complexes formed are $[BiI_7^{4-}]$, $[BiI_6^{3-}]$, $[BiI_4^{-}]$, and a solvated species of $[BiI_3]$. No evidence has been found of the existence of the species $[BiI_5^{2-}]$ previously reported. A logical reinterpretation of the previous results is presented which confirms the nonexistence of this complex. The successive formation constants of the various complexes have been established together with their individual absorption spectra. The results show that in the analytical determination of bismuth by the chlorimetric iodide method, three complexes—$[BiI_7^{4-}]$, $[BiI_6^{3-}]$, and $[BiI_4^{-}]$—are responsible for the absorbance.

Introduction

In a previous paper[3] it was reported that a spectrophotometric study of the formation of bismuth iodide complexes had led to results which were incompatible with the published values[4] for the formation constants of the complexes presumed to be involved. From the formation constants, it is possible to calculate the concentrations of all of the complexes present at any fixed iodide concentration. Hence, from a knowledge of the absorbance of bismuth solutions of known iodide concentration, it is possible to calculate the molar absorptivities of each complex at the appropriate wavelength. The results of such calculations have shown that either the complex BiI_5^{2-} fluoresces at 337 $m\mu$ or the formation constants are in error.

Babko and Golub[5] claim a lower figue than that given by Ahrland and Grenthe for the value of β_6, but this has been dismissed by the latter authors on the grounds that the bismuth electrodes are likely to be less stable than the bismuth amalgam electrodes, that such high concentrations of nitric acid were used that a definite risk of oxidation of the metal of the electrode must have existed, and lastly that sulfite was used as a reducing agent, thus introducing an additional ligand and at the same time reducing the acid concentration.

In the previous paper,[3] the present author dealt with the formation of BiI^{2+}. The present report presents the evidence for the formation of the higher complexes.

Experimental Section

Material and Apparatus.—All chemicals used were analytical reagent grade. Bismuth oxide was prepared by converting recrystallized bismuth nitrate to the oxide by heating to constant weight in a platinum basin at 500°.

Solutions of bismuth perchlorate were prepared by dissolving the oxide in sufficient warm 70% w/w perchloric acid to give a final concentration of 1 M and then diluting to the required volume with distilled water. The concentration of the solution and purity of the bismuth oxide was checked by spectrophotometric comparison, using the iodide method, with a solution prepared from spectrographically pure bismuth trioxide, as prepared and analyzed by Spex Industries Inc.

Stock solutions of sodium iodide were prepared by dissolving the weighed quantity of the salt in distilled water from which dissolved oxygen had been removed by aspiration with oxygen-free nitrogen.

Perchloric acid used for adjusting the hydrogen ion concentration and for the preparation of sodium perchlorate was Baker Analyzed 70% w/w. The density of each new batch was measured and the concentration obtained from tables.[6] Periodic checks were made by titration of suitably diluted samples with standardized sodium hydroxide.

Solutions prepared from Frederic Smith and from Fischer Chemicals sodium perchlorate were found to be yellow and therefore unsuitable. Consequently, solutions were prepared by careful neutralization of a weighed amount of 70% w/w perchloric acid with a weighed equivalent amount of sodium bicarbonate. The carbonic acid was decomposed by heating and dissolved CO_2 removed by boiling and by nitrogen aspiration. The pH was finally adjusted to 7 with a Baker Analyzed sodium hydroxide solution.

In all these experiments the distilled water referred to was prepared in a conventional large-scale laboratory distillation apparatus and then passed through a mixed-bed ion-exchange column.

A Cary Model 14 spectrophotometer was used for recording spectra and for accurate measurement of absorbance. Usually the absorbance was taken straight from the recorded spectra, but on a few occasions, especially in regions of the spectrum where the absorbance was changing rapidly with wavelength, measurements were made with the instrument set at a fixed wavelength.

Measurements were made using 10.00-mm matched cells and carried out at a constant temperature of 24 ± 1°.

The hypophosphorous acid used as a reducing agent was a purified 50% w/w solution. It was found during this work that, once opened, these solutions deteriorated rapidly. After use, the bottles were purged with nitrogen and then kept tightly stoppered.

The nitrogen was the purest form readily available. Last traces of oxygen were removed by bubbling the gas through two scrubbers containing vanadous sulfate as recommended by Meites.[7] Finally, it was passed through a scrubber containing distilled water, to remove any acid or vanadium.

Results and Discussion

General Characteristics of the Absorption Spectra.—Solutions having the concentrations indicated in Table

(1) Taken in part from the Ph.D. (London) Thesis of A. J. Eve, University College of Rhodesia and Nyasaland, Rhodesia, Feb 1964.

(2) Part of this work was carried out while on sabbatical leave in the Department of Chemistry and the Laboratory for Nuclear Science, Massachusetts Institute of Technology, in collaboration with D. N. Hume.

(3) A. J. Eve and D. N. Hume, *Inorg. Chem.*, **3**, 276 (1964).

(4) S. Ahrland and I. Grenthe, *Acta Chem. Scand.*, **11**, 1111 (1957).

(5) A. K. Babko and A. M. Golub, *Sb. Statei Obshch. Khim., Akad. Nauk SSSR*, **1**, 64 (1953).

(6) "Handbook of Chemistry and Physics," Chemical Rubber Publishing Co., Cleveland, Ohio, 1960.

(7) L. Meites and T. Meites, *Anal. Chem.*, **20**, 984 (1948).

I were prepared, and absorptions were measured in 10-mm quartz cells *vs.* distilled water. Corresponding blank solutions containing all constituents other than the bismuth were prepared at the same time and measured in the same manner. Except where noted, the acid concentration was kept constant at 1 *M* and the ionic strength at 2 *M*, allowance being made for the partial ionization of the hypophosphorous acid. The latter ionic strength was chosen to enable comparison to be made with previous work.

TABLE I

SOLUTIONS FOR ANALYSIS: REAGENT CONCENTRATIONS $(M)^a$

Solution	[I]	[HClO$_4$]	[NaClO$_4$]
1	1.4	0.55	0
2	1.2	0.76	0
3	1.0	0.97	0
4	0.8	1.00	0.17
5	0.4	1.00	0.57
6	0.189	1.00	0.77
7	0.1	1.00	0.87
8	0.07	1.00	0.90
9	0.04	1.00	0.93
10	0.0085	1.00	0.96
11	0.007	1.00	0.96
12	0.005	1.00	0.96

^{a} In each case [Bi] $= 7.17 \times 10^{-5}$ M and [H$_3$PO$_2$] $= 0.47$ M.

tained by Newman and Hume for the chloride and bromide complexes[8,9] reveals that the iodide spectra are considerably more complex in this wavelength region. Whereas both the chloride and bromide spectra contain only one major absorption band, in the spectra of the iodide complexes there are two, with maxima at 337 and 460 mμ and two smaller bands at 310 and 402.5 mμ.

The same gradual shift of the peak at 465 mμ to shorter wavelengths with decreasing iodide concentration is, however, observed. This indicates that lower complexes than the one dominantly present at 1.4 *M* iodide must be formed.

Calculation of Successive Formation Constants.— For a discussion of the over-all method of application, reference should be made to the first paper by Newman and Hume.[10] In this paper, all equation numbers are those originally used.

Essentially the method of application is to convert the metal quantitatively into the highest species by increasing the ligand concentration, thus enabling the calculation of the molar absorptivity of the highest complex. The ligand concentration is then gradually reduced which results in the ionization of the complex. By applying the equations derived by Newman and
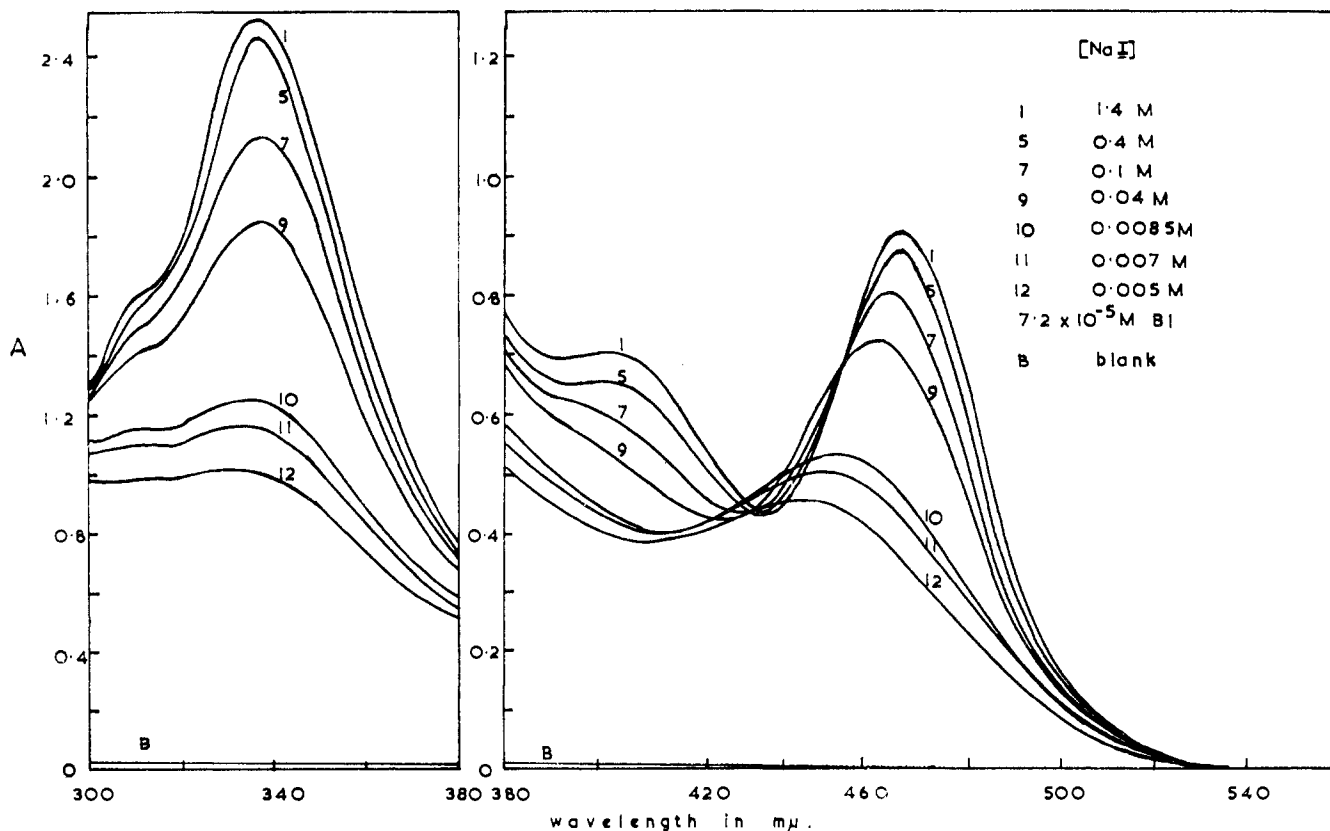

Figure 1.—Variation of the absorbance spectrum of bismuth iodide complexes with iodide concentration.

The absorption spectra of the bismuth solutions and that of the most concentrated blank solutions are shown in Figure 1. To avoid confusion only some of the spectra are shown. The numbers on the curves correspond to the numbers of the solutions in Table I.

Comparison of the family of curves with those ob-

Hume one can calculate the formation constants and molar absorptivities of each species in turn.

From Figure 2, it is obvious that even at a potassium

(8) L. Newman and D. N. Hume, *J. Am. Chem. Soc.*, **79**, 4576 (1957).
(9) L. Newman and D. N. Hume, *ibid.*, **79**, 4581 (1957).
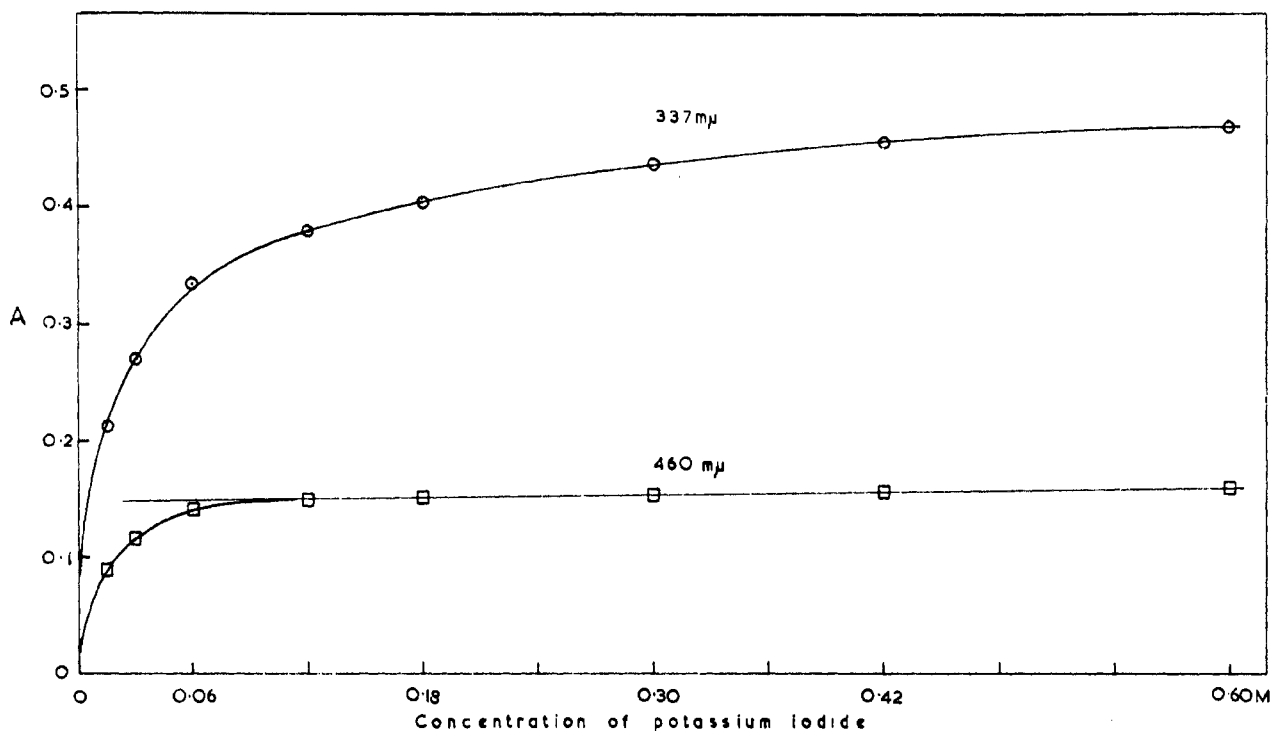(10) L. Newman and D. N. Hume, *ibid.*, **79**, 4571 (1957).

Figure 2.—Variation of absorbance with potassium iodide concentration.

iodide concentration of 0.6 M the highest species is still partially ionized, and the metal cannot be converted completely into this complex. It is also interesting to note that at 460 mμ one reaches a limiting absorbance at a lower iodide concentration than at 337 mμ. Reference to Figure 1 will show that this is because the former wavelength is very close to an isosbestic point for the top complexes.

A further complication arises in the case of iodide complexes of bismuth which was not present in the case of the chloride complexes.[8] Although it is not obvious from Figure 1, calculation has shown that even at 500 mμ both of the higher complexes absorb. This necessitates the use of eq C12 for two species being present with two absorbing

$$A = K_n(A' - A)X^m + A''$$

where A, A', and A'' are the absorbance, the limiting absorbance of the highest complex, and the limiting absorbance of the second highest complex, respectively; m and K_n are the number of ligands lost in the first ionization and the successive formation constant of the highest complex which contains n ligands; and X is the total ligand concentration.

Since in this case it is not possible to determine A', a value has to be assumed. A value for m is also assumed but it should be pointed out that here the choice is limited to a small integer.

From Figure 1 it may be seen that the most favorable wavelengths for study are likely to be 470, 402.5, and 337 mμ. Of these, 402.5 mμ has the advantage of being at the maximum of a very broad band where the least possible error from the mechanics of the recorder is introduced.

A plot of eq C12 using differing values for A' is shown in Figure 3. The five most concentrated solutions conform to the assumption of two species present with two absorbing, within the limits of the experimental accuracy, when A' has a value between 0.950 and 1.200 and $m = 1$. This results in a value of K_n between 0.15 and 0.08 M^{-1}.

The possibility that $m = 2$ was also considered but was ruled out on the grounds that results obtained from measurements at different wavelengths were inconsistent.

Below an iodide concentration of 0.4 M a third species is introduced which was found to absorb at 402.5 mμ and calculations were therefore carried out using eq C9 for three species present, all three absorbing

$$A = K_{n-m}[(A' - A)K_nX^m + (A'' - A)]X^p + E_{n-m-p}M_t$$

The last term may be replaced by A''', the limiting absorbance of the third complex.

Two possibilities were considered: $m = 1$, $p = 1$; $m = 1$, $p = 2$. This is further complicated by the range of possible values obtained for A' and K_n.

A plot of eq C9, shown in Figure 4, shows quite clearly that $p = 2$ since on this assumption a straight line is obtained. Curve 3 also shows the effect of assuming the maximum of value A', 1.200, suggested by the previous experiments at high iodide concentration. The lower limit of $A' = 0.950$ and $K_n = 0.15$ results in greater departure from linearity. Thus it was possible by this calculation to fix the value of A' at 1.000 and K_n at 0.13 ± 0.03 M^{-1}. The slope of the line obtained with these values of A' and K_n is 268 which is the value of K_{n-1}. The intercept fixes the value of A'' at 0.485.
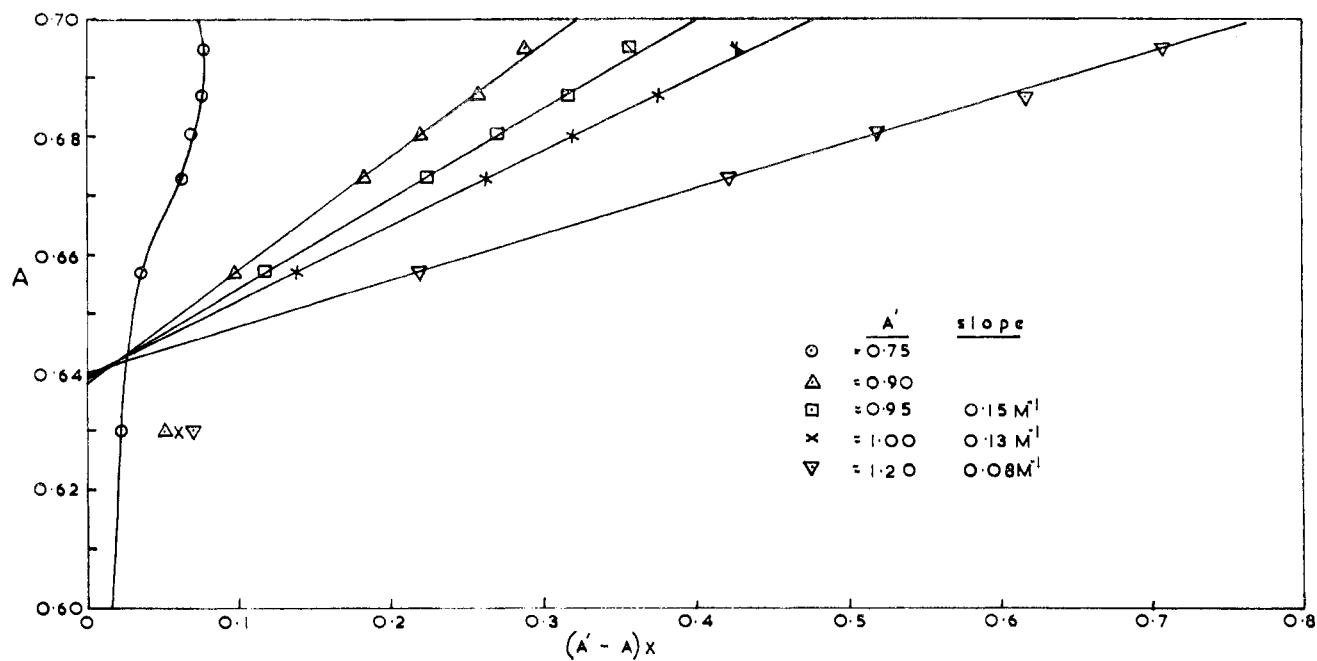
Figure 3.—Determination of K_n, m, and A' at 402.5 mμ.   Two species present both absorbing; $m = 1$.
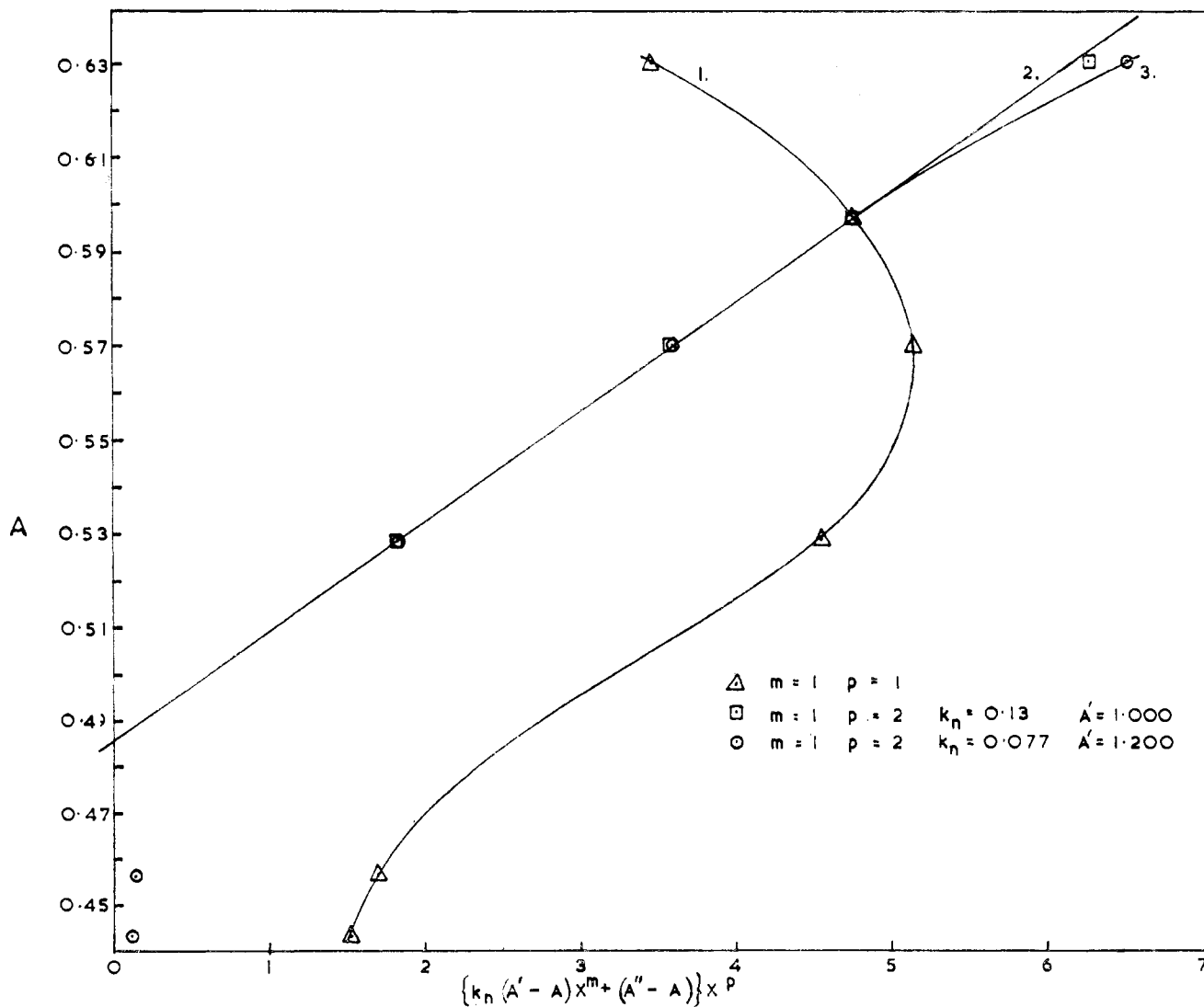
Figure 4.—Determination of K_{n-m}; $m = 1$.

Calculations Based on Measurements at Other Wavelengths.

—Confirmation of the results given above was obtained from measurements at other wavelengths. It has been suggested previously that a further region which could be expected to give accurate results is that between 460 and 470 mμ. This has the advantage over measurements at 402.5 mμ of low blank values with consequently less possibility of error from this source.

The results obtained, given in Table II, refer to a bismuth solution of 15 ppm ($7.2 \times 10^{-5} M$).

TABLE II

SUMMARY OF RESULTS FOR K_n, K_{n-1}, A', A'', AND A'''

Wavelength, mμ	A'	A''	A'''	K_n, M^{-1}	K_{n-1}, M^{-2}
500	0.313	0.132	0.130	0.15	230^a
402.5	1.00	0.639	0.485	0.13	268
465	1.20	0.849	0.641	0.14	269
470	1.28	0.798	0.575	0.14	265

^{a} The experiments which gave this set of data were carried out with iodide concentrations up to 2 M and at a constant ionic strength of 3 M. This made it possible to keep the acid concentration constant at 1 M for all solutions.

The Ionization of BiI_{n-3}.

—The results of the calculations for solutions 10–12 deviate from the straight line representing the absorbance of mixtures of BiI_n, BiI_{n-1}, and BiI_{n-3}. This indicates that a fourth species is being formed. Since the band in the region of 440 mμ is still moving to shorter wavelengths, the species is evidently soluble and a complex similar to those already mentioned and is not a solid.

As Newman and Hume have pointed out, the introduction of a fourth species leads to equations which are unmanageable. However, from the values of the successive formation constants already obtained, it may be calculated that less than 0.1% of the total bismuth is present in the form BiI_n below an iodide concentration of 0.04 M. In addition, the molar absorptivities of the species are of the same order of magnitude. In this case therefore, the system may be approximated to one of three species only, that is, BiI_{n-1}, BiI_{n-3}, and BiI_{n-3-q}.

The assumption that one iodide is involved in the transition leads to a reasonable approximation to a straight line, while the assumption that q has a value of 2 leads to a definite curve. The series of complexes formed under these conditions are, therefore, BiI_n, BiI_{n-1}, BiI_{n-3}, and BiI_{n-4}. The best straight line gives values of K_{n-3} of $2.77 \times 10^2 M^{-1}$ and A'''' for this wavelength of 0.292. Similar calculations at 465 and 470 mμ gave values of K_{n-3} of 2.82 and 2.63 $\times 10^2 M^{-1}$, respectively, and a limiting absorbance of the new species of zero.

Experiments in the Absence of a Reducing Agent.

—It has been shown[3] that hypophosphorous acid is capable of forming weak complexes with bismuth in acid solution. The possibility of the formation of mixed-ligand complexes containing the reducing agent has been ruled by experiments, similar to those discussed above, carried out in the absence of the reducing agent and dissolved oxygen.
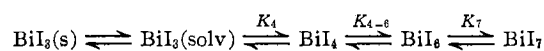
No significant difference could be detected between the absorbance spectra of corresponding solutions above an iodide concentration of 0.007 M. It may be assumed, therefore, that the reducing agent cannot compete with the iodide as a ligand, and, even in competition with water, the effect is negligible.

Stability of Complexes in Solution—Precipitation of Bismuth Trioxide.

—The absorbance spectra of solutions containing 0.45 M reducing agent and iodide at a concentration of 0.04 M or above were found to be reproducible after a period of 2 months. Similarly in the absence of the reducing agent and oxygen the corresponding solutions were stable for at least 2 days. No attempt was made to keep these solutions for longer periods. This range of iodide concentration corresponds to the presence of the top three complexes.

At lower iodide concentrations a precipitate formed which, over a period of a few days, grew to hexagonal platelike crystals with a metallic luster. The iodide concentration at which the precipitate forms, the speed with which it forms, and the amount formed were found to depend on the concentration of hypophosphorous acid present.

The Value of n.

—The black precipitate formed at low iodide concentrations is BiI_3. Since the absorbance maxima of solutions containing the fourth species do not shift to shorter wavelength during the slow precipitation stage, it is reasonable to assume that this species is a solvated form of BiI_3 or a mixed-ligand complex containing three iodide ions and one or more $H_2PO_2^-$ ions. In the absence of further clarification the formula $BiI_3(solv)$ is used. This assumption would fix the value of n, in the range of iodide concentration studied, to a value of 7. The transitions involved are therefore

$$BiI_3(s) \rightleftharpoons BiI_3(solv) \underset{}{\overset{K_4}{\rightleftharpoons}} BiI_4 \underset{}{\overset{K_{4-6}}{\rightleftharpoons}} BiI_6 \underset{}{\overset{K_7}{\rightleftharpoons}} BiI_7$$

The conclusions are in agreement with the findings of Ahrland and Grenthe in that in both cases the dominant species in the range of iodide concentration covered is BiI_6.

Solutions of Bismuth Iodide Complexes and Beer's Law.

—The most fundamental requirement of a spectrophotometric study is the adherence of the absorbance of solutions to Beer's law. All of the equations derived by Newman and Hume applied here are based partially on this law. Furthermore, in the derivation of their equations, the assumption has been made that polymeric species are not formed. The formation of polymeric species would be indicated by failure of the law for solutions at high bismuth concentrations. Burnett[11] has claimed that at an iodide concentration of 0.0602 M (1% KI) Beer's law is obeyed by measurements at 460 mμ. Lisicki and Boltz[12] using an iodide concentration of 0.34 M claim that the iodide method should be limited to between 0.6 and 6 ppm when meas-

(11) B. B. Burnett, University Microfilms, Ann Arbor, Mich., Publication No. 6992.
(12) N. M. Lisicki and D. F. Boltz, *Anal. Chem.*, **27**, 1722 (1955).

urements are made at 337 mμ. It may be presumed that they found that Beer's law is not followed outside these limits.

For these reasons adherence to Beer's law was tested at a number of representative iodide concentrations. Concentrations of 1.2, 0.2, 0.04, and 0.007 M iodide were selected for study.

Solutions were prepared containing these total iodide concentrations, 5, 20, 50, 100, and 0 ppm of bismuth, 0.45 M hypophosphorous acid, and 1 M perchloric acid and sodium perchlorate to bring the total ionic strength to 2.2 M.

Consideration of the Beer's law plots at the four iodide concentrations and the spectra from which they were obtained led to the following observations.

(1) At high iodide concentrations, 1.2 M, Beer's law is strictly obeyed at all wavelengths where measurements are possible up to a bismuth concentration of at least 100 ppm (4.78 $\times$ 10^{-4} M).

(2) As the iodide concentration decreases, Beer's law begins to fail. At moderate concentrations, 0.2 M iodide, the failure occurs only at and above bismuth concentrations of 100 ppm but is adhered to strictly up to at least 50 ppm. When the concentration of iodide is fixed at 0.04 M, failure occurs above 15 ppm, while at an iodide concentration of 0.007 M, adherence even up to 15 ppm is doubtful.

(3) At an iodide concentration of 0.007 M a precipitate appeared in the 50- and 100-ppm bismuth solutions.

(4) If a straight line is drawn through zero and the absorbance at 5 ppm and if one then takes deviations of subsequent points above this line as positive and those below as negative, then the following observation may be made. Failure of Beer's law is always positive on the long-wavelength side of any absorbance band and negative on the short-wavelength side.

(5) A shift occurs in the position of the bands in the absorbance spectra to longer wavelengths as the bismuth concentration is increased but only in the case of the lower two iodide concentrations.

(6) At high bismuth concentrations, 100 ppm, absorbance at some wavelengths is higher in the case of the 0.04 M iodide solution than for the 1.2 or 0.2 M solutions.

The reason for the failure of Beer's law under certain circumstances as presented in the above observations may be discussed in the light of subsequent experience under a number of headings.

(i) **Complexes Present at Different Iodide Concentrations.**—As has already been shown, between iodide concentrations of 0.4 and 2 M only the complexes BiI$_7$ and BiI$_6$ are present when the total bismuth concentration is 15 ppm or below. Below an iodide concentration of 0.4 M and above 0.04 M a third complex, BiI$_4$, is added to the system. Below 0.04 M two forms of a fourth species are added, namely, BiI$_3$-(solv) and solid bismuth triiodide. Certainly at a concentration of 0.005 M the solutions become unstable and this has been attributed to the reaction

$$\text{BiI}_3(\text{solv}) \rightleftharpoons \text{BiI}_3(\text{s})$$
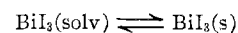
Increasing the total bismuth concentration will naturally increase the absolute amount of total BiI$_3$ present. Since the hypophosphorous acid content is constant, the amount of bismuth triiodide precipitate, relative to the amount in solution, as BiI$_3$(solv), will increase with increasing bismuth concentration.

A second possible solid species which may be present especially at low iodide and high bismuth concentrations is solid, finely divided bismuth metal, as a result of reduction by hypophosphorous acid.

(ii) **Effect on Absorption Spectra of the Presence of Solid Species.**—There are two opposed effects of the presence of a solid species.

First, the conversion of the solvated BiI$_3$ to a precipitate and the reduction of bismuth complexes or ions to the metal will reduce the concentration of absorbing species and bring about a reduction of the absorbance over the full range of wavelengths.

Second, the presence of solid material will scatter light, the extent of scattering increasing slightly as one moves to shorter wavelengths. This will be registered on the recorder as an increase in absorbance over the whole range of wavelengths, the increase being greater at shorter wavelengths. This will also affect the position of the bands in the absorbance spectra, moving them by a very small amount to shorter wavelengths which is, in fact, the opposite of what is observed.

Of the two effects on the absorbance noted above the second is slightly greater and undoubtedly responsible to a certain extent for the positive deviations from Beer's law. This cannot, however, account for the negative deviations.

(iii) **Beer's Law and Mixture of Complexes.**—It can readily be shown that mixtures of monatomic complexes will obey Beer's law if the iodide concentration is constant and the molar absorptivities remain constant.

In the solutions used for these experiments the total iodide concentration was kept constant. The bismuth concentration varied from 5 ppm (2.39 $\times$ 10^{-5} M) to 100 ppm (4.78 $\times$ 10^{-4} M). At a total iodide concentration of 1.2 M when all of the bismuth is converted to BiI$_6$ plus BiI$_7$, at most (4.78 $\times$ 10^{-4}) $\times$ 7 M or approximately 0.003 M iodide would be used in complex formation. This is less than 0.3% of the total and the concentration of iodide may be regarded as being constant within the limits of experimental error.

At lower iodide concentrations this does not hold for solutions of high bismuth concentration. The effect of a reduction of iodide is to increase the concentrations of the lower species relative to the higher. This in turn would bring about a reduction of absorbance at most wavelengths (cf. the absorption spectra of the constituents, Figure 6). It would also result in a shift of the absorption bands to shorter wavelengths with consequent positive deviations from Beer's law on the short-wavelength side of all bands and a negative deviation on the other side. This is, in fact, the opposite of what is observed.

(iv) **Shifting of the Absorbance Bands.**—The shift-

ing of the absorbance bands in the spectra to longer wavelengths is obviously the key to the positive deviations from Beer's law on the one side of the bands and negative deviation on the other.

The position of an absorbance band in the spectrum of a mixture of complexes is dependent on the relative concentrations of the individual complexes. Provided the ratio of the concentrations of the individual complexes is constant, the position of the composite band will be fixed and is independent of the total concentration of each complex. Since the relative concentration of monomeric complexes is dependent on iodide concentration only, it follows that at constant iodide concentration the positions of bands should not change.

It has already been pointed out that the slight decrease in iodide concentration which takes place would move the band in the opposite direction to that noted.

It was suggested above that when the BiI_3 is first formed it remains in solution as a solvated species which depends on the presence of hypophosphorous acid. In the experiments being discussed here the hypophosphorous acid concentration is kept constant. Therefore as the absolute amount of the BiI_3 species is increased, with increasing bismuth concentration, without a corresponding increase in the solvating material, a relatively greater amount of BiI_3 will exist in the solid as opposed to the solvated form in solution. These two forms of BiI_3 do not have the same absorbance spectra, *i.e.*, molar absorptivities.

Thus while at constant iodide concentration the relative concentrations of the various complexes is constant, the average effective molar absorptivity of the third species is decreasing. This effectively reduces the "pull" by this species to shorter wavelengths and the absorption bands move to longer wavelengths causing positive deviations from Beer's law on the high-wavelength side of the band and a negative deviation from Beer's law on the low-wavelength side, as shown in Figure 5.

One may conclude that polymeric species are not formed at these concentrations unless they have absorbance spectra almost identical with those of the monomeric species which is unlikely. Also, these experiments lend weight to the hypothesis that BiI_3 in the presence of hypophosphorous acid exists in two forms, $BiI_3(s)$ and $BiI_3(solv)$ in solution.

Resolved Absorption Spectra of the Complexes.— The establishing of the values of the successive formation constants makes it possible to calculate the resolved spectra of each complex by a more simple method than that using the Newman–Hume equations.

It has been shown that in the range of iodide concentrations from 0.4 to 2 M only the top two species are present in detectable amounts. Thus from

$$\frac{[BiI_7]}{[BiI_6][I]} = 0.14; \quad [BiI_7] + [BiI_6] = [Bi]_{total}$$

the individual concentrations of the two complexes may be calculated at any iodide concentration in the
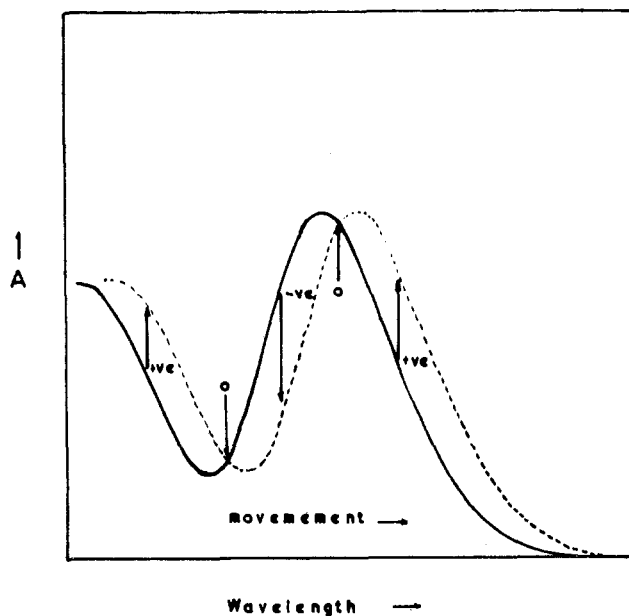

Figure 5.—Deviations from Beer's law. Effect of moving bands to longer wavelengths.

above range. Two concentrations were selected, 0.4 and 1.0 M. The absorbances, A_1 and $A_{0.4}$, of solutions of these complexes at iodide concentrations of 1.0 and 0.4 M and at any particular wavelength are given by

$$A_1 = E_7[BiI_7]_1 + E_6[BiI_6]_1$$
$$A_{0.4} = E_7[BiI_7]_{0.4} + E_6[BiI_6]_{0.4}$$

E_7 and E_6 are the molar absorptivities at the particular wavelength being studied. Substituting the limiting absorbance at the appropriate wavelength divided by the total bismuth concentration for E_7 and E_6 and substituting for the concentration of the complexes, one can solve for the limiting absorbances of BiI_7 and BiI_6.

By similar reasoning the concentration of three species present at an iodide concentration of 0.04 M may be calculated. The concentration of BiI_7 was found to be only 0.02% of the total and was therefore ignored. From the absorbance of the solution at any wavelength, one can calculate the limiting absorbance of BiI_4.

The limiting absorbance spectrum of $BiI_3(solv)$ was calculated in a similar manner from the absorbance spectrum of a solution having an iodide concentration of 0.007 M. Thus the values of A', A'', A''', and A'''' may be obtained at any wavelength by measuring the total absorbance, at that wavelength, of the 1.0, 0.4, 0.04, and 0.007 M iodide solutions.

The resolved absorbance spectra of the four top complexes each at a concentration of 7.2×10^{-5} M are shown in Figure 6.

It should be born in mind that errors in the determination of the values of the successive formation constants lead to errors in the calculation of the value of the limiting absorbance of each species and that these errors are accumulative. Furthermore, it has been shown that the neutral third species probably does not exist as a simple hydrated complex in solution but as a complex involving hypophosphorous acid. For these
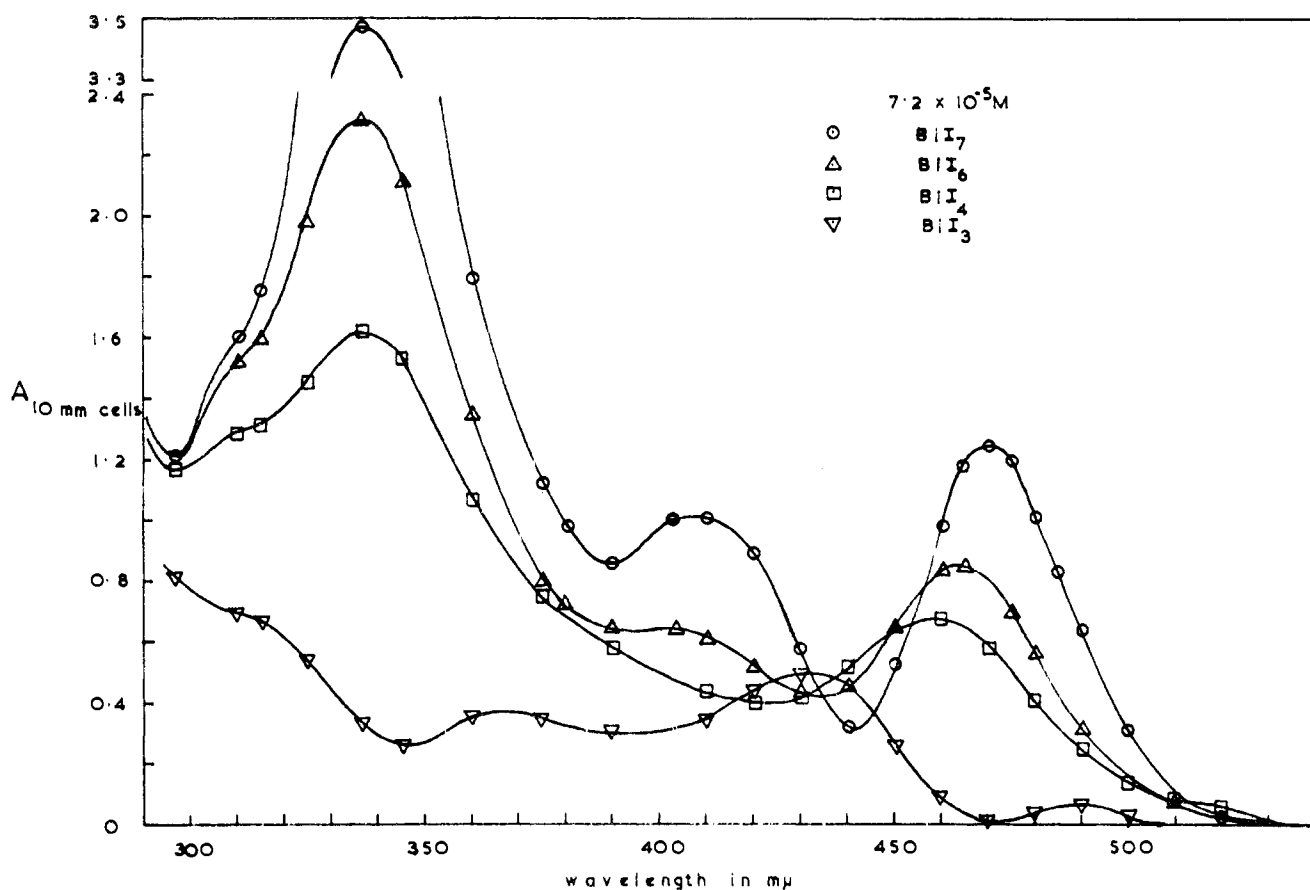
Figure 6.—Resolved spectra of bismuth iodide complexes.

reasons no great degree of accuracy can be claimed, or is claimed, for the spectrum of BiI_3, given in Figure 6.

Comparison with Previously Published Results.— The results published by Ahrland and Grenthe and those of Babko and Golub are presented in the form of over-all formation constants. Since the value of K for the reaction $BiI_3(solv) \rightleftharpoons BiI_3(s)$ is not known, it is not possible to calculate β values from the successive formation constants given above. Thus no comparison is possible with the work of Babko and Golub, who report only the value 3.2×10^{11} for the sixth formation constant (β_6). From the results of Ahrland and Grenthe, however, it is possible to calculate the values of successive formation constants and to compare them with the results reported here. Summarizing the two sets of results, we have for Ahrland and Grenthe

$$BiI_3(s) \xrightleftharpoons{K'_4} BiI_4 \xrightleftharpoons{K'_5} BiI_5 \xrightleftharpoons{K'_6} BiI_6$$
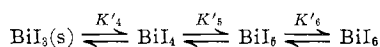
$K'_6 = 100 \ M^{-1}; \quad K'_5 = 70.8 \ M^{-1}; \quad K'_4 = 7.23 \times 10^4 \ M^{-1}$

and from the present work

$$BiI_3(solv) \xrightleftharpoons{K_4} BiI_4 \xrightleftharpoons{K_{4-6}} BiI_6 \xrightleftharpoons{K_7} BiI_7$$
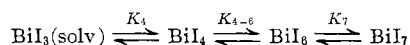
$K_7 = 0.14 \ M^{-1}; \quad K_{4-6} = 270 \ M^{-2}; \quad K_4 = 260 \ M^{-1}$

Comparison of these two sets of results leads to the following observations and conclusions.

The previous report made no reference to a species higher than $[BiI_6{}^{3-}]$. This is understandable since the highest iodide concentration used was only 0.1 M.

At this concentration only 1.2% of the total bismuth would have been present as $[BiI_7{}^{4-}]$ and would not have been detected.

Comparison of K_4 and K'_4 is not possible since they undoubtedly refer to different reactions. If it may be assumed that both values are correct, then, on combination, we obtain for the reaction $BiI_3(solv) \rightleftharpoons BiI_3(s)$ a value of an equilibrium constant of the order of 2.8 $\times$ 10^2.

In the present work no evidence could be found of the existence of the species $[BiI_5{}^{2-}]$ and this led to a careful reexamination and reinterpretation or the results of Ahrland and Grenthe.[4]

Reference to Table IX in the original paper[4] shows that over a considerable range of iodide concentration the value of X'_6 is constant; *i.e.*, the slope at the point of intersection, β_5, is zero indicating the nonexistence of the fifth species. This finding may be confirmed by a consideration of the results of the solubility studies. Since the method of calculation applied is one of extrapolation to an iodide concentration of infinity the results of most significance in the extrapolation are those at high ligand concentration. From a graphical reexamination of the results reported on pp 1124 and 1125 of the original paper[4] it would appear that the inclusion of the four most significant values of the function LX'_5 leads to an intercept of zero indicating the absence of the species $[BiI_5{}^{2-}]$.

Combination of the published figures for β_6, β_5, and β_4 gives a value of K_{4-6} of 7080 M^{-2} which is in fair

agreement with the result of 270 M^{-2} reported here when one considers that previously published figures for β_6 have differed by a factor of 2×10^7.

It is suggested, therefore, that there is no conclusive evidence for the existence of the species BiI_5^-, and

$$\frac{[BiI_7^{4-}]}{[BiI_6^{3-}][I^-]} = 1.4 \ (\pm 0.1) \times 10^{-1} \ M^{-1}$$

$$\frac{[BiI_6^{3-}]}{[BiI_4^-][I^-]^2} = 2.70 \ (\pm 0.05) \times 10^2 \ M^{-2}$$

$$\frac{[BiI_4^-]}{[BiI_3(solv)][I^-]} = 2.6 \ (\pm 0.1) \times 10^2 \ M^{-1}$$

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Vibrational Spectra and Force Constants of Zn(NCO)₄²⁻, Zn(NCS)₄²⁻, and Zn(NCSe)₄²⁻ [1]

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The Raman spectra and supplementary infrared data are reported for the tetrahedral tetraisocyanate, -isothiocyanate, and -isoselenocyanate complex anions of the type $Zn(NCX)_4^{2-}$, X = O, S, Se. Vibrational assignments are given. A complete vibrational analysis and force constant calculation was carried out *via* Wilson's *F–G* matrix method using a general valence force field. Off-diagonal *F* matrix elements were included in certain cases. A significant increase in the C–X (X = O, S, Se) force constant is observed upon coordination of N–C–X⁻. The C–N force constant is less affected. The potential energy distribution among the symmetry coordinates was calculated for each species and considerable mixing is evident in the low-energy modes of $Zn(NCSe)_4^{2-}$.

Introduction

There have recently been a number of infrared studies of metal pseudohalide complexes[2–6] in which assignments were made of the bands occurring below 600 cm⁻¹. In order to put these assignments on a firmer basis we have obtained Raman spectra and additional infrared data on zinc complexes of three pseudohalides. With fairly complete vibrational data in hand, we carried out complete vibrational analyses and force constant calculations for these complexes.

Experimental Section

The anions were studied in the form of their tetraethylammonium salts. The preparations of these compounds have been described previously: $[(C_2H_5)_4N]_2[Zn(NCO)_4]$,[7] $[(C_2H_5)_4N]_2$-$[Zn(NCS)_4]$,[4] and $[(C_2H_5)_4N]_2[Zn(NCSe)_4]$.[8] The tetraethylammonium cation was chosen for two reasons: (a) its large size confers on the compounds a high solubility in organic oxy solvents (*i.e.*, about 100% w/w in nitromethane) and (b) it has no absorption in the 700–100-cm⁻¹ region in the infrared. The spectra were run in organic solvents to eliminate the solvolysis effects possible in aqueous solutions.

The infrared spectra in the range 3000–200 cm⁻¹ were obtained with a Beckman IR 12 spectrophotometer and in the range 200–130 cm⁻¹ with a Perkin-Elmer 301 spectrophotometer. Raman spectra were obtained with a Cary 81 spectrophotometer.

Considerable experimental difficulty was encountered in an

attempt to obtain the Raman spectrum of the isoselenocyanate complex, since it tended to decompose fairly rapidly in the tube, depositing a thin film of a red material (presumably red elemental selenium or polymeric selenocyanogen) on the walls.

Results

The vibrational frequencies observed are listed in Table I.

The infrared results for $[(C_2H_5)_4N]_2[Zn(NCO)_4]$ were taken from ref 2, except for ν_{11} which was observed in nitromethane solution. (The numbering and descriptions of the fundamental vibrations are those of Miller and Carlson.[9]) The Raman results were obtained on a saturated nitromethane solution. The uncertainty in the position of ν_3 is because of the overlap of ν_3 and ν_{11}.

The data for the isothiocyanato complex are the most complete of the three ions studied. The infrared and Raman spectra for $Zn(NCS)_4^{2-}$ are shown in Figures 1 and 2. We have not observed any combinations which might involve the inactive T_1 modes. The lowest energy E and T_2 fundamentals were also not observed; however, our calculations (*vide infra*) indicate that these N–Zn–N bending modes occur at very low frequencies (<40 cm⁻¹). Some doubt must remain about the assignments of ν_5 and ν_{13}, since the band at 168 cm⁻¹ represents a solid-state infrared measurement. It is possible that the band at 150 cm⁻¹ observed in the Raman spectrum of a solution is the T_2 mode (Raman and infrared active) shifted from its position in the solid state. However, none of the other T_2 funda-

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