it is believed that the actual value is within one unit of 33.0.

Acknowledgment.—The authors are indebted to K. L. Elmore and L. H. Hull for constructive criticism of the paper.

Summary

Conductance measurements for phosphoric acid were made over a wide range of concentration.

Conductance measurements for sodium and potassium dihydrogen phosphate were made from dilute solutions practically up to saturation.

The cation transference numbers were measured in dilute orthophosphoric acid.

The limiting conductance of the dihydrogen phosphate ion was determined to be 33.0 ± 1.0.

WILSON DAM, ALABAMA RECEIVED OCTOBER 20, 1948

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

A Spectrophotometric Investigation of Bismuth Thiocyanate Complexes[1]

BY WM. DAVID KINGERY[2] AND DAVID N. HUME

Both the normal salt, $Bi(SCN)_3 \cdot 14H_2O$, and a series of red complex salts with the type formulas $M^{I}_3[Bi(SCN)_6]$ and $M^{II}_3[Bi(SCN)_6]_2$ are well known and have been prepared as crystalline compounds by previous workers.[3,4] The amber to red color obtained by addition of excess alkali thiocyanate to an acidic bismuth nitrate or chloride solution has been observed to migrate to the anode in transference experiments[4] and is generally assumed to be due to the presence of the $Bi(SCN)^{\equiv}_6$ ion. The color reaction is quite sensitive and has been suggested for the colorimetric determination of small amounts of bismuth.[5] The existence of $TlBi(SCN)_4$ has also been claimed,[4] leading to the inference that the $Bi(SCN)^-_4$ ion may also exist in solution.

The purpose of this research has been to determine the bismuth thiocyanate complexes present in solution by means of spectrophotometric analysis. A combination of the method of continuous variations, introduced by Job[6] and further developed by Vosburgh and Cooper,[7] with a logarithmic analysis similar to that used by Bent and French[8] has served to demonstrate the existence of several complex ions in the mixture and permit their stability constants to be measured.

Experimental

Measurements.—Absorption measurements below 355 mμ were made with a Beckman model DU Quartz Photoelectric Spectrophotometer. Measurements at wave lengths above 355 mμ were made with a Coleman model 14 Photoelectric Spectrophotometer using a Coleman PC 6 filter for all readings given, except those at 400 mμ shown in Fig. 2, which were made using a Coleman PC 4 filter. The same cells were used for all measurements on each instrument, and oriented in the same direction. In all cases, measurements were made with reference to a blank solution containing all constituents save one, namely, the color-forming constituent in lowest concentration. This technique served to compensate for the effects due to small amounts of impurities in the reagents. All measurements were made at room temperature, 20–25°, and the measurements of optical density are accurate within about 1% under the conditions used in this investigation.

Materials.—Solutions were prepared from freshly opened bottles of commercial C.P. bismuth oxide, perchloric acid and sodium thiocyanate. Small amounts of color-forming impurities varied with each container. However, by using materials from the same containers for all measurements involving intercomparisons, and by the uniform use of "blank" corrections, any small effects of these impurities were cancelled.

Perchloric acid was used for acidification since it transmits well in the ultraviolet as well as in the visible section of the spectrum, and is known to have little or no tendency to form complexes.

Results and Discussion

A large number of mixtures of bismuthyl perchlorate and sodium thiocyanate in perchloric acid were prepared and their absorption characteristics determined. The bismuth concentration was varied between 0.00003 and 0.8 *M*, and the thiocyanate concentration was varied between 0.00005 and 4.0 *M*. When all the measurements were corrected to a common path length for comparison, it was found that curves for all intermediate concentrations and ratios of bismuth to thiocyanate fell between two extremes. The solutions with very low thiocyanate and high bismuth concentrations showed maximum absorption in the vicinity of 270 mμ and no absorption above 350 mμ. The other limiting case, the solutions with very high thiocyanate and low bismuth concentrations, showed absorption peaks at 335 and 270 mμ with the absorption extending well into the visible region (Fig. 1). All curves for high thiocyanate solutions were observed to have the same shape above 350 mμ suggesting that only one complex was absorbing in this region. Similarly, with very high bismuth to

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[2] Present address: Division of Ceramics, Department of Metallurgy, Massachusetts Institute of Technology, Cambridge 39, Massachusetts.

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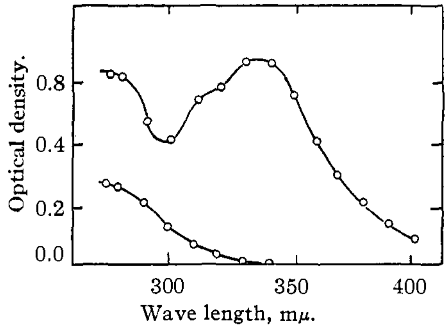

Fig. 1.—Limiting absorption curves of bismuth–thiocyanate mixtures: upper curve—0.000030 *M* Bi, 4.0 *M* NaSCN, 0.02 *M* $HClO_4$ against 4.0 *M* NaSCN, 0.02 *M* $HClO_4$ as the reference solution. Lower curve—0.000050 *M* NaSCN, 0.8 *M* Bi, 5.0 *M* $HClO_4$ against 0.8 *M* Bi, 5.0 *M* $HClO_4$; path 10.00 mm.

thiocyanate ratios, the shape of the curve was observed to be independent of thiocyanate concentration if below 0.01 *M*. This was taken as indicating the probable existence of only one ion absorbing significantly under these conditions.

Application of the Method of Continuous Variations.—For an equilibrium reaction such as

$$A + nB = AB_n$$

a series of equimolar mixtures prepared by adding x liters of B to $(1 - x)$ liters of A will in general have varying optical densities. If Y, the difference between the value of optical density found and the value calculated for no reaction, is plotted against x, a maximum or minimum will be obtained when $n = x/(1 - x)$. This is the "method of continuous variations."[6,7]

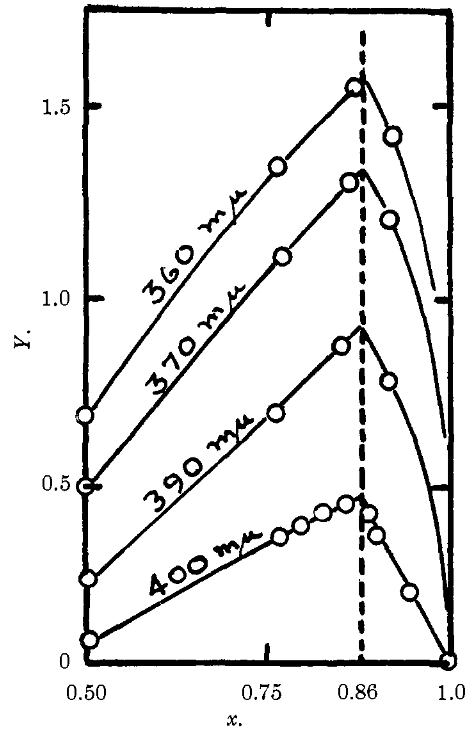

Fig. 2.—Method of continuous variations, bismuth hexathiocyanate: $(1 - x)$ 0.1 *M* Bi in 0.4 *M* $HClO_4$, and x 0.1 *M* NaSCN in 0.4 *M* $HClO_4$.

When 0.1 *M* bismuth and 0.1 *M* thiocyanate solutions in 0.4 *M* perchloric acid were mixed and examined spectrophotometrically at wave lengths of 360, 370, 380, 390, and 400 mμ, the curves shown in Fig. 2 were obtained. The maximum observed when the fraction of thiocyanate in the mixture equals 0.86 ± 0.01, indicates the formation of the bismuth hexathiocyanate ion, $\mathrm{Bi(SCN)_6^{\equiv}}$, which has a theoretical maximum at 0.857. On examination of mixtures of solutions 0.005 *M* in bismuth and 0.005 *M* in thiocyanate (in 0.1 *M* perchloric acid) at wave lengths of 275, 280, 285, and 290 mμ, the curves shown in Fig. 3 were obtained. Here the maximum is obtained when the fraction of thiocyanate in the mixture equals 0.50 ± 0.05, corresponding to the formation of the bismuth monothiocyanate ion, $\mathrm{BiSCN^{++}}$ which should lead to a maximum at 0.50.

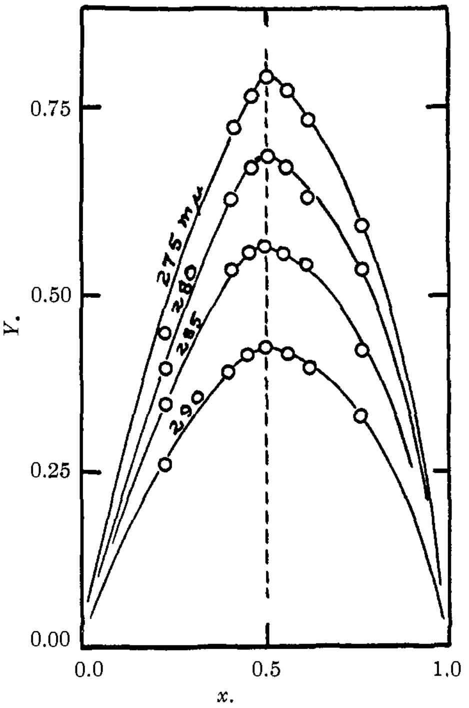

Fig. 3.—Method of continuous variations, bismuth monothiocyanate: $(1 - x)$ 0.005 *M* Bi in 0.1 *M* $HClO_4$, and x 0.005 *M* NaSCN in 0.1 *M* $HClO_4$.

Since no evidence was found for complexes higher than the hexathiocyanate, the extinction coefficient of the hexathiocyanate ion could be determined by measurements in solutions containing very high thiocyanate to bismuth ratios. For solutions 0.000025 *M* in bismuth, and increasing thiocyanate concentration, the plot

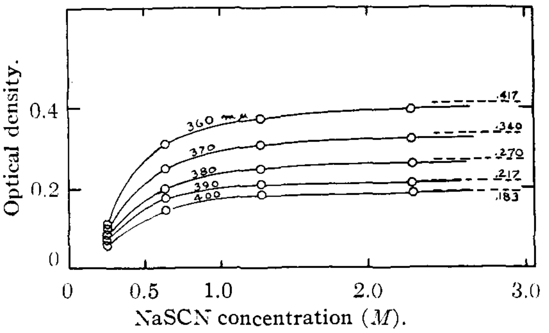

Fig. 4.—Optical density of 0.000025 *M* Bi (0.02 *M* $HClO_4$) and increasing thiocyanate concentration, asymptotic limits indicated.

shown in Fig. 4 was obtained. The asymptotes approached correspond to the optical densities of 0.000025 *M* bismuth hexathiocyanate ion. The products of cell length (approx. 2 cm. in the Coleman Spectrophotometer) and extinction coefficient were found to be 16600, 13600, 10800, 8700, and 7400 at wave lengths of 360, 370, 380, 390, and 400 mμ, respectively, thus providing a means of measuring bismuth hexathiocyanate concentration.

A similar series of experiments at high bismuth to thiocyanate ratios was used to estimate the extinction coefficients of the $BiSCN^{++}$ ion. In order to repress hydrolysis of the bismuth in the more concentrated solutions, it was necessary to work in 5.0 *M* perchloric acid. Since the highest bismuth concentrations obtained were insufficient to yield reliable values of the extinction coefficients by simple extrapolation of the curves, a method of successive approximations was employed. The chemical reaction involved is

$$Bi^{III}_{(\text{uncomplexed})} + SCN^- \rightleftharpoons BiSCN^{++}$$

At constant acidity, the degree of hydrolysis of the free bismuth or bismuthyl ion is constant and proportional to the total concentration of uncomplexed bismuth. Hence we may write

$$[BiSCN^{++}]/[SCN^-][Bi_{(\text{uncomplexed})}] = k_1$$

The observed values of the optical density at each wave length were used to fit the unknown constants in the system: the extinction coefficient and k_1.

The results, obtained with the Beckman Spectrophotometer and a path length of 10.00 mm., are shown in Fig. 5. The molecular extinction coefficients at 275, 280, 290 and 300 mμ were found to be 5720, 5580, 4400, and 2520, respectively. The average value of k_1 obtained was 10.7, with an estimated uncertainty, due to the physical measurements, of ± 0.5.

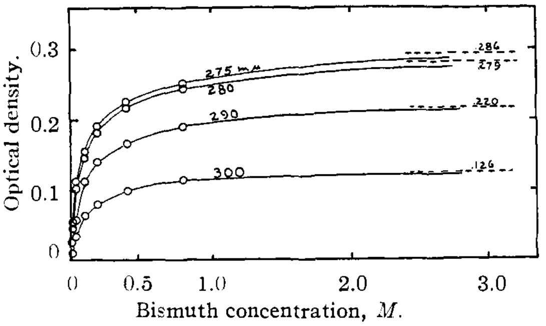

Fig. 5.—Optical density of 0.000050 *M* NaSCN (5.0 *M* $HClO_4$) and increasing bismuth concentration, calculated asymptotic limits indicated.

Application of the Logarithmic Plot Method.—In a concentration range where a single reaction such as

$$AB_n + mB = AB_{(n+m)}$$

predominates, useful information may be obtained by converting the mass action expression $[AB_{n+m}]/[AB_n][B]^m = k_{n+m}$ to the logarithmic form

$$\log \frac{[AB_{n+m}]}{[AB_n]} = \log k_{n+m} + m \log [B]$$

It is seen that a plot of $\log ([AB_{n+m}]/[AB_n])$ against $\log [B]$ should yield a straight line with a slope of m and an intercept equal to $\log k_{n+m}$. This treatment was applied to solutions containing only uncomplexed bismuth and the monothiocyanate complex ($m = 0$, $n = 1$) in 0.4 *M* perchloric acid, with the result shown in Fig. 6. Here, actually, the $\log ([BiSCN^{++}]/[SCN^-])$ was plotted against the $\log [Bi^{III}]$ for convenience. The observed slope was 1.00 ± 0.05 and the value of k_1 equalled 14 ± 0.5. The difference from the value in 5.0 *M* perchloric acid is surprisingly small.

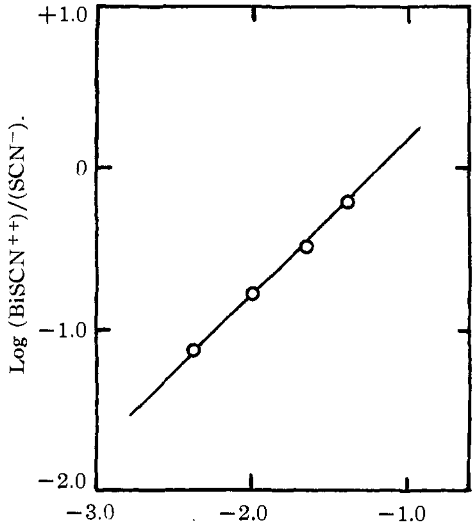

Fig. 6.—Variation of $\log (BiSCN^{++})/(SCN^-)$ with log [Bi uncomplexed]: 0.000050 *M* NaSCN in 0.4 *M* $HClO_4$; slope equals 1.00.

A similar treatment of the data obtained by measurements on the $Bi(SCN)_6$ ion at low bismuth and high thiocyanate ion concentrations yielded

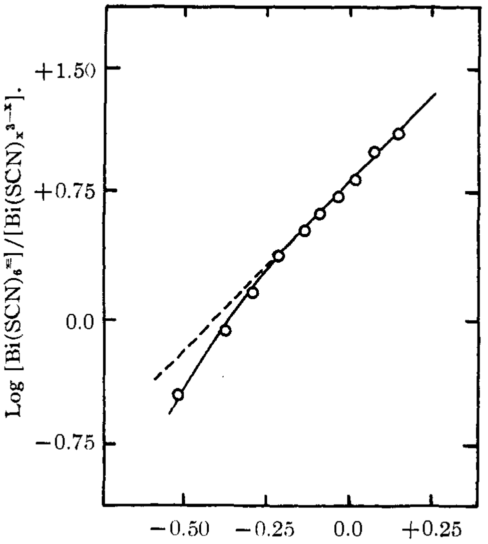

Fig. 7.—Variation of log $[\mathrm{Bi(SCN)_6^{\equiv}}]/[\mathrm{Bi(SCN)_x^{3-x}}]$ with log $(\mathrm{SCN^-})$: 0.000050 *M* bismuth in 0.02 *M* $\mathrm{HClO_4}$; slope equals 2.00.

the result shown in Fig. 7. The slope of 2.00 ± 0.05 obtained with values of the thiocyanate concentration higher than 0.5 *M* clearly indicates $n = 2$ and shows the existence of the colorless $\mathrm{Bi(SCN)_4^-}$ ion in these solutions. Conversely, it may be seen that no appreciable amount of pentathiocyanate complex is formed. The equilibrium constant, k_6, for the reaction

$$\mathrm{Bi(SCN)_4^-} + 2\mathrm{SCN^-} = \mathrm{Bi(SCN)_6^{\equiv}}$$

was found to be 6.6 ± 0.1 in 0.4 *M* perchloric acid. From this value and the directly determined concentration of the hexathiocyanate ion, the concentration of tetrathiocyanate ion in equilibrium with the hexathiocyanate ion was calculated for a considerable number of thiocyanate concentrations between 0.3 and 3 *M*. The results are shown graphically in Fig. 9. At thiocyanate concentrations greater than 0.5 *M*, the tetra- and hexa-complexes account for all the bismuth present, but below 0.5 *M* a significant amount is present in another form or forms.

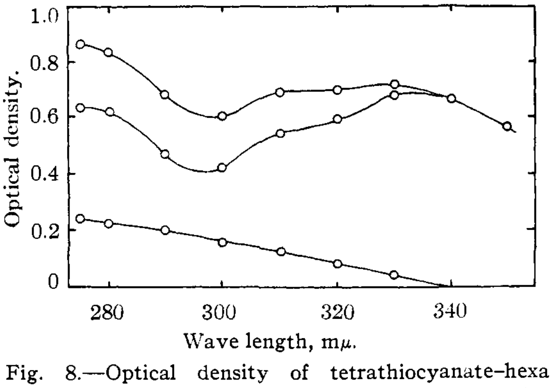

Fig. 8.—Optical density of tetrathiocyanate–hexathiocyanate mixture: upper curve, total optical density; middle curve, calculated optical density of bismuth hexathiocyanate; lower curve, difference; optical density of bismuth tetrathiocyanate.

Examination of the absorption curves of bismuth in thiocyanate mixtures showed that although the extinction coefficients of the hexathiocyanate ion were independant of thiocyanate concentration at wave lengths greater than 340 mμ, increased absorption appeared at wave lengths below 340 mμ, particularly when the thiocyanate concentration was less than 1.0 *M* (Fig. 8). In 0.5 *M* thiocyanate, for example, the optical density at 340 mμ indicated the presence of 3.07 × 10^{-5} *M* hexathiocyanate ion. From k_6, the concentration of tetrathiocyanate in the equilibrium mixture must be 1.88 × 10^{-1} *M*. The differences between the observed absorption curve of the mixture and the calculated absorption curve for the hexathiocyanate give the absorption curve of the tetrathiocyanate ion and a means of determining its extinction coefficients. These were found to be 1020, 960, 570, and 220 at 280, 300, 320, and 330 mμ, respectively. Further examination of the absorption curves showed that the unidentified constituent in Fig. 9 absorbed only below 300 mμ. The asymmetry of the curves in Fig. 3 can probably be attributed to this absorption.

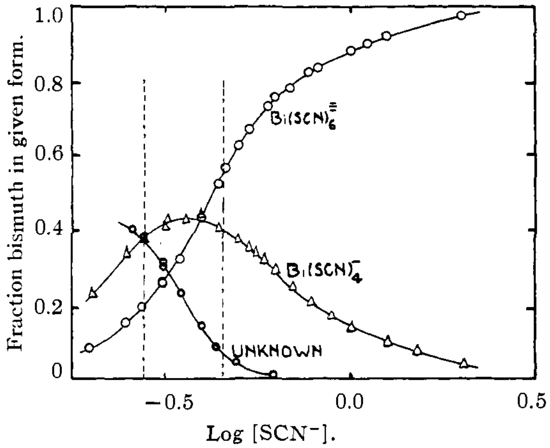

Fig. 9.—Complexes formed with varying thiocyanate concentrations.

If the unidentified portion of the bismuth in thiocyanate solutions of intermediate concentrations were present predominantly in the form of a single ionic species, treatment of the data of Fig. 9 by the logarithmic plot method should yield an interpretable straight line. This was tried and the result (Fig. 10) was a straight line with a slope of 2.1 ± 0.1 between 0.25 and 0.50 *M* thiocyanate. This indicates that the unaccounted for bismuth is essentially all in the form of the dithiocyanate complex, and conversely, that un-ionized bismuth thiocyanate is not formed in any appreciable amount. The

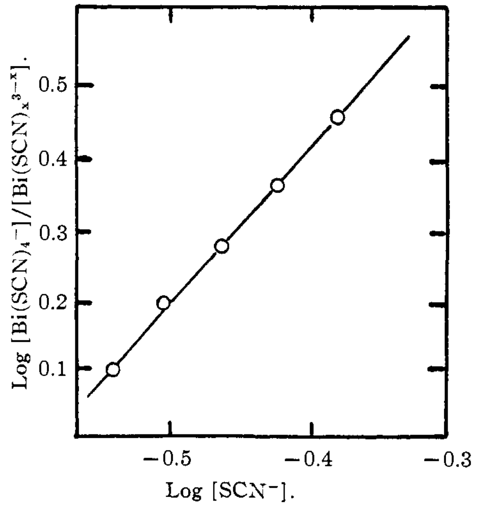

Fig. 10.—Variation of log $[Bi(SCN)_4^-]/[Bi(SCN)_x^{3-x}]$ with log $[SCN^-]$ in 0.4 *M* $HClO_4$; slope equals 2.06.

equilibrium constant k_4 was found to be equal to 14 ± 1 from this plot.

From the known values of k_1, k_4 and k_6, and the measured extinction coefficients, it was then possible to calculate the distribution of bismuth between the various forms as a function of thiocyanate concentration from 0.001 to 0.01 *M* and from 0.06 to 8.0 *M*. The overlapping of absorption curves of the four complex ions prevented direct resolution of the mixtures obtained between 0.01 and 0.06 *M* thiocyanate. The curves in Fig. 11 were obtained by plotting the calculated distribution and interpolating between 0.01 and 0.06 *M*. This entailed little difficulty since none of the curves involved had maxima in this comparatively short range. The accuracy of the interpolation in the monothiocyanate and dithiocyanate curves was checked by taking several points in this region and applying the logarithmic plot method (Fig. 12). The resulting straight line with slope of 0.96 confirms the correctness of the fit of the curves in Fig. 11 to the experimental data. The corresponding equilibrium constant, k_2, for the reaction

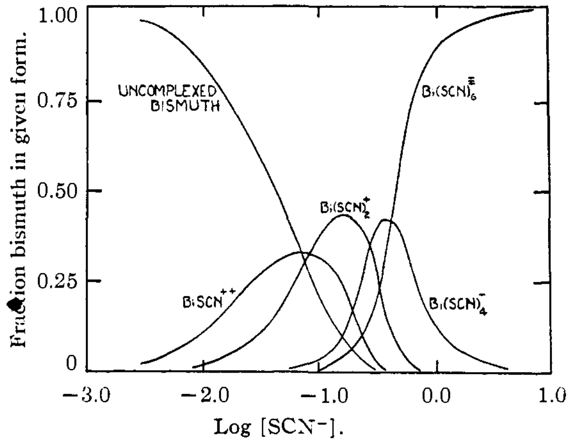

Fig. 11.—Bismuth thiocyanate complexes formed in 0.4 *M* $HClO_4$ at varying thiocyanate concentrations.

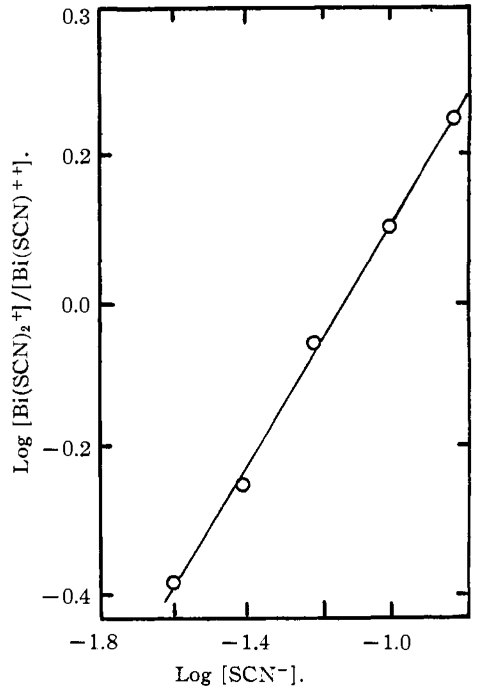

Fig. 12.—Variation of log $[Bi(SCN)_2^+]/[Bi(SCN)^{++}]$ with log $[SCN^-]$ in 0.4 *M* $HClO_4$; slope equals 0.96.

$$BiSCN^{++} + SCN^- = Bi(SCN)_2^+$$

was found to be 13 ± 1.

Summary

A combination of the method of continuous variations and a method of logarithmic plotting was found useful in the spectrophotometric elucidation of the structure of bismuth thiocyanate complex ions in perchloric acid solutions.

1. It was found that in solution, the tri- and pentathiocyanate complexes of bismuth, exist in negligible amounts in comparison to the mono-, di-, tetra- and hexathiocyanate complexes.
2. The fraction of bismuth present in the uncomplexed form and in the form of mono-, di-, tetra- and hexathiocyanate complexes was determined as a function of the thiocyanate concentration in 0.4 *M* perchloric acid solution (Fig. 11).
3. Equilibrium constants were determined in 0.4 *M* perchloric acid solution and found to be:

$k_1 = [BiSCN^{++}]/[SCN^-][Bi_{uncomplexed}] = 14 \pm 0.5$
$k_2 = [Bi(SCN)_2^+]/[SCN^-][BiSCN^{++}] = 13 \pm 1.0$
$k_4 = [Bi(SCN)_4^-]/[SCN^-]^2[Bi(SCN)_2^+] = 14 \pm 1.0$
$k_6 = [Bi(SCN)_6^{\equiv}]/[SCN^-]^2[Bi(SCN)_4^-] = 6.6 \pm 0.1$

CAMBRIDGE, MASSACHUSETTS

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