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A Study of Thiocyanatoargentate(I) Ions by a Solubility Method

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The solubility of silver thiocyanate has been measured as a function of potassium thiocyanate concentration up to 2.2 *m* at constant ionic strength. Three complex ions, $\text{Ag}(\text{SCN})_2^-$, $\text{Ag}(\text{SCN})_3^-$ and $\text{Ag}(\text{SCN})_4^-$ have been shown to exist in these solutions and their formation constants have been evaluated for two different reference states, one being a 2.2 *m* solution of potassium nitrate, the other an infinitely dilute solution. For the former reference state at 25°, the formation constants of the di-, tri- and tetrathiocyanatoargentate ions were found to be 3.7×10^7 , 1.2×10^9 and 1.2×10^{10} , respectively.

The ready solubility of silver thiocyanate in solutions containing free thiocyanate ion has generally been assumed to be a result of the formation of stable complex thiocyanatoargentate ions. Hellwig² who was the first to measure the solubility of silver thiocyanate as a function of alkali thiocyanate concentration, made no attempt to interpret the data quantitatively, and Randall and Halford³ who essentially repeated Hellwig's work were able to conclude only that their data could not be explained by assuming the formation of the dithiocyanato ion alone. Ferrell, Ridgeon and Riley⁴ obtained from potentiometric titrations, data which they felt could be interpreted at least qualitatively in terms of the formation of mono-, di- and tri-thiocyanato complex ions with formation constants of the order of 10^{11} . Several investigators have shown the existence of compounds of potassium and silver thiocyanates in the solid state: namely, $\text{AgSCN} \cdot \text{KSCN}$,⁵ $\text{AgSCN} \cdot 2\text{KSCN}$ ^{5b,c,d} and $\text{AgSCN} \cdot 3\text{KSCN}$,^{5c,d} this last substance being unstable in the solid state. It was the purpose of the present investigation to measure at constant ionic strength the solubility of silver thiocyanate in potassium thiocyanate over a wide range of thiocyanate concentrations, and to determine if possible the nature of the complex ions formed and their formation constants.

Experimental

Materials.—The silver thiocyanate was prepared from standard solutions of reagent grade silver nitrate and recrystallized reagent grade potassium thiocyanate, both made up in conductivity water. For the solubility determinations in solutions up to 0.5 *M* in potassium thiocyanate, the well-washed silver thiocyanate was stored until used in a 2 *M* solution of recrystallized reagent grade potassium nitrate in conductivity water. Just before use, it was washed with the particular thiocyanate solution to be used, then bottled with this latter solution. For the solubility determinations in solutions more concentrated than 0.5 *M* in potassium thiocyanate, the above procedure of washing with the thiocyanate solution was impractical due to the high solubility of silver thiocyanate; therefore, the well-washed silver thiocyanate was dried to constant weight at 110°, and the dry solid bottled with the particular thiocyanate solution. Solutions containing thiocyanate at concentrations above 0.04 *M* were prepared from reagent grade potassium nitrate and thiocyanate, and distilled water was used. For thio-

cyanate concentrations below 0.04 *M*, recrystallized reagents in conductivity water were used.

Preparation of Saturated Solutions.—Borosilicate glass bottles, 125-ml. capacity waxed on the inside, and coated with black lacquer on the outside were used. The neoprene stoppers were waxed at the end in contact with the solution. The bottled mixtures were brought to equilibrium by mechanical rotation through a 15-cm. radius at the rate of 30 r.p.m. in a water thermostat at $25 \pm 0.05^\circ$. The saturated solutions were separated from the solids by centrifuging; this was found preferable to filtration through fritted glass, and tests proved that the separation was excellent in solutions which were 2.2 *m* in ionic strength. Occleshaw^{5d} has shown that for solutions even more concentrated than 2 *m* in potassium thiocyanate, silver thiocyanate is the stable solid phase at equilibrium. This fact was confirmed in the present work in the following way. The solid phase after it had reached equilibrium with a 2 *M* solution of potassium thiocyanate was analyzed gravimetrically for silver by weighing as silver chloride. The equilibrium phase was found to contain 65.0% silver, the theoretical value for AgSCN being 65.02%.

Tests of Equilibrium.—The period of time required for the attainment of equilibrium was determined for various initial concentrations of potassium thiocyanate. Equilibrium was approached from under saturation in all cases except that of the 0.005 *M* solution of potassium thiocyanate; for it, equilibrium was approached from both directions. From the results, given in Table I, one week was chosen as the equilibrium period for solutions 0.5 *M* or more in potassium thiocyanate, and two weeks for solutions less concentrated than 0.5 *M*.

The period required for attainment of equilibrium is evident for all the solutions in Table I except for the 0.04 *M* potassium thiocyanate solution; for it, a graph of the molarity of dissolved silver versus the period of time needs to be plotted whereupon it becomes evident that equilibrium is approached sufficiently closely after two weeks of mixing.

TABLE I

RATES OF APPROACH TO EQUILIBRIUM SILVER THIOCYANATE-POTASSIUM THIOCYANATE-POTASSIUM NITRATE SYSTEMS

All solutions 2 *M* in ionic strength, $T = 25^\circ$

Initial molarity of KSCN	Period of mixing in days	Measured molarity of dissolved silver	Method of analysis for silver	Equilibrium from:
2.0	1	0.444	Gravimetric	Below
2.0	6	0.443	Gravimetric	Below
0.3	1	3.28×10^{-3}	Polarographic	Below
.3	4	3.27×10^{-3}	Polarographic	Below
.3	10	3.28×10^{-3}	Polarographic	Below
.08	2	1.23×10^{-4}	Polarographic	Below
.08	16	1.27×10^{-4}	Polarographic	Below
.04	2	2.72×10^{-5}	Polarographic	Below
.04	16	3.07×10^{-5}	Polarographic	Below
.005	7	1.46×10^{-6}	Colorimetric	Below
.005	35	1.49×10^{-6}	Colorimetric	Above
.005	36	1.45×10^{-6}	Colorimetric	Below

Methods of Analysis.—The equilibrium solutions were freed of solid phase by centrifuging, and then aliquots were analyzed for silver by one of three methods devised espe-

(1) From the Doctoral Dissertation of G. C. B. Cave, 1951. Procter and Gamble Fellow, 1950-1951.

(2) K. Hellwig, *Z. anorg. Chem.*, **25**, 157 (1900).

(3) M. Randall and J. O. Halford, *THIS JOURNAL*, **52**, 178 (1930).

(4) E. Ferrell, J. M. Ridgeon and H. L. Riley, *J. Chem. Soc.*, 1121 (1936).

(5) (a) G. Bodländer and W. Eberlein, *Z. anorg. Chem.*, **39**, 197 (1904); (b) H. W. Foote, *Am. Chem. J.*, **30**, 330 (1903); *Z. physik. Chem.*, **46**, 79 (1903); (c) H. L. Wells and H. F. Merriam, *Am. Chem. J.*, **28**, 265 (1902); (d) V. J. Occleshaw, *J. Chem. Soc.*, 2404 (1932).

cially for the purpose. For solutions 0.5 *M* or more in thiocyanate, a gravimetric method was used; it consisted in the destruction of all the dissolved thiocyanate by boiling with nitric acid for one-half hour, neutralization of almost all of the excess acid, addition of a few drops of 2 *M* potassium thiocyanate, and the eventual weighing of the silver as the thiocyanate. For solutions from 0.04 to 0.5 *M* in thiocyanate, the concentration of silver was measured with a Sargent Model XXI recording polarograph, a mixture 1 *M* in potassium nitrate and 1 *M* in potassium thiocyanate serving as the supporting electrolyte.⁶ For solutions 0.04 *M* or less in thiocyanate, the latter was destroyed with nitric acid and the silver determined colorimetrically by the *p*-dimethylaminobenzalrhodanine method suitably modified to permit its use in solutions initially 2 *M* in potassium nitrate.⁷ The equilibrium solutions were analyzed also for total thiocyanate by precipitating and weighing it as silver thiocyanate. Densities of solutions, both before contact with silver thiocyanate and after equilibration with this solid phase, were measured in the usual way at 25° with 25-ml. specific gravity bottles.

A value for the solubility of silver thiocyanate in water also was required. For this purpose a nephelometric method was developed. Equilibrium was approached from above and from below saturation, the concentration of the suspension of silver thiocyanate being determined by use of a multiplier-phototube nephelometer of our own design to measure the intensity of the Tyndall beam. Proper precautions were taken to minimize the suspended dust in the solutions by using redistilled conductivity water and operating in an essentially dust-free atmosphere. However, the silver thiocyanate sol proved a difficult one to work with at the very low concentrations (about 10⁻⁶ *M*) necessary, leading to an uncertainty of about ±3% in the solubility reported; but this degree of accuracy was quite adequate for the present purpose, as will be evident below.

Experimental Results

These results consist of the measured solubilities of silver thiocyanate in solutions of potassium thiocyanate made up to 2.2 *m* in ionic strength with potassium nitrate, and of the measured concentrations of the thiocyanate in these solutions. For solutions up to 0.5 *m* in potassium thiocyanate, only the initial thiocyanate concentrations are

TABLE II

EXPERIMENTAL RESULTS AND COMPUTED VALUES OF FUNCTIONS DEFINED BY EQUATIONS (6) AND (7)

The value for the solubility in 0.02 *m* potassium thiocyanate was omitted from this table because of the large inherent error in the polarographic method at this low concentration of silver.

Molal solubility of AgSCN		KSCN, molality	10 ⁴ S _{Ag} /m _{SCN} ⁻	(10 ⁴ S _{Ag} /m _{SCN} ⁻) ^{-2.5}	Free SCN ⁻ , molality (calc.)
Measured S _{Ag} ⁺	Calc. eq. (9)				
1.62 × 10 ⁻⁶	1.62 × 10 ⁻⁶	0.00548	2.96	84	0.00548
3.65 × 10 ⁻⁶	3.52 × 10 ⁻⁶	.01033	3.53	100	.01033
3.00 × 10 ⁻⁵	2.95 × 10 ⁻⁵	.04133	7.27	116	.04127
3.36 × 10 ⁻⁵	3.37 × 10 ⁻⁵	.04440	7.58	115	.04434
7.99 × 10 ⁻⁵	7.52 × 10 ⁻⁵	.06662	12.0	143	.06646
1.39 × 10 ⁻⁴	1.40 × 10 ⁻⁴	.08885	15.7	149	.08854
2.38 × 10 ⁻⁴	2.32 × 10 ⁻⁴	.1111	21.5	171	.1105
3.56 × 10 ⁻⁴	3.58 × 10 ⁻⁴	.1334	26.8	183	.1326
7.24 × 10 ⁻⁴	7.22 × 10 ⁻⁴	.1779	41.1	219	.1760
1.28 × 10 ⁻³	1.27 × 10 ⁻³	.2224	58.4	255	.2191
2.21 × 10 ⁻³	2.18 × 10 ⁻³	.2744	82.2	297	.2686
2.28 × 10 ⁻³	2.24 × 10 ⁻³	.2774	83.9	300	.2715
3.70 × 10 ⁻³	3.63 × 10 ⁻³	.3343	114	344	.3246
8.26 × 10 ⁻³	7.57 × 10 ⁻³	.4443	195	453	.4240
0.0146	0.0134	.5572	280	534	.5202
.0146	.0132	.5536	282	540	.5177
.0376	.0308	.7783	540	770	.6970
.0981	.0716	1.114	1050	1122	.934
.2684	.1750	1.688	2113	1863	1.270
.5061	.3090	2.252	3282	2127	1.542

(6) G. C. B. Cave and D. N. Hume, *Anal. Chem.*, **24**, 558 (1952).

(7) G. C. B. Cave and D. N. Hume, *ibid.*, **24**, 1503 (1952).

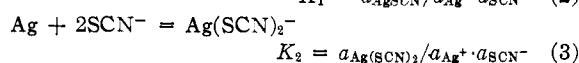
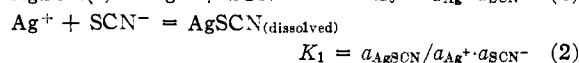
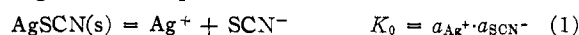
reported since the analyses of three equilibrium solutions (0.005, 0.04 and 0.1 *m* in potassium thiocyanate) showed that the differences between the initial and the equilibrium concentration of the thiocyanate were of the order 0.7% of the concentration present, and hence were not significant for the subsequent theoretical treatment of these data.

Table II gives in column 1 the measured solubility of silver thiocyanate in the corresponding potassium thiocyanate solution given in column 3; all concentrations have been converted to molalities, and all solutions were initially 2.2 *m* in ionic strength, through the addition of potassium nitrate.

From nephelometric measurements, the solubility of silver thiocyanate in water was estimated to be 1.1 × 10⁻⁶ *m*. The error in this value is probably of the order ± 0.1 × 10⁻⁶ *m*.

Theoretical Interpretation of the Solubility Measurements.—It is assumed for the lower concentrations of thiocyanate at least, that only mononuclear complex ions exist; the results of Bodländer and Eberlein^{8a} seem to substantiate this.

The first members of the series of possible thermodynamic formation constants and their corresponding chemical equations are



etc.

K_0 is the activity product, variously symbolized in the literature.

Conforming to usual practice, the symbol for the free silver ion has been used exclusively in equations (1) to (3). However, it seems more reasonable to suppose that this ion in water exists preponderantly as the tetrahydrate⁸; in potassium nitrate solution silver ion may even be present in part as weakly-bound nitrate complexes, but apparently this has not been investigated experimentally. In the present work it will be presumed that the silver ion exists as the tetrahydrate, so that Ag-(H₂O)₄⁺ is to be understood wherever Ag⁺ appears. The consequence of this presumed hydration is that the activity of water, raised to the appropriate power, will occur in the numerator of equations (2) to (3), etc., and in the denominator of equation (1). The effect of this factor, although negligible in dilute solutions, may become significant at high salt concentrations and should be considered whenever complex formation takes place with metal ions.

By introducing molal activity coefficients, denoted by γ , and by denoting the molal solubility of silver thiocyanate by S_{Ag} , and the equilibrium molality of the thiocyanate ion by m_{SCN^-} , we have

$$S_{\text{Ag}} = \frac{K_0}{\gamma_{\text{Ag}^+} \gamma_{\text{SCN}^-} m_{\text{SCN}^-}} + \frac{K_0 K_1}{\gamma_{\text{AgSCN}}} + \left[\frac{K_0 K_2 \gamma_{\text{SCN}^-}}{\gamma_{\text{Ag}(\text{SCN})_2^-}} \right] m_{\text{SCN}^-} + \left[\frac{K_0 K_3 \gamma^2 \text{SCN}^-}{\gamma_{\text{Ag}(\text{SCN})_3^-}} \right] m_{\text{SCN}^-}^2 + \left[\frac{K_0 K_4 \gamma^3 \text{SCN}^-}{\gamma_{\text{Ag}(\text{SCN})_4^-}} \right] m_{\text{SCN}^-}^3 + \dots \quad (4)$$

This equation relates the solubility of silver thio-

(8) H. B. Jonassen and P. C. Yates, unpublished results reported at ONR Symposium on Complex Ions, Chicago, 1950.

cyanate, S_{Ag} , to the equilibrium molal concentration of the thiocyanate ion, m_{SCN^-} , and contains explicitly the thermodynamic formation constants, K_1, K_2, K_3, K_4 —of all the possible mononuclear complex ions.

Since the lowest molality of thiocyanate ion to be used is $0.00548 M$, for which the solubility of silver thiocyanate is $1.62 \times 10^{-6} M$, and since the activity product, K_0 , is 1.13×10^{-12} when calculated from the e.m.f. data of Pearce and Smith,⁹ the first term on the right side of equation (4) is negligible in comparison with S_{Ag} , for all the data to be used.

When the solubility of silver thiocyanate is plotted against the corresponding molality of the thiocyanate ion, and a short extrapolation made toward zero molality of added thiocyanate ion, then it is evident that the intercept of the curve on the solubility axis is of the order $10^{-7} M$ or less. Hence, since the first term on the right side of equation (4) is negligible, the second term is also negligible except possibly for one solubility measurement, that of silver thiocyanate in $0.0548 M$ potassium thiocyanate. As additional confirmation of this conclusion, the solubility of silver thiocyanate in water has been found in the present work by a nephelometric method to be about $1.1 \times 10^{-6} m$, while the activity product of 1.13×10^{-12} computed from the data of Pearce and Smith⁹ leads to a value of $1.06 \times 10^{-6} m$ for the concentration of silver ions in an aqueous solution saturated with silver thiocyanate. Therefore, the molality of undissociated silver thiocyanate is negligible in comparison with the values to be used for S_{Ag} . The above arguments are not, of course, to be interpreted as meaning that silver thiocyanate molecules are necessarily absent in the equilibrium solutions.

For convenience the bracketed terms in equation (4) will be symbolized A, B, D , etc., and the solubility multiplied by 10^4 , whence for thiocyanate solutions $0.005 M$ or more, equation (4) becomes

$$S_{Ag} \times 10^4 = Am_{SCN^-} + Bm_{SCN^-}^2 + Dm_{SCN^-}^3 + \dots \quad (5)$$

It is necessary to determine if the parameters A, B, D, \dots , etc., are functions of the composition of the equilibrium solution, at constant pressure and temperature. Certainly for a constant activity of the water, the thermodynamic formation constants K_0 to K_4 (and any higher) are independent of the composition of the equilibrium solution at any one temperature and pressure.

It remains only to consider how the activity coefficients vary with changing composition of solution. All the relevant activity coefficients are for negative ions; and the stoichiometric molality of potassium ions is $2.2 m$ for every solution. Moreover, at least for solutions up to $0.5 m$ in potassium thiocyanate the ionic strength is essentially constant, although at higher molalities the ionic strength will increase as the concentrations of polyvalent complex ions become significant. Therefore, Brønsted's theory of "specific ionic interaction"¹⁰ was assumed to be valid up to at least $0.5 m$ in thiocyanate. On this basis, the activity coefficient of the thiocyanate ion should have been

reasonably constant, and close to the mean activity coefficient of a $2.2 m$ potassium thiocyanate solution alone; for it was estimated by Kielland¹¹ that the activity coefficients of potassium and of thiocyanate ions are almost exactly equal up to an ionic strength of 0.1. Brønsted's theory would indicate that the activity coefficients of any thiocyanatoargentate ions were reasonably constant also, providing their molalities were low; at relatively high molalities, they would produce an increase in ionic strength.

Equation (5) may be transformed to the following two equivalent forms

$$\frac{S_{Ag} \times 10^4}{m_{SCN^-}} = A + Bm_{SCN^-} + Dm_{SCN^-}^2 + \dots \quad (6)$$

$$\frac{S_{Ag} \times 10^4 - A}{m_{SCN^-}} = B + Dm_{SCN^-} + \dots \quad (7)$$

In order to evaluate the constants, A, B and D , the functions were plotted using first measured and then, in successive approximations, corrected values for the free thiocyanate molalities. Values for A and B were obtained by extrapolation; D by use of the slope of the straight line which fortunately resulted for equation 7 below $0.4 m$ thiocyanate. After three approximations, calculated and observed solubilities agreed, within experimental error, up to about $0.4 m$ thiocyanate. The complete data for the third and final approximation are given in Table II.

Figure 1 is a plot of the values computed by using the left side of equation (6) against the final calculated molality of the free thiocyanate ion;

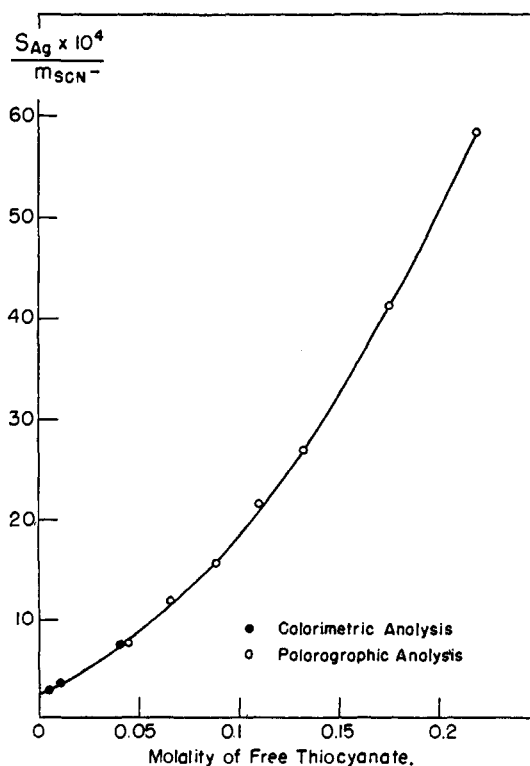


Fig. 1.—Plot of equation (6) as a function of free thiocyanate concentration.

(9) J. N. Pearce and L. Smith, *THIS JOURNAL*, **59**, 2063 (1937).

(10) J. N. Brønsted, *ibid.*, **44**, 877 (1922); **45**, 2898 (1923).

(11) J. Kielland, *ibid.*, **59**, 1675 (1937).

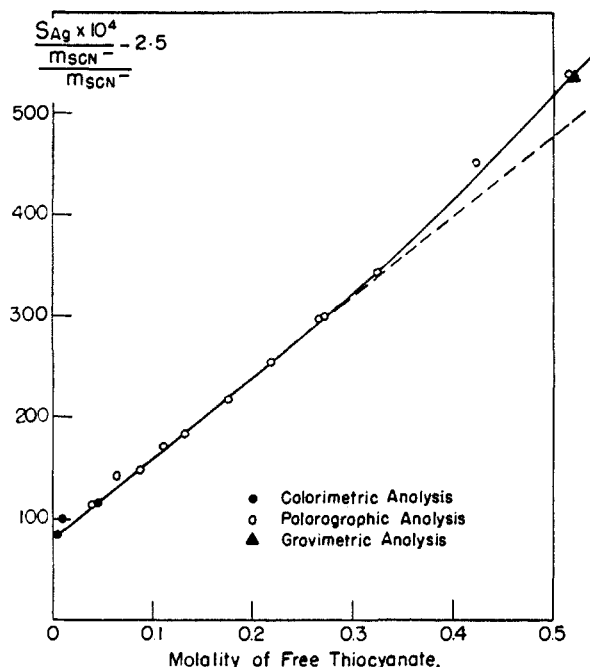


Fig. 2.—Plot of equation (7) as a function of free thiocyanate concentration.

from this curve $A = 2.5$. Figure 2 is a plot of the values computed by using the left side of equation (7) against the equilibrium molality of thiocyanate ion; from this curve $B = 80$ and $D = 790$. An inspection of Fig. 2 shows that for all points below $0.4 M$ in thiocyanate, there is nothing to suggest that the curve is significantly different from a straight line. Therefore, the closed-form equation

$$S_{Ag} \times 10^4 = 2.5m_{SCN^-} + 80m^2_{SCN^-} + 790 m^3_{SCN^-} \quad (9)$$

is necessary and sufficient to represent the solubility measurements below $0.4 m$ in thiocyanate. The solubility behavior up to this concentration can then be interpreted as being due to the existence of three species of thiocyanatoargentate ions, namely $Ag(SCN)_2^-$, $Ag(SCN)_3^{2-}$ and $Ag(SCN)_4^{3-}$. The proportions of these ions present at various molalities of free thiocyanate computed from the values of A , B and D are shown graphically in Fig. 3.

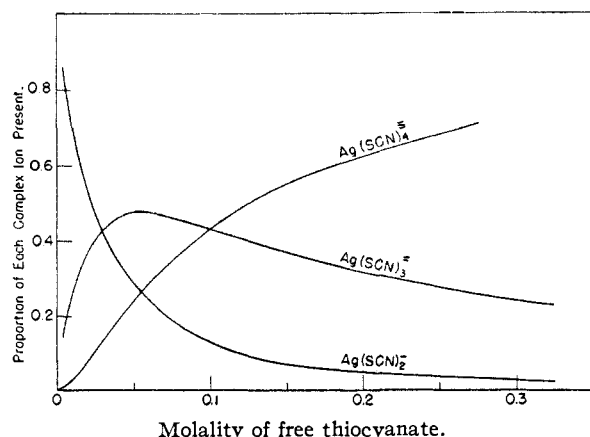


Fig. 3.—Distribution of dissolved silver among the several complex ions as a function of free thiocyanate concentration.

There are two plausible explanations why the curve of Fig. 2 deviates systematically from the straight line, above about $0.4 m$ in thiocyanate; one is that the B and the D of equation (5) may really be functions of the equilibrium molality of the thiocyanate ion. The other is that additional species of complex ion exist. There are no experimental results, either published or in the present work, which permit an unequivocal exclusion of either of these proposed explanations. Mathematically, the problem reduces to having only two equations of condition, namely, (5) and (8), but having at least three unknowns, B , D and m_{SCN^-} .

From the work of Scatchard¹² and Scatchard and Prentiss¹³ on mixtures of electrolytes, it seems doubtful that variations in the values of the relevant activity coefficients can account completely for the deviations depicted in Fig. 2.

By assuming the existence of additional mononuclear complex ions higher than the trivalent one, an analytical expression can be obtained to represent the measured solubilities more closely for a short concentration range above $0.4 m$ than does the series terminating in the cubic term in m . However, this cannot properly explain the deviations, since the fundamental problem is to explain an increase, not a decrease, in the ratio of the equilibrium molalities of silver to free thiocyanate. The solubility data at the higher molalities of thiocyanate, therefore, point to the existence of polynuclear complexes of which $Ag_3(SCN)_6^{3-}$ is a likely example. The formation constants of this, and several other possible species of polynuclear complexes, are inextricably a part of the parameters B and D of equation (5). Therefore, the solubility data alone cannot provide an unambiguous picture of what and how many complex ions are contributing to the observed effect at high thiocyanate concentrations.

Estimation of the Thermodynamic Formation Constants.—These were estimated for $Ag(SCN)_2^-$, $Ag(SCN)_3^{2-}$ and $Ag(SCN)_4^{3-}$ on the basis that the silver ion exists as a tetrahydrate, and with an infinitely dilute solution as the thermodynamic reference state. On substituting the values found for A , B and D and introducing explicitly the activity of the water we have

$$K_2 = 2.5 \times 10^{-4} \frac{\gamma_{Ag(SCN)_2^-}}{\gamma_{SCN^-} K_0 a_{H_2O}^2}$$

$$K_3 = 0.008 \frac{\gamma_{Ag(SCN)_3^{2-}}}{\gamma_{SCN^-}^2 K_0 a_{H_2O}}$$

$$K_4 = 0.079 \frac{\gamma_{Ag(SCN)_4^{3-}}}{\gamma_{SCN^-}^3 K_0} \text{ and}$$

$$K_0 = \frac{[a_{Ag(H_2O)^+}][a_{SCN^-}]}{a_{H_2O}^4}$$

The activity of the water was calculated to be 0.950 for a $2.2 m$ solution of potassium nitrate; this value was found in the usual way, by using the value 0.653 for the osmotic coefficient of a $2.2 m$ solution of potassium nitrate, interpolated from the osmotic coefficients given by Robinson and Stokes.¹⁴

(12) G. Scatchard, *Chem. Revs.*, **19**, 309 (1936).

(13) G. Scatchard and S. S. Prentiss, *THIS JOURNAL*, **56**, 2320 (1934).

(14) R. A. Robinson and R. H. Stokes, *Trans. Faraday Soc.*, **45**, 612 (1949).

The standard potential of the silver thiocyanate electrode was calculated from the e.m.f. data of Pearce and Smith¹⁰ and the values of -0.3338 v. for the potential of the $0.1 N$ calomel electrode¹⁵ and 0.769 for the activity coefficient of potassium thiocyanate in $0.1 M$ solution.¹⁵ The resulting value, $E^0 = -0.0921$ v., combined with MacInnes' value for the standard potential of the silver-silver ion electrode¹⁶ and the correction for the activity of water in $0.1 M$ potassium thiocyanate gave for the activity product of silver thiocyanate

$$K_0 = (a_{\text{Ag}(\text{H}_2\text{O})_4^+} a_{\text{SCN}^-})/a^{\text{H}_2\text{O}} = 1.13 \times 10^{-12}$$

The data of Pearce and Smith were selected in preference to those of others because they appeared to involve the fewest and least important correction factors.

In order to estimate the activity coefficient of the thiocyanate ion, Brønsted's theory of "specific ion interaction" was assumed, and the evidence given by Kielland¹¹ that the potassium and thiocyanate ions have essentially equal activity coefficients in dilute solutions of potassium thiocyanate was taken to imply that this would also be true in moderately concentrated solutions. This led to the conclusion that the activity coefficient of the thiocyanate ion, in solutions $2.2 m$ both in ionic strength and in concentration of potassium ion, will be 0.553 , by interpolation in the values for the activity coefficient of potassium thiocyanate, given by Robinson and Stokes.

The activity coefficient of the dithiocyanatoargentate ions was assumed equal to that of the free thiocyanate ions.

For the other thiocyanatoargentate ions, the usual Debye-Hückel expression was used to obtain approximate values of the activity coefficients in solutions $2.2 m$ in ionic strength. The "effective ionic diameters" of the complex ions were assumed to be equal, and a reasonable value was estimated to be 6 \AA . Thus at 25° , the molal activity coefficient for $\text{Ag}(\text{SCN})_3^-$ was calculated to be 0.17 , and for $\text{Ag}(\text{SCN})_4^{2-}$, 0.019 .

(15) D. A. MacInnes, "The Principles of Electrochemistry," Reinhold Publ. Corp., New York, N. Y., 1939, p. 248.

(16) D. A. MacInnes, *ibid.*, p. 254.

On substituting the values found above for the activity of the water, the activity product of silver thiocyanate, and the activity coefficients of the various negative ions, the following values result for the thermodynamic formation constants of the mono-, di- and trithiocyanatoargentate ions

$$\frac{[a_{\text{Ag}(\text{SCN})_2(\text{H}_2\text{O})_2^-}][a_{\text{H}_2\text{O}}]^2}{[a_{\text{Ag}(\text{H}_2\text{O})_4^+}[a_{\text{SCN}^-}]^2} \equiv K_2 = 2.4_6 \times 10^8$$

$$\frac{[a_{\text{Ag}(\text{SCN})_3(\text{H}_2\text{O})^-}][a_{\text{H}_2\text{O}}]^3}{[a_{\text{Ag}(\text{H}_2\text{O})_4^+}[a_{\text{SCN}^-}]^3} \equiv K_3 = 4.1_4 \times 10^9$$

$$\frac{[a_{\text{Ag}(\text{SCN})_4^{2-}}][a_{\text{H}_2\text{O}}]^4}{[a_{\text{Ag}(\text{H}_2\text{O})_4^+}[a_{\text{SCN}^-}]^4} \equiv K_4 = 7.8_6 \times 10^9$$

Instead of choosing the thermodynamic reference state to be a solution which is infinitely dilute with respect to a particular solute, it may be expedient to choose the reference state to be a solution which is $2.2 m$ in potassium nitrate, and to adopt this state as the standard state for the water. It is then necessary to compute a value of K_0 referred to this new reference state. This was done by applying Brønsted's theory, and by assuming that the activity coefficients of the anion and of the cation were equal for silver nitrate and for potassium thiocyanate. Then, on using the data of Robinson and Stokes for the mean activity coefficients of $2.2 m$ solutions of silver nitrate and of potassium thiocyanate, it was calculated that in a $2.2 m$ solution of potassium nitrate saturated with silver thiocyanate, $\gamma_{\text{Ag}^+} = 0.300$ and $\gamma_{\text{SCN}^-} = 0.553$.

Hence, referred to a $2.2 m$ potassium nitrate solution as the reference state, the formal formation constants defined above becomes

$$K_0' = 6.75 \times 10^{-12}$$

$$K_2' = 3.7 \times 10^7$$

$$K_3' = 1.2 \times 10^9$$

$$K_4' = 1.2 \times 10^{10}$$

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