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

A Polarographic Study of the Cadmium Thiocyanate Complexes[1]

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The half-wave potential of the cadmium ion was determined in potassium nitrate-potassium thiocyanate mixtures over the range of 0.1–2.0 *M* thiocyanate at an ionic strength of 2.00. Application of a previously described method of mathematical analysis to the data revealed the existence of four reaction products: $CdSCN^+$, $Cd(SCN)_2$, $Cd(SCN)_3^-$ and $Cd(SCN)_4^=$ with formation constants of 11, 56, 6 and 60, respectively.

In order to provide data for a test of the method for the determination of consecutive formation constants described in the previous paper,[4] the half-wave potential of cadmium as a function of thiocyanate concentration was measured with high precision. The range of thiocyanate concentrations used was 0.1 to 2.0 *M* and the solutions were kept at an ionic strength of 2.00 with potassium nitrate in order to minimize changes in the activity coefficients with composition of solution. Previous work had shown both that the cadmium–thiocyanate system was a promising one for this type of study[4] and that complex formation between cadmium and nitrate is negligible in this range of concentration.[5]

Experimental

Apparatus.—Measurements were made with a Sargent Recording Polarograph, Model XXI. Corning marine barometer tubing was used for the capillary, which had a value of 1.91 for $m^{2/3}t^{1/6}$ at the potential of the S.C.E. The conventional "H" cell was employed with the solution to be examined in one arm and saturated potassium nitrate in the other arm. The two arms of the "H" cell were separated by a sintered glass disk and an agar plug saturated with potassium nitrate. The connection to the saturated calomel reference electrode was through a flexible saturated potassium chloride salt bridge dipping into the saturated potassium nitrate arm of the "H" cell.[6] The resistance of the cell system was found to be 256 ohms as measured by a 1000-cycle a.c. bridge. This resistance did not change noticeably as the composition of the thiocyanate–nitrate mixture was varied.

A constant-temperature water-bath held at 30 ± 0.1° was used for all measurements, and the calomel reference electrode was kept immersed in the bath. The potential of the calomel electrode was checked against a new Beckman calomel cell, both dipping into saturated potassium chloride, and was found to agree within 1 millivolt. The water-bath dropping mercury cathode, and one side of the 115 a.c. input to the polarograph were all grounded. This was found to be necessary for stable operation.

Materials.—Reagent-grade cadmium nitrate, potassium thiocyanate and potassium nitrate were used without further purification. The potassium thiocyanate solutions were prepared by weighing out the correct amounts of solid salt. The concentration was always checked by titration and the solutions used were uniformly within 0.5% of the desired value. Nitrogen was used to exclude air from the polarographic cell.

Measurement of Half-wave Potential.—The polarograph was always set with an initial voltage of −0.35 and a span voltage of 0.5. The sensitivity used was 0.04 μa./mm., with no damping. The initial and final potentials on the polarogram were measured to within 0.1 mv. with a portable Rubicon potentiometer. The use of a small span voltage resulted in an expansion of the curve so that many drops fell during the rising portion. All current measurements used in calculation were of apparent maximum current, taken just as the drop fell. Since the average of the pen excursions on a recording-potentiometer type of polarograph such as the Sargent Model XXI does not give the same approximation to the hypothetical average current as is obtained with a long period galvanometer, there is no particular benefit obtained by averaging the pen excursions. The apparent maximum current (maximum pen excursion) is much more readily determined and the precision obtained is very good. The half-wave potential of a normal, reversible wave is theoretically the same regardless of whether the maximum or the average current is measured, since the average current is simply six-sevenths of the maximum current. This we have verified experimentally. The diffusion current and diffusion current constant is, however, a function of the method of current measurement and this must be taken into consideration when comparing results obtained on different types of instruments. The half-wave potentials were found by plotting the logarithm of $i/(i_d - i)$ (where i is the current corresponding to the particular voltage and i_d is the diffusion current, corrected for residual current) against applied voltage (corrected for iR drop in the cell). A point was plotted for each individual drop on the rising part of the curve and at least six values were used along the mid-portion of the curve. The plot of the log term against voltage invariably resulted in a straight line with negligible scatter of points and a slope of 0.030 ± 0.001. The half-wave potential was taken as that value of the voltage for which the log term was zero. Since all points on the rising portion of the wave are given equal weight, the half-wave potential may be interpolated with considerable accuracy. It was found possible to estimate the half-wave potential in any given experiment to 0.1 mv., and duplicate experiments showed that the reproducibility was of the order of 1 mv., the agreement frequently being well within 1 mv. In one series on cadmium in 0.5 *M* potassium thiocyanate and 1.5 *M* potassium nitrate, measurements were made on five separately prepared samples, which gave individual results of −0.6125, −0.6143, −0.6138, −0.6143 and −0.6147 volt. The observed half-wave potentials are corrected for iR drop but still involve junction potential of unknown magnitude. The junction potential is a composite of the potential across the saturated potassium chloride–saturated potassium nitrate boundary and the saturated potassium nitrate–potassium nitrate, potassium thiocyanate boundary. Although unknown, this potential probably changes by an insignificant amount in these studies and therefore is eliminated in taking differences.

Results and Discussion

In Table I are given the experimentally determined half-wave potentials and the diffusion currents, together with the calculated values of $F_j(X)$ which are also plotted in Figs. 1 and 2. These are obtained from Equations 17, 18 and 19, ref. 4, where (X) is used to denote the molar concentration of potassium thiocyanate. The assumption that the change in half-wave potential observed is due entirely to complex formation with no contribution from changing liquid junction potential is implicit in the interpretation of the data. This assumption is felt to be valid because the only junction which changes is the junction between the potassium nitrate–thiocyanate mixture and saturated potassium nitrate. As the

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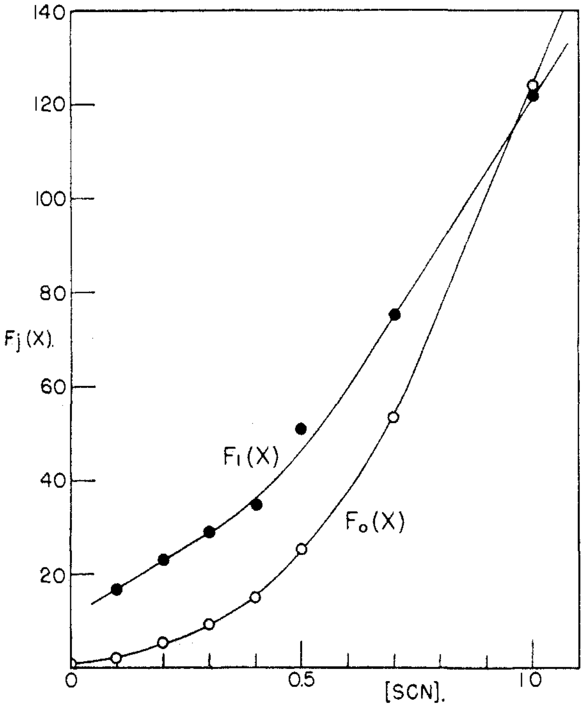

Fig. 1.—Values of $F_0(X)$ and $F_1(X)$ for cadmium in thiocyanate medium.

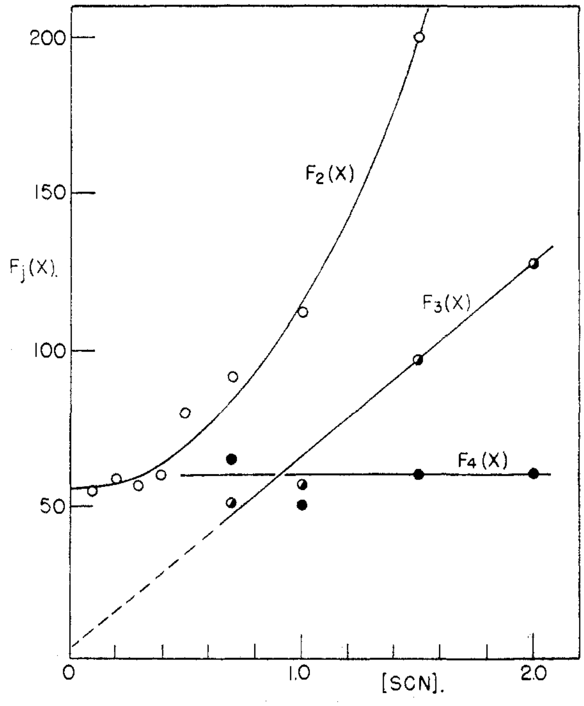

Fig. 2.—Values of $F_2(X)$, $F_3(X)$ and $F_4(X)$ for cadmium in thiocyanate medium.

limiting equivalent conductances of potassium nitrate and thiocyanate are not greatly different, the variation in junction potential here should never be large. It should be observed that the variations will be smallest in the low range of thiocyanate concentrations where the significant data for the evaluation of K_1 and K_2 are taken, while in the high range of thiocyanate concentration, the larger values of $\Delta E_{1/2}$ used to calculate K_3 and K_4 will be much less sensitive to junction potential errors.

TABLE I

ANALYSIS OF $E_{1/2}$ OF CADMIUM IN THIOCYANATE MEDIUM

KSCN, M	$E_{1/2}$, v.	i_l, μa.	$F_0(X)$	$F_1(X)$	$F_2(X)$	$F_3(X)$	$F_4(X$
0.0	−0.5724	7.56	(1.00)	...	...	...	..
.1	.5847	7.34	2.65	16.5	55	...	..
.2	.5943	7.29	5.57	22.8	59	...	..
.3	.6011	7.24	9.44	28.1	57	...	..
.4	.6071	7.22	15.00	35.0	60	...	..
.5	.6142	7.08	26.4	50.8	80	...	..
.7	.6235	7.08	53.8	75.4	92	51	65
1.0	.6343	7.07	123.6	122.6	112	56	50
1.5	.6516	7.06	467	311	200	96	60
2.0	.6646	7.03	1274	637	313	128	60
			K_0 = 1.00	K_1 = 11	K_2 = 56	K_3 = 6	K_4 = 60

Since values for the several activity coefficients which appear in the equations are at present unavailable, all activity coefficients were treated as if equal to unity. This results in values for the several formation constants which are not true thermodynamic equilibrium constants, but which include the undetermined activity coefficients. Since both the ionic strength and the potassium ion concentration were kept constant throughout the series of measurements, the ionic atmosphere, and therefore the several activity coefficients, probably changed very little. For this reason, the formal formation constants which are calculated here have genuine physical significance. Should values for the various activity coefficients become available at some future time, the true thermodynamic equilibrium constants could be calculated from the formal constants reported in this paper.

The plot of $F_0(X)$ is a curve, but the plot of $F_1(X)$ is essentially a straight line up to 0.4 M thiocyanate, indicating that in this region the only constituents present in significant amounts are the aquo cadmium ion, the monothiocyanate complex and unionized cadmium thiocyanate. The curvature of $F_1(X)$ above 0.4 M thiocyanate indicates a significant contribution by higher complexes. Extrapolation of a large scale plot of $F_1(X)$ to zero thiocyanate concentration yielded a value of 11.0 for K_1. Substitution of this value and calculation of $F_2(X)$ resulted in a curve which on extrapolation leads to a value of between 55 and 57 for K_2. This is in good agreement with the initial slope of $F_1(X)$ which gives a value of 56 for K_2.

Experimental errors in the determination of $\Delta E_{1/2}$ are magnified in the successive calculations of the several $F(X)$ functions, particularly for low concentration of complexing agent, and by the time $F_2(X)$ was obtained, a pronounced scatter was apparent in the points corresponding to concentrations below 0.5 M. Fortunately, however, successively accumulated errors are always in the same direction, and it is therefore easy to observe which points are high and which low with respect to the smooth curve. This knowledge, together with the limiting slope of the previous $F_j(X)$ curve, may be utilized to draw a better curve than would be otherwise possible. Considerable confidence may therefore be placed in the shape and position of the $F_2(X)$ curve found in this investigation even though the points at lower concentrations show considerable scatter. The most probable value of the limiting slope of $F_2(X)$ was estimated to be 6, and the maximum possible limiting slope at all consistent with the data to be less than 15.

When values of $F_3(X)$ were calculated, the points below 0.5 *M* thiocyanate had become so uncertain that they were disregarded. The remaining points, however, approximated a straight line which extrapolated readily to give a value of K_3 between 0 and 10, in good agreement with the value of 6 obtained by the limiting slope method. The slope of this line was found to be 55 and a plot of the values of $F_4(X)$, using a value of 6 for K_3, gave a horizontal straight line with an intercept corresponding to a K_4 in the range of 55–65. Although there was a considerable scatter of points below 1.5 *M* thiocyanate, no trend from the horizontal could be detected. The conclusion is therefore drawn that in solutions containing free thiocyanate ion in concentrations up to 2.0 *M*, only the species Cd^{++}, $CdSCN^+$, $Cd(SCN)_2$, $Cd(SCN)_3^-$ and $Cd(SCN)_4^=$ exist. The distribution of cadmium among the five species for various concentrations of free thiocyanate ion has been calculated and is plotted in Fig. 3.

The experimental uncertainty in the determined values of the several formation constants is estimated to be ±0.5 for K_1, ±2 for K_2, ±5 for K_3 and ±10 for K_4. Due to the nature of the method of calculation, these uncertainties increase in absolute magnitude for successively calculated formation constants. It should be observed that the smallest value of $\Delta E_{1/2}$ used was 12.3 mv. and that any reasonable experimental error in this measurement (*e.g.*, 1 mv.) would not change the value of K_1 more than 0.5 unit. Naturally, if the complexes formed are very weak (*e.g.*, *K* of 1 or 2), the shifts in half-wave potential will be very small and the errors involved correspondingly larger. If the complexes involved were extremely stable, difficulty would arise because the application of the method requires that the concentration of the complexing agent be large in comparison with the metal ion concentration. It is to the study of series complexes of moderate and comparable stability that the method is best suited.

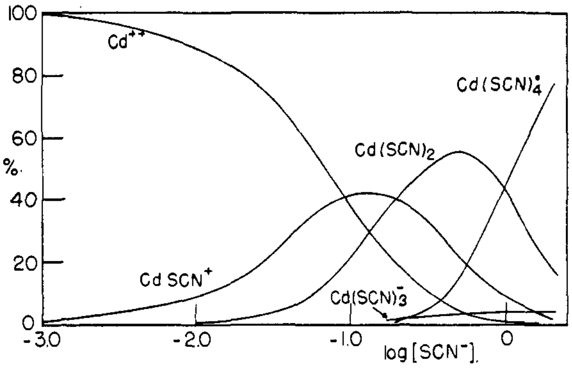

Fig. 3.—Percentage of cadmium in various forms as a function of free thiocyanate ion concentration.

Prior to this investigation, Brintzinger and Ratanarat[7] reported the existence of the $Cd(SCN)_4^=$ ion by dialysis experiments in 1.5 *M* thiocyanate medium. Grossmann[8] obtained $K_2Cd(SCN)_4 \cdot 2H_2O$ as a crystalline solid together with the analogous ammonium and rubidium compounds, but the sodium compound was found to be $NaCd(SCN)_3 \cdot 3H_2O$. Aside from the previous measurements by DeFord,[4] the only quantitative data available are those of Leden[9] who, by potentiometric measurements, concluded that the adducts $CdSCN^+$, $Cd(SCN)_2$ and $Cd(SCN)_3^-$ are formed with formation constants equal to 24.5, 96 and 380, respectively, at an ionic strength of 3.0. The values for K_1 and K_2 are of the same order of magnitude as those found in this investigation, but the conclusions regarding the higher complexes do not agree. Leden, however, worked only in the range of 0.01 to 0.6 *M* thiocyanate and with cadmium concentrations between 5 × 10^{-3} and 0.1 *M*. The higher complexes make up an insignificant proportion of the total below 0.3 *M* (Fig. 3) and in Leden's work only one higher concentration was examined. The much higher ratios of thiocyanate to cadmium employed in the present investigation would tend to favor the detection of higher complexes and probably accounts for his failure to find the very stable tetrathiocyanate complex. The earlier data of DeFord, taken at variable ionic strength, yielded the values of K_1 = 16, K_2 = 63 and K_3 = 1, which are of the same order of magnitude as those found in this investigation, but the fact that definite conclusions could not be drawn regarding the number and stability of higher complexes emphasizes the necessity of controlling the ionic strength.

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