Although in a different melt and at a different temperature, the order of magnitude of the constants is such as to indicate relative agreement, particularly when the lower temperature of this work is considered. Van Artsdalen,[5] from cryoscopic measurements in sodium nitrate, reports that the monochloro- and trichloro-complexes of lead and cadmium are not thermodynamically important. The data reported herein indicate that four complexes are important in the case of cadmium and only two, the monochloro- and the dichloro-, are important in the case of lead.

An effort was made to obtain data on the bromo-complexes of lead and cadmium. In the presence of bromide in the melt, the polarographic waves for lead and cadmium exhibit maxima, precluding any accurate determination of the halfwave potentials with the addition of bromide (KBr) to the melt. It appears however that the monobromo-complex is about twice as stable as the corresponding monochloro-complex and that the dibromo-complex is about five times as stable as the corresponding dichloro-complex in the case of cadmium and about the same order of stability as the dichloro-complex in the case of lead. Van Artsdalen[3] reports that the dissociation constant for $CdCl_2$ is about ten times as great as that for $CdBr_2$.

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TROY, NEW YORK

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF KANSAS]

Voltammetric Studies of Metal Complexes with a Rotated Platinum Electrode. I. The Monoöxalatosilver(I) Complex

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Voltammetry at a rotating platinum electrode has been used to study the complex formed between silver(I) and oxalate ions. From half-wave potential measurements at different oxalate concentrations, the formula of the complex was found to be $AgC_2O_4^-$. With the use of an extrapolation technique a pK_{inst} of 2.41 was obtained for the complex.

Introduction

A large number of complex metal ions have been studied by means of voltammetry at a dropping mercury electrode (polarography). Kolthoff and Lingane have reviewed this subject.[1] Polarography, unfortunately, cannot be used to study the stability of complexes of metal ions which have standard potentials in the vicinity of or more positive than, the dissolution potential of mercury. To circumvent this inherent difficulty in the polarographic technique this study using voltammetry at a rotating platinum electrode was undertaken. Since the standard reduction potential of the silver(I) ion–silver couple (+ 0.7995 v. *vs.* N.H.E.) is very close to that for the mercury(I)–mercury couple (+ 0.7986 v.), it was believed that the investigation of the complexes of silver would demonstrate the usefulness of the solid electrode technique.

The reduction of silver(I) ion to the metallic state on a platinum electrode is similar to the case in polarography of the reduction of the simple ion of a metal which is insoluble in mercury.[2] If one assumes that the activity of the deposited metal is constant and independent of the current density, the potential at any point on the potential–current curve, E_i, is given by

$$E_i = E^0{}_{Ag} - \frac{RT}{nF}\ln\frac{k}{f} + \frac{RT}{nF}\ln(i_d - i) \qquad (1)$$

where $E^0{}_{Ag}$, k, f and i are, respectively, the ordinary standard potential of silver, the proportionality constant relating the diffusion current, i_d, to the concentration of the metal ion in the bulk of the solution, the activity coefficient of the silver ion at the electrode surface, and the current at any given potential, E_i. If the $[Ag^+]$ is kept low and the supporting electrolyte concentration is kept high so that the ionic strength is essentially constant, one may assume that the activity coefficient will not vary with changes in silver ion concentration. If the constants are grouped together and the measurements are made at 25°, equation 1 becomes

$$E_i = E' + 0.059\log(i_d - i) \qquad (2)$$

Equation 2 gives the relationship between the instantaneous potential and current and will be discussed later in connection with the reversibility of the reaction. At the half-wave potential $E_{1/2}$ equation 2 becomes

$$E_{1/2} = E'' + 0.059\log\frac{[Ag^+]}{2} \qquad (3)$$

Where $E'' = E' + 0.059\log k$. When uncomplexed silver ions are reduced, equation 3 is used to evaluate E'' If a silver complex is formed

$$Ag^+ + yX^{-q} = AgX_y{}^{1-qy} \qquad (4)$$

one can write an expression for the instability constant K_{inst}

$$K_{inst} = \frac{[Ag^+][X^{-q}]^y}{[AgX_y{}^{1-qy}]} \qquad (5)$$

By solving equation 5 for $[Ag^+]$, substituting the resulting expression into equation 3, and rearranging terms, one obtains

$$pK_{inst} = \frac{E'' - E_{1/2}}{0.059} - y\log[X^{-q}] + \log\frac{1}{2}[AgX_y{}^{1-qy}] \qquad (6)$$

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[1] I. M. Kolthoff and J. J. Lingane, "Polarography," Vol. I, Interscience Publishers, Inc., New York, N. Y., 1952, p. 189.

[2] *Ibid.*, p. 203.

Equation 6 gives the relationship between the instability constant and known or measurable quantities.

Preliminary paper electrophoresis studies with saturated sodium oxalate as the supporting electrolyte gave definite indication of a negatively charged complex of silver(I) and oxalate. But because of the very low solubility of $Ag_2C_2O_4$ and the low stability of the negatively charged complex, no quantitative data could be obtained from this work. It was decided, therefore, to study the silver(I) ion–oxalate system by voltammetry at a rotating platinum electrode.

Experimental

Reagents and Solutions.—The lithium and silver perchlorates were G. Frederick Smith reagent grade and the sodium oxalate was Mallinckrodt A.R. grade. All solutions were prepared by volumetric dilution of stock solutions and were made 1 *M* with respect to $LiClO_4$ in order to keep the ionic strength nearly constant. The silver ion–oxalate solutions were used on the same day they were prepared since there were indications that the silver complex underwent a photochemical reaction on standing for long periods of time. All solutions were protected from excessive exposure to light.

Apparatus.—The platinum electrodes were prepared by fusing *ca.* 1 mm. diameter platinum wire into Pyrex glass tubes and making electrical contact by filling the tubes with mercury. The electrodes were rotated at *ca.* 600 r.p.m. with a Sargent synchronous rotator. The cell used was a standard H-cell with the two compartments separated by a sintered glass disc. A saturated calomel electrode was used as both auxiliary and reference electrode.

The current–voltage curves all were obtained on a continuous recording Polarograph Model XV, made by E. H. Sargent and Company. The resistance of the cell was measured before each run with a Model RC-1B Industrial Instruments, Inc., conductivity bridge. This resistance was used to obtain the *iR* correction, which was subtracted from each $E_{1/2}$ value. All solutions were polarographed at 25.0 ± 0.1°.

Procedure.—Before each run the platinum electrode was cleaned in a uniform manner. First, the silver metal from the previous run was removed at + 0.45 v. *vs.* S.C.E. Then the electrode was rotated in concentrated nitric acid and next immersed in cleaning solution. The electrode now was rinsed in distilled water, and the platinum oxide film on the electrode was removed by electrolysis at + 0.2 v. *vs.* S.C.E. in a 1 *M* lithium perchlorate solution. After another distilled water rinse the electrode was ready for use.

Both compartments of the H-cell were filled with the solution to be examined. The side arm of the calomel reference electrode which had a filter paper plug was placed in one of the compartments. This technique was used to prevent contamination of the solution being examined with chloride ions.

Solutions were deaerated with purified nitrogen before each polarographic run. Under the conditions at which the silver ions were reduced in this study, clean waves without maxima were obtained.

Results and Discussion

From equation 2 it can be seen that if the reduction of silver(I) is reversible at the rotating platinum electrode, a plot of E_i *vs.* log $(i_d - i)$ should yield a straight line with a slope of 0.059. The reduction of both uncomplexed and complexed silver ion gave excellent straight line plots. The average of eight such reversibility plots for uncomplexed silver ion was 0.056 ± 0.007. This is in excellent agreement with the theoretical value of 0.059 and in good agreement with the value obtained by Ferrett and Phillips.[3] The slope for the reversibility plot of 2×10^{-5} *M* silver ion (complexed) in 3.0×10^{-2} *M* sodium oxalate was 0.064. The value is also in good agreement with the theoretical slope.

TABLE I

DATA FOR UNCOMPLEXED SILVER ION[a]

Elect. no.	$[Ag^+] \times 10^5$, *M*	$E_{1/2}$, v. *vs.* S.C.E.	E'',[c] v. *vs.* S.C.E.	i_d, μamp	$i_d/[Ag^+]$, μamp/*M*
1	1.40	0.177	0.481	2.50	1.78
1	2.00	.192	.487	3.56	1.78
1	2.00	.190	.485	3.54	1.77
1	4.00	.202	.480	6.84	1.71
1	4.00	.202	.480	7.00	1.75
2	4.00	.205	.483	[b]	[b]
3	5.00	.210	.481	[b]	[b]
4	5.00	.214	.485	[b]	[b]
1	6.00	.219	.487	10.4	1.74
1	8.00	.225	.484	15.0	1.87
1	10.0	.232	.484	20.0	2.00
1	20.0	.250	.486	49.2	2.46

[a] All measurements at 25.0 ± 0.1° with 1 *M* $LiClO_4$ supporting electrolyte. [b] This value is of interest only when comparing measurements made on the same electrode. [c] The average value of *E* is 0.484 ± 0.002 v. *vs.* S.C.E.

The data used to determine the constant potential term E'' (equation 3) are presented in Table I. The average value obtained for twelve solutions of uncomplexed silver ion was 0.484 ± 0.002 v. *vs.* S.C.E. This constant was independent of the platinum electrode used in the determination.

A plot of the diffusion current *vs.* the silver ion concentration showed that these two quantities are directly proportional to each other below a $[Ag^+]$ of 6.0×10^{-5} *M* in 1 *M* lithium perchlorate. From examination of the quantity $i_d/[Ag^+]$ in Table I one can see clearly an increase in this ratio above a $[Ag^+]$ of 6.0×10^{-5} *M*. The reason for this effect is not completely understood at the present time but two explanations are offered. First, at the higher silver ion concentrations enough metal may be plated out onto the electrode to appreciably change its surface area and thereby increase the current. It is also possible that at concentrations above 6×10^{-5} *M* silver ion the proportionality constant *k* may not be truly constant and independent of concentration. It is interesting to note that when the electrode was not cleaned of all the silver from the preceding reduction, a wave with a maximum was obtained. The maximum current was frequently over twice that of the diffusion current.

If one is investigating a very stable complex or if very high concentrations of the ligand are used so as to keep the log $^1/_2[AgX_y{}^{1-qy}]$ term constant, the slope of the plot of the half-wave potential, $E_{1/2}$, *vs.* 0.059 log $[X^{-q}]$ should yield *y*, the number of bound ligands (see equation 6). This type of plot is made for the silver ion–oxalate system in Fig. 1. The slopes of sections 1, 2, 3 and 4 are 0.90, 0.80, 0.72 and 0.57, respectively. The dashed line is the theoretical line for the one–one complex of oxalate and silver(I). Because of the low stability of the silver–oxalate complex, the term log $^1/_2$-$[AgX_y{}^{1-qy}]$ is not constant as required for this plot. However, at points (A) and (B), 92 and

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(3) D. J. Ferrett and C. S. G. Phillips, *Trans. Faraday Soc.*, **51**, 390 (1955).

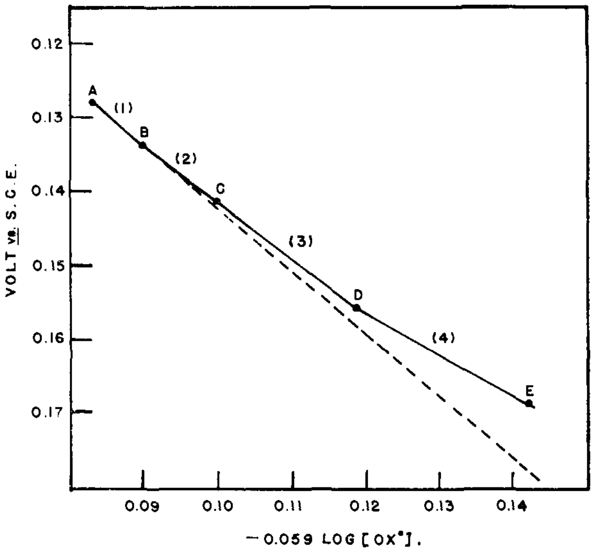

Fig. 1.—Plot of $E_{1/2}$ *vs.* −0.059 log [Oxalate] for the determination of the ligand number.

89%[4] of the silver is complexed and therefore the slope between them should be closest to the actual y value. From Fig. 1 the formula of the silver-oxalate complex would then be $AgC_2O_4^-$.

If the silver complex is fairly stable, so that the concentration of the complex is very nearly the same as the concentration of the silver ion added, one can substitute the known and measured quantities into equation 6 and calculate pK_{inst}. On the other hand, if the complex is relatively unstable, as is the case with $AgC_2O_4^-$, an extrapolation technique must be used to determine the complex ion concentration. One first assumes that all the silver added is complexed and then from equation 6 determines an apparent pK (pK_{app}). As the oxalate concentration is increased, the pK_{app} approaches the true pK_{inst} because the equilibrium is being shifted toward a higher percentage of silver complex. A plot of pK_{app} *vs.* oxalate concentration should give a line which at high oxalate concentrations is asymptopic to the value of the true pK_{inst}. Such a plot is shown in Fig. 2. From this graph the value of the true pK_{inst} for the $AgC_2O_4^-$ complex is estimated as 2.41. For a final check on the accuracy of the graphically obtained pK_{inst} value, the silver complex concentrations were calculated using the value of 2.41 for pK_{inst} in equation 5. The calculated silver complex concentrations were then used in solving equation 6 for the true pK_{inst}. If the graphic value is correct, one should obtain the same pK_{inst} value for the different oxalate concentrations. The calculated pK_{inst} values are found in Table II. The average value for ten runs are 2.41 ± 0.02 pK units. This is in excellent agreement with the graphic value and therefore the values are self-consistent.

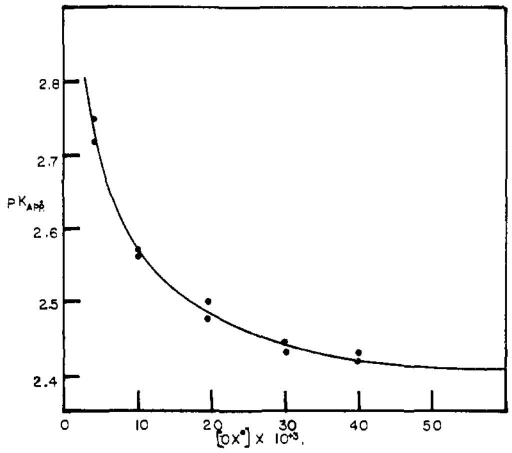

Fig. 2.—Variation in pK apparent with oxalate ion concentration.

TABLE II

DATA FOR COMPLEXED SILVER ION[a]

Initial [Oxalate⁼] × 10^3, M	$E_{1/2}$, v. *vs.* S.C.E.	pK_{app}	[Ag complex][b] × 10^5, M	Calcd.[c] pK_{inst}
4	0.170	2.72	1.01	2.44
4	.168	2.75	1.01	2.41
10	.156	2.57	1.44	2.43
10	.155	2.56	1.44	2.42
20	.141	2.51	1.67	2.40
20	.143	2.48	1.67	2.43
30	.135	2.43	1.77	2.40
30	.134	2.45	1.77	2.38
40	.129	2.42	1.84	2.39
40	.128	2.43	1.84	2.40

[a] All runs were made at 25.0 ± 0.1° with 1 M $LiClO_4$ and 2 × 10^{-5} M $AgClO_4$ initially added. [b] This value was calculated using the experimentally determined value of 2.41 for pK_{inst}. [c] The average value for the calculated pK_{inst} is 2.41 ± 0.02.

The above investigation also was carried out in 0.1 M $LiClO_4$ as supporting electrolyte. E'' values of 0.489 ± 0.003 v. *vs.* S.C.E. were obtained for uncomplexed silver ion. An average value of 2.40 ± 0.04 for pK_{inst} was found for the mono-oxalatosilver(I) complex. Both E'' and pK_{inst} are in excellent agreement with the above results.

Attempts to determine the stability constants of silver cyanide and silver thiosulfate complex were unsuccessful because of the appearance of the background wave before the silver complexes could be reduced.

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[4] These percentages have been calculated using the experimentally determined value of 2.41 for pK_{inst} of $AgC_2O_4^-$.