tion in the concentration region of 0.01 to 1 M sodium nitrate in ethylenediamine and a cadmium ion concentration of 3×10^{-4} M. The data for the singly charged thallous ion at a concentration of 3×10^{-4} M follow the theoretical slope above about 0.2 M sodium nitrate but fall considerably below the expected change at lower concentrations of sodium nitrate. Apparently, ion-pair association of Tl^+ with NO_3^- is predominant only at the higher concentrations of sodium nitrate, but at lower concentrations thallous ion is increasingly dissociated. If the reducible species were essentially completely dissociated, then the $E_{1/2}$ would change comparatively little with supporting electrolyte concentration and the plot would be approximately horizontal, as is the case in aqueous solution if the anion of the supporting electrolyte does not form complexes with the reducible ion. The greater degree of ion-pair association of Cd^{++} than Tl^+ in the more dilute sodium nitrate solutions is understandable on the basis of its higher charge and smaller size.

Experimental

The general experimental procedures used to study the polarographic characteristics of metal ions in ethylenediamine have been described previously.[7,8] The ethylenediamine used was dried by refluxing over sodium and then distilled. Sodium nitrate, reagent grade and vacuum dried, was used as supporting electrolyte at concentrations of 1.0, 0.25, 0.10 and 0.010 molar. The chlorides of cadmium and thallium were used to supply these cations at concentrations of about 3×10^{-4} M.

The polarograms were recorded at 25° using a Sargent Model XXI Polarograph and a two-compartment, demountable H-type cell. The cell compartments were separated by a 25 mm. diameter, fine sintered-glass disk. One compartment contained a reference electrode composed of saturated zinc amalgam in contact with ethylenediamine containing 0.25 M LiCl and saturated with respect to zinc chloride.[7] The potential of the dropping mercury electrode was varied with respect to this zinc reference electrode. (The potential of this zinc reference electrode has been found in this Laboratory to be −1.226 volts *vs.* the mercury pool in ethylenediamine containing 0.25 M LiCl and −1.17 volts *versus* the pool in ethylenediamine containing 0.25 M $NaNO_3$.)

Resistances of all solutions were measured with a Serfass conductivity bridge and the half-wave potentials corrected for iR drops. Approximate resistances for the 1.0, 0.25, 0.1 and 0.01 M $NaNO_3$ solutions (in ethylenediamine) were, respectively, 1800, 3000, 6000 and 35,000 ohms.

Acknowledgments.—The author is grateful to Dr. R. E. Bayer and Mr. J. E. Siefker for their help in obtaining the experimental results and to the U. S. Atomic Energy Commission for a grant (AT 11-1-256) in partial support of this work.

BLOOMINGTON, INDIANA

---

[8] W. B. Schaap, A. E. Messner and F. C. Schmidt, THIS JOURNAL, **77**, 2683 (1955).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, RENSSELAER POLYTECHNIC INSTITUTE]

Polarographic Determination of Formation Constants of Complex Ions in Fused $LiNO_3$–KNO_3

BY JOE H. CHRISTIE AND ROBERT A. OSTERYOUNG

RECEIVED AUGUST 28, 1959

A polarographic study of the chloro-complexes of Pb(II), Cd(II) and Ni(II) has been made with the dropping mercury electrode in a fused $LiNO_3$–KNO_3 mixture at 180°. Respectively, 3, 4 and 2 chloro-complexes were found for these ions yielding these formation constants: Pb(II), $K_1 = 42$, $K_2 = 3$; Cd(II), $K_1 = 200$, $K_2 = 15$, $K_3 = 40$, $K_4 = 5$; Ni(II), $K_1 = 26$, $K_2 = 2$, $K_3 = 10$. The results are compared with other available data.

Introduction

The feasibility of using the dropping mercury electrode (d.m.e.) in fused nitrate melts was demonstrated several years ago by Steinberg and Nachtrieb.[1] Their work indicated that in sufficiently low melting systems the d.m.e. could be utilized in much the same way that it is in aqueous solutions. One use of the polarographic technique in aqueous solutions has been to study complex ions; in certain instances, formation constants for complex ionic species may be determined.[2]

The existence of complex ions in fused salts has been demonstrated, most recently by Gruen[3] and Van Norman,[4] and data on the formation constants for various species have been obtained.[5–8]

It appears that the metal halide complex ions formed in fused salts are characterized by rather weak formation constants. An aqueous polarographic technique for the study of such complexes was derived by DeFord and Hume.[9] The present work is an attempt to apply this method to the determination of formation constants of metal halide complexes in a $LiNO_3$–KNO_3 fused salt system.

Experimental

Reagent grade chemicals were used in all cases. The $LiNO_3$–KNO_3 eutectic system (38.56 mole % $LiNO_3$, m.p. 139°)[10] was prepared from vacuum-oven dried material. In all cases the eutectic material was mixed, fused and filtered through a fine sintered glass frit. Metal ions were added to this mixture as the metal nitrates dried under vacuum at 100°. Additions of chloride were made to the

---

[1] M. Steinberg and N. H. Nachtrieb, THIS JOURNAL, **72**, 3558 (1950).

[2] I. M. Kolthoff and J. J. Lingane, "Polarography," Vol. I, Interscience Publishers, Inc., New York, N. Y., 1952, pp. 211-215.

[3] D. M. Gruen and R. L. McBeth, *J. Phys. Chem.*, **63**, 393 (1959).

[4] J. D. Van Norman and R. A. Osteryoung, unpublished results.

[5] E. R. Van Artsdalen, *J. Phys. Chem.*, **60**, 172 (1956).

[6] S. N. Flengas and E. Rideal, *Proc. Roy. Soc.* (*London*), **A233**, 443 (1956).

[7] F. R. Duke and M. L. Iverson, *J. Phys. Chem.*, **62**, 417 (1958). *Anal. Chem.*, **31**, 1233 (1959).

[8] D. Neil, Ph.D. Thesis, Rensselaer Polytechnic Institute (1959).

[9] D. D. DeFord and D. N. Hume, THIS JOURNAL, **73**, 5321 (1951).

[10] "International Critical Tables," Vol. IV, 1st Ed., McGraw-Hill Book Co., New York, N. Y., 1928, p. 67.

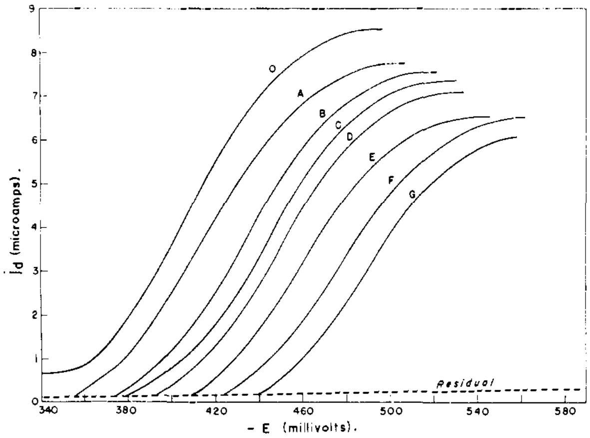

Fig. 1.—Shifts in polarographic waves with increasing chloride concentrations: 1.01×10^{-3} *m* $Pb(NO_3)_2$; concentration of added chloride: 0, none; A, 0.0248 *m;* B, 0.0607 *m;* C, 0.0975 *m;* D, 0.149 *m;* E, 0.225 *m;* F, 0.303 *m;* G, 0.743 *m.*

melt with weighed amounts of vacuum dried potassium chloride.

The melt was contained in a 100 ml. beaker and was placed in a tubular furnace consisting of a Vycor core (58 mm. diameter) wound with Nichrome wire and covered with insulating cement. A mercury thermometer was dipped into the melt to measure the temperature which was maintained at 180° by means of a Variac.

The reference electrode compartment consisted of a small Pyrex tube, sealed at one end with a fine fritted disc. The tube was placed in the melt and was filled with $LiNO_3$—KNO_3 mixture containing 3.86 mg. of KCl per gram of eutectic. The same concentration of KCl was used in all cases. The melt in the fritted compartment was saturated with silver chloride and a silver wire was immersed in the reference compartment, giving a silver–silver chloride electrode.

The capillary for the d.m.e. was a 3–5 sec. polarographic capillary, 21 cm. long (E.H. Sargent and Co., Chicago, Ill.). This was sufficiently long that while one end dipped into the melt, the other end was well out of the furnace. Contact to a mercury reservoir was made with Tygon tubing attached to the capillary. A drop time of about 4.5 sec. resulted at a head of 68 cm. of Hg at −0.35 v. *vs.* the Ag–AgCl reference electrode. All polarograms were recorded in the conventional manner with a Sargent Model XXI Recording Polarograph.

Potentials were checked by stopping the polarograph at given intervals and measuring the applied e.m.f. with a Rubicon Potentiometer (Cat. No. 2700).

In making a run a weighed amount of potassium nitrate–lithium nitrate mixture was placed in the 100 ml. beaker, together with the filled reference compartment and brought up to temperature in the furnace. A residual current was run and a weighed amount of metal nitrate was added. Polarograms were then run as weighed amounts of potassium chloride were added.

In the case of nickel, it was found that when nickel nitrate was added to the melt, a black precipitate, presumably nickel oxide, formed. To forestall this, nickel nitrate was mixed with the eutectic, fused and filtered through a sintered glass frit, removing the precipitated material. Thus, the exact concentration of nickel in the melt was not known; it is estimated from the wave height that the concentration of nickel was of the order of millimolal (moles/1000 g). A knowledge of the exact amount of nickel in the melt is, however, not necessary in the following treatment.

Results and Discussions

The residual currents obtained were linear over the useful range from about 0 volt (mercury dissolution) to −0.8 volt *vs.* the Ag–AgCl reference electrode (reduction of alkali metal or nitrate). The maximum current obtained in this range was about 0.3 μamp. (at −0.8 v.). Normal polarograms with no maxima were obtained for the reduction of Ni(II), Pb(II) and Cd(II). The slopes of the plots of E *vs.* log $(i_d - i/i)$ were 0.047, 0.052 and 0.052 for the reduction of Ni(II), Cd(II) and Pb(II) $(2.303RT)/F = 0.090$ at 180°). respectively. These reductions thus appear to be reversible. Shifts of the halfwave potentials to more negative values were noted as increasing amounts of chloride were added. The polarograms in Fig. 1 show the shifts in the waves relative to the uncomplexed material as KCl was added to the melt containing lead nitrate.

Table I indicates i_d for the reduction of Cd(II), Ni(II) and Pb(II), corrected for residual current and the slight dilution of the melt by added KCl *vs.* the concentration of added KCl.

TABLE I

VARIATION OF i_d AND $E_{1/2}$ WITH CHLORIDE CONCENTRATION

Cd(II)			Pb(II)			Ni(II)		
$[Cl^-]$, mole 1000 g.	Δ $E_{1/2}$, mv.	i_d, μamp.	$[Cl^-]$, mole 1000 g.	Δ $E_{1/2}$, mv.	i_d, μamp.	$[Cl^-]$, mole 1000 g.	Δ $E_{1/2}$, mv.	i_d, μamp.
0.0	...	18.1	0.0	..	8.64	0.0	..	20.4
.0166	24.8	17.2	.0248	10.4	8.08	.0098	9.1	20.6
.0264	42.9	17.4	.0607	25.5	7.79	.0296	12.3	20.5
.0420	59.3	18.8	.0975	34.0	7.64	.0615	16.3	19.9
.0604	78.2	19.0	.149	41.9	7.55	.123	29.7	19.5
.0801	84.4	18.5	.225	46.5	6.91	.244	48.9	19.4
.102	106.4	18.5	.303	63.3	7.01	.416	70.0	18.7
.161	134.8	18.0	.373	65.3	7.05	.582	80.3	18.5
.240	155.7	17.7	.481	70.1	7.05			
.336	180.6	17.6	.743	84.5	6.84			
.446	200.2	17.2						
.590	217.2	17.0						

It is to be noted that the diffusion current decreases somewhat as the concentration of added chloride increases. This effect is most striking in the case of lead; in the cases of nickel and cadmium, the percentage change in i_d is not so great but the diffusion current does decrease at higher concentration of added chloride. The slight increase in the diffusion current at lower concentration of chloride may be due to the dissolution of a slight amount of metal oxide in equilibrium with the metal ion in the melt. This redissolution would tend to offset the slight decrease in the diffusion current due to the formation of complex ions. The decrease in the diffusion current is taken as an indication of the formation of a complex ion or a series of complex ions; it might be expected that as the size of the average species diffusing to the electrode increases, the diffusion coefficient would decrease, resulting in a decrease in the diffusion limited current. To ascertain that the currents were diffusion controlled i_d was determined at varying mercury column heights and log i_d *vs.* log h (height of mercury column) was plotted. A slope of 0.498 for the least squares line indicated a diffusion controlled current.[11]

The $\Delta E_{1/2}$ for each of the reductions are shown in Table I. The $E_{1/2}$ for the various reductions varied from one run to another, probably due to variations in the reference cell. This variation is not serious, however, since $\Delta E_{1/2}$ is used in the treatment of the data.

An attempt was made to treat the data by the method of DeFord and Hume.[9] It was necessary

---

(11) Ref. 2, p. 85.

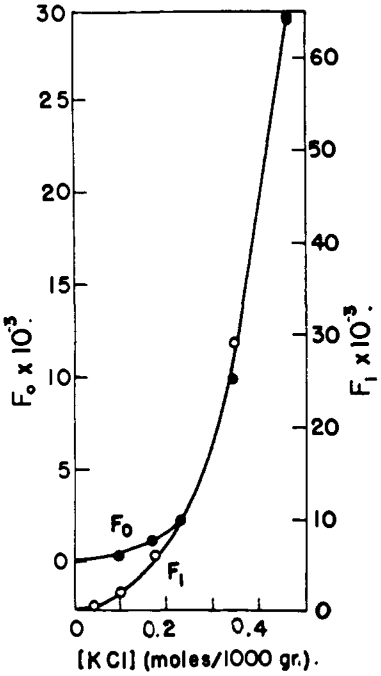

Fig. 2.—Values of F_0 and F_1 for cadmium chloro-complexes.

to assume that activity coefficients of the metal ions were unity and that the reductions were polarographically reversible. For details of the treatment, the reader is referred to the original paper of DeFord and Hume.[9]

The plots of the F functions for the chloro-complexes of cadmium are shown in Figs. 2 and 3, where

$$F_0 = \text{antilog}\left\{\frac{1}{2.303}\,\frac{nF}{RT}\,[(E_{1/2})_s - (E_{1/2})_c] + \log (i_d)_s/(i_d)_c\right\} = \sum_{i=0}^{i} \beta_i C_X^{i} \quad (1)$$

$$F_1 = \frac{F_0 - \beta_0}{C_X} = \sum_{i=1}^{i} \beta_i C_X^{i-1} \quad (2)$$

$$F_2 = \frac{F_1 - \beta_1}{C_X} = \sum_{i=2}^{i} \beta_i C_X^{i-2} \quad (3)$$

$$F_3 = \frac{F_2 - \beta_2}{C_X} = \sum_{i=3}^{i} \beta_i C_X^{i-3} \quad (4)$$

R, T, n and F have their usual significance; $(E_{1/2})_c$ is the halfwave potential of the metal ion in the presence of the complexing species X; $(E_{1/2})_s$ is the halfwave potential of the metal ion in the absence of the complexing agent X; $(i_d)_s/(i_d)_c$ is the ratio of the diffusion currents in the absence and presence of X; β^i is the formation constant for the ith species and C_X^{i} is the concentration of the complexing agent X raised to the ith power. Thus

$$\beta_0 = 1 \quad (5)$$

$$\beta_1 = K_1 = \frac{[MX^{n-1}]}{[M^{+n}]\,[X^-]} \quad (6)$$

$$\beta_2 = K_1K_2 = \frac{[MX_2^{n-2}]}{[M^{+n}]\,[X^-]^2} \quad (7)$$

$$\beta_3 = K_1K_2K_3 = \frac{[MX_3^{n-3}]}{[M^{+n}]\,[X^-]^3} \quad (8)$$

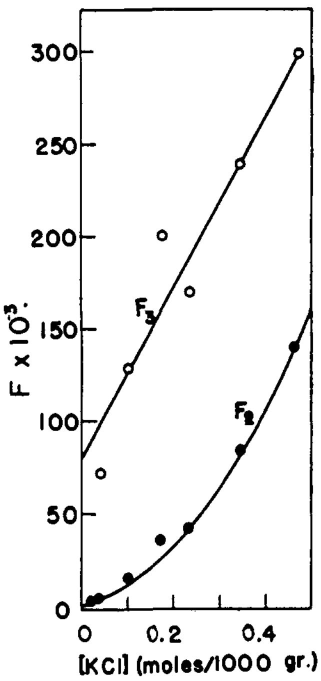

Fig. 3.—Values of F_2 and F_3 for cadmium chloro-complexes.

where the K's are the successive formation constants for the complex series MX^{n-1}, MX_2^{n-2}, etc. A plot of F_0 *vs.* the concentration of the complexing agent yields a curve with intercept at 1 and a limiting slope equal to β_1. A plot of F_1 *vs.* concentration of complexing agent has an intercept β_1 and a limiting slope β_2. The plot of the F function for the next to the last complex (F_{i-1}) will be a straight line of slope β_i and the plot of the F function for the last complex will be a straight line parallel to the abscissa.

Table II gives the experimentally obtained values for the successive formation constants for the Pb(II), Ni(II) and Cd(II) chloro-complexes. Each value shown is the average of two or three separate determinations, the range being ± 30% for K_1 and K_2 and ± 60% for K_3 and K_4.

TABLE II

FORMATION CONSTANTS OF CHLORO-COMPLEXES IN $LiNO_3$–KNO_3 AT 180°

Metal ion	K_1	K_2	K_3	K_4
Ni^{++}	26	2	10	..
Cd^{++}	200	15	40	5
Pb^{++}	42	3	..	..

TABLE III

FORMATION CONSTANTS IN $NaNO_3$–KNO_3[a]

Species	Temperature, °C. 250	275	300
PbCl[b]	18	8	6
$PbCl_2$	2	3	3
$PbCl_3^-$	2	1	1
CdX^+[b]	20	..	24
CdX_2	5	..	5

[a] Taken from Duke and Iverson (ref. 7). [b] X is either Cl or Br.

The data for the Pb(II) and Cd(II) complexes may be compared roughly with the results obtained by Duke and Iverson[7] shown in Table III.

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 $CdBr_2$.

Acknowledgment.—This work was supported in part by the U. S. Atomic Energy Commission under Contract AT (30-3)-241).

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

BY SHELDON H. COHEN, REYNOLD T. IWAMOTO AND JACOB KLEINBERG

RECEIVED SEPTEMBER 15, 1959

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

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

---

[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.