[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Polarography in Liquid Ammonia. IV. The Polarography of Thallium(I), Copper (II), and Ammonium Ions and of Molecular Oxygen

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In previous papers, the polarographic behavior of alkali metal ions,[2] tetraalkylammonium ions,[3] and the mercury pool anode[4] have been described. Several other electrode reactions of special interest in polarography were studied in the present investigation.

Experimental

The apparatus and technique have been previously described.[4] Thallous ion was used as the pilot ion for the measurement of the half-wave potential of the ammonium ion. In the other experiments, the previously established potential of the mercury anode[4] was used for reference.

Reagent grade cupric chloride, ammonium nitrate and potassium nitrate were dried at 110° for several hours. Tetrammine cupric bromide was prepared by dissolving pure cupric bromide in dilute aqueous ammonia, recrystallization from the same medium, and drying at 100° in an atmosphere of anhydrous ammonia.

Results and Discussion

Reduction of Thallous Ion.—In the presence of a trace of methyl cellulose as a maximum suppressor, thallous ion gave a well-developed polarographic wave (Fig. 1). The plot of log $(i_d - i)/i$ *versus* E was a straight line with a reciprocal slope of 0.057 as compared with the theoretical value of 0.047 at −36°. The reduction process seems to be essentially reversible, although no data on the electrode potential of thallium in liquid ammonia appear to be available for comparison. The half-wave potential was previously evaluated to be 0.15 volt with respect to the lead–0.1 N lead nitrate electrode, or 0.46 volt with respect to the normal hydrogen electrode.[3]

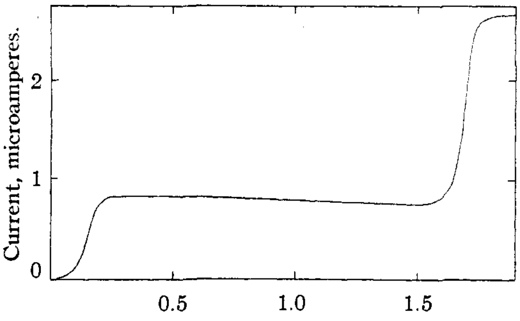

Fig. 1.—Polarogram of 3×10^{-4} M TlCl, 7×10^{-4} M NH_4NO_3 in saturated tetrabutylammonium iodide, trace of methyl cellulose.

To compare the observed and calculated values of the diffusion current, the conductivity measurements of Franklin and Kraus[5] on thallous nitrate were used. Extending the measured values to infinite dilution with the aid of data on potassium nitrate solutions, a value of 167 cm.^{2} ohm^{-1} equiv.$^{-1}$ was estimated for the equivalent ion conductance of the thallous ion at infinite dilution at −33.5°. Using the data of Pleskov and Monosson[6] for the alkali metals at −40°, and assuming that the same temperature coefficient prevails for the thallous ion as for the alkali metal ions, a value of 164 cm.^{2} ohm^{-1} equiv.$^{-1}$ was estimated for a temperature of −36°. The diffusion coefficient was calculated to be 3.47×10^{-5} cm.^{2} sec.$^{-1}$. From the Ilkovic equation, the calculated value for i_d/C was 3.30, as compared with an average observed value of 3.21 ± 0.08 μ amp. mmole^{-1} liter^{-1} (Table I).

TABLE I

DIFFUSION CURRENTS OF COPPER AND THALLIUM, METHYL CELLULOSE USED AS MAXIMUM SUPPRESSOR

Salt	C, mmole/l.	Supporting electrolyte	i_d, μ amp.	i_d/c
TlCl	0.289	0.1 M KNO_3	0.906	3.13
TlCl	.310	Satd. KCl	0.982	3.17
TlCl	.699	0.1 M NH_4Cl	2.34	3.34
$CuCl_2$	.580	0.1 M KNO_3	1.37	2.36
$Cu(NH_3)_4Br_2$	.507	0.1 M KNO_3	1.23	2.46

Reduction of Copper(II) Ion.—The polarographic reduction curve of copper(II) ion in the presence of a trace of methyl cellulose is shown in Fig. 2. The double wave showed two equal reduction steps, corresponding to the successive reduction to the copper(I) ion and to the amalgam. The half-wave potentials were −0.15 and −0.52 v. with respect to the mercury pool anode, or +0.16 and −0.21 v. with respect to the

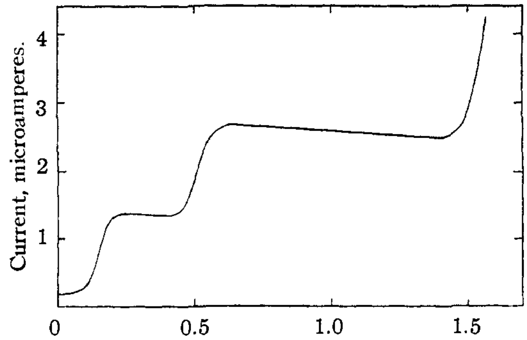

Fig. 2.—Polarogram of cupric bromide in 0.1 N potassium nitrate.

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(1) Abstracted from the Ph.D. Thesis of Carlyle E. Shoemaker. 1949.

(2) Laitinen and Nyman, THIS JOURNAL, **70**, 2241 (1948).

(3) Laitinen and Nyman, *ibid.*, **70**, 3002 (1948).

(4) Laitinen and Shoemaker, *ibid.*, **72**, 663 (1950).

(5) Franklin and Kraus, *ibid.*, **27**, 191 (1905).

(6) Pleskov and Monosson, *Z. physik. Chem.*, **156**, 176 (1931).

lead–0.1 N lead nitrate electrode, or 0.47 and 0.10 v. with respect to the normal hydrogen electrode. The reciprocal slopes of the plots of log $(i_d - i)/i$ *versus* E were 0.049 and 0.066, respectively, for the first and second waves, indicating that the first step is reversible but that the second step deviates appreciably from reversible behavior.

The first half-wave potential should be very close to the standard potential of the cupric–cuprous ion electrode (neglecting differences of activity coefficients and diffusion coefficients of the two ions).[7] Apparently no measurement of the potential of the cupric–cuprous ion electrode has been made, although Johnson and Wilsmore[8] have measured the potential of the thermodynamically unstable copper–cupric nitrate electrode.

The half-wave potential of the second reduction wave is related to the standard potential of the copper–cuprous ion electrode. In aqueous solution, the standard potential for the reaction

$$Cu(NH_3)_2^+ + e^- \rightleftarrows Cu + 2NH_3$$

is −0.11 volt.[9] The half-wave potential for the reaction

$$Cu(NH_3)_2^+ + e^- + Hg \longrightarrow Cu(Hg) + 2NH_3$$

in the presence of 1 M ammonia is −0.25 volt, with respect to the hydrogen electrode.[10]

At a constant temperature, the difference between these two values should be independent of solvent, because it arises from two concentration effects, namely, the dilution of cuprous ion and copper from unit activity to the approximately equimolar concentration existing at the surface of the dropping electrode at the half-wave point.

Pleskov[11] measured the e.m.f. of the cell in liquid ammonia at −50° and found it to be

$$\begin{array}{c} Cu^+ \mid CuI \mid KNO^3 \mid Pb(NO_3)_2 \mid Pb^- \\ (0.1\ N) \quad (Satd.) \quad (0.1\ N) \end{array}$$

0.0524 volt. Using the Nernst equation, a value of 0.097 volt for the standard potential of the copper cuprous ion electrode was calculated.[12] With reference to the normal hydrogen electrode a value of 0.41 volt is obtained.

The disagreement between this value and the value of 0.24 volt estimated from the second half-wave potential may be attributed largely to the lack of completely reversible behavior in the second polarographic reduction step, but may also be caused in part by the neglect of temperature difference in the comparison.

The observed diffusion currents (Table I) were in essential agreement with the calculated values. From the conductivity data of Franklin[13] for tetrammine cupric nitrate, the equivalent ionic conductance of the cupric ion at infinite dilution in liquid ammonia at −36° was estimated to be 170 cm.^{2} ohm^{-1} equiv.$^{-1}$, corresponding to a diffusion coefficient of 1.8 × 10^{-5} cm.^{2} sec.$^{-1}$ and a value of i_d/C of 2.38, as compared with an average observed value of 2.40 ± 0.05 μ amp. mmole^{-1} liter^{-1}.

Reduction of Ammonium Ion.—In a supporting electrolyte of saturated tetrabutylammonium iodide, the polarographic wave was characterized by a pronounced maximum. Methyl red had little or no effect on the maximum, but methyl cellulose proved to be an excellent maximum suppressor.

A typical polarogram of ammonium ion in the presence of thallous ion is shown in Fig. 1. A plot of log $(i_d - i)/i$ against E was a straight line with a reciprocal slope of 0.050 to 0.062, as compared with the theoretical value of 0.047 for a reversible one-electron process at −36°.

The half-wave potential was determined by using the thallous ion as a pilot ion. The measured values as well as those calculated against the lead–0.1 N lead nitrate electrode are given in Table II.

TABLE II

POLAROGRAPHIC REDUCTION OF AMMONIUM NITRATE IN SATURATED TETRABUTYLAMMONIUM IODIDE; METHYL CELLULOSE AS MAXIMUM SUPPRESSOR

C, mmole/l.	Half-wave potential, volts vs. $E^1/_2$(Tl$^+$)	vs. Pb/Pb^{++}	i_d, μ amp.	i_d/C
0.375	−1.52	−1.37	0.994	2.65
.436	−1.52	−1.37	1.120	2.57
.374	−1.53	−1.38	1.15	3.07

The average value is −1.37 volts against the lead electrode, or −1.06 volts against the normal hydrogen electrode.

The conductivity data of Franklin and Kraus[14] for ammonium and alkali metal salts at −33.5° were used to calculate the diffusion coefficient of ammonium ion. The equivalent conductance values for potassium nitrate, sodium nitrate, sodium bromide and ammonium bromide were extrapolated to infinite dilutions from a plot of equivalent conductance against the square root of concentration. The values obtained were 354, 315, 312 and 316 cm.^{2} ohm^{-1} equiv.$^{-1}$, respectively. Taking the value of Franklin and Cady[15] for the transference number of nitrate ion in potassium nitrate, the equivalent ionic conductance of the nitrate ion was calculated to be 177. By difference the value for sodium ion is equal to 158. Comparing sodium bromide and ammonium bromide, the equivalent ionic conduc-

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(7) Kolthoff and Lingane, "Polarography," Interscience Publishers, New York, N. Y., 1941.

(8) Johnson and Wilsmore, *Trans. Faraday Soc.*, **3**, 70 (1907).

(9) Latimer, "The Oxidation States of the Elements on Potentials in Aqueous Solutions," Prentice-Hall, Inc., New York, N. Y., 1938.

(10) Stackelberg and Freyhold, *Z. Elektrochem.*, **46**, 120 (1940).

(11) Pleskov, *Acta Physicochim.* (*U. S. S. R.*), **13**, 659 (1940).

(12) Pleskov and Monosson, *J. Phys. Chem.* (*U. S. S. R.*), **4**, 696 (1933).

(13) Franklin, *Z. physik. Chem.*, **69**, 272 (1909).

(14) Franklin and Kraus, THIS JOURNAL, **27**, 191 (1905).

(15) Franklin and Cady, *ibid.*, **26**, 499 (1904).

tance of the ammonium ion is 142 at −33.5°, or 139 cm.^{2} ohm^{-1} equiv.$^{-1}$ at −36°, assuming that the temperature coefficient is equal to that for sodium and potassium ion. The calculated diffusion coefficient is 2.95×10^{-5} cm.^{2} sec.$^{-1}$. From the Ilkovic equation the calculated value of i_d/C is 2.38 μ amp. millimole^{-1} liter^{-1}, as compared to the observed value of 2.8 ± 0.2.

As in the case of the alkali metal ions,[2] the higher observed value may be attributed at least partly to migration effects because the concentration of indifferent electrolyte was only about fifteen times that of the reducible ion.

The polarographic reduction of ammonium ion is exactly comparable to that of alkali metal ions. The half-wave potential of ammonium ion is intermediate between those of lithium and sodium ions.

It is evident from the observed diffusion currents that the solvated ammonium ion diffuses an entity through liquid ammonia, and that the transfer of protons from one solvent molecule to another is therefore relatively slow.

Reduction of Oxygen.—It has been definitely established that the first step of reduction of oxygen by solutions of alkali metals in liquid ammonia results in the formation of insoluble superoxides[16] which have been shown by magnetic susceptibility measurements to contain the O_2^- ion.[17a,b,c] It was of interest to determine whether the reduction of oxygen at the dropping mercury electrode proceeds through two one-electron steps, followed by a two-electron reduction of the peroxide ion, or whether two two-electron reduction steps occur in liquid ammonia as in aqueous solution.

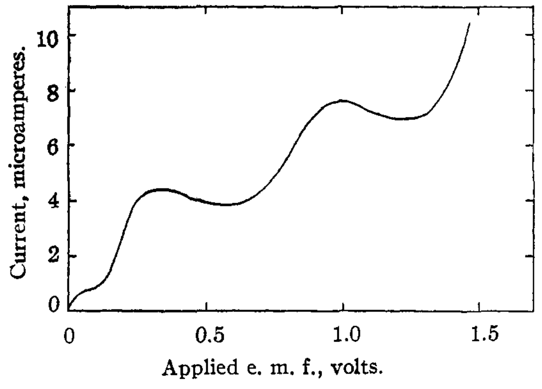

Fig. 3.—Polarogram of oxygen in 0.005 *N* potassium iodide.

The polarogram of oxygen (Fig. 3) in 0.005 *N* potassium iodide shows two waves of equal height, each distorted somewhat by a maximum. The half-wave potentials were −0.19 v. and −0.79 v., respectively, referred to the mercury pool anode, or 0.43 and −0.17 volt, respectively, with respect to the hydrogen electrode. The reciprocal slopes of the plots of log $(i_d - i)/i$ against E were 0.048 for the first wave and 0.078 for the second.

The general appearance of the curve is very similar to that observed in aqueous solution, where the two waves correspond to the reduction of oxygen to peroxide and hydroxide, respectively.

The reduction of oxygen was also studied in a highly concentrated solution of ammonium nitrate at 0°. Thirty grams of ammonium nitrate was dissolved in liquid ammonia to form about 48 ml. of solution. The first reduction step started at zero applied e.m.f., indicating that it had been shifted to a potential more positive than that required for anodic dissolution of mercury. The second wave did not change appreciably in shape or location.

An attempt was made to study the reduction of the peroxide ion. Freshly prepared sodium peroxide was too insoluble in supporting electrolytes of potassium nitrate, sodium nitrate or lithium nitrate to be detected polarographically. In the presence of ammonium nitrate, the peroxide decomposed, and two reduction waves of oxygen were observed.

Summary

1. Thallous ion and ammonium ion are reduced in liquid ammonia at the dropping mercury electrode to form the amalgams. Cupric ion is reduced first to the cuprous ion and then to the amalgam. Oxygen is reduced first to peroxide and then to hydroxide, with no evidence of superoxide ion formation.

2. The electrode processes for thallous ion, ammonium ion, and for the reduction of cupric ion to cuprous ion are essentially reversible. The second step of the copper(II) ion reduction and both steps of oxygen reduction are irreversible.

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RECEIVED APRIL 27, 1950

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[16] (a) Joannis, *Compt. rend.*, **116**, 1370 (1893); (b) Rengade, *Ann. chim. phys.*, [8] **11**, 348 (1907); (c) Kraus and Whyte, THIS JOURNAL, **48**, 1781 (1926); (d) Kraus and Parmenter, *ibid.*, **56**, 2384 (1934); (e) Schechter, Sisler and Kleinberg, *ibid.*, **70**, 267 (1948); (f) Schechter, Thompson and Kleinberg, *ibid.*, **71**, 1816 (1949).

[17] (a) Neuman, *J. Chem. Phys.*, **2**, 31 (1934); (b) Ehrlich, *Z. anorg. Chem.*, **252**, 370 (1944); (c) Stephanou, Schechter, Argersinger and Kleinberg, THIS JOURNAL, **71**, 1819 (1949).