ability to form complexes with the polyphosphates (1) quaternary ammonium ions, which form no complexes; (2) alkali metal and similar cations, which form weak complexes; and (3) the other metal ions which form strong complexes. The *p*H titration data was also discussed in terms of dissociation constants.

RUMFORD, R. I. RECEIVED AUGUST 14, 1948

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

Polarography in Liquid Ammonia. III. The Mercury Pool Anode[1]

BY H. A. LAITINEN AND C. E. SHOEMAKER[2]

In the first and second papers[3] of this series, a mercury pool anode in a saturated solution of tetrabutylammonium iodide in liquid ammonia was used as the reference electrode for polarographic measurements. The potential of the anode was measured against a lead electrode in 0.1 *N* lead nitrate. Using the data of Pleskov and Monosson[4] for the potential of the lead electrode with reference to the standard hydrogen electrode, it was possible to relate the polarographic data to the hydrogen electrode.

It is well known that in polarographic work in aqueous solution, the mercury pool anode potential is markedly affected by the nature and concentration of substances which form insoluble salts or stable complex ions with mercurous or mercuric ions.[5] In the absence of such depolarizing substances, the anode potential is determined by the concentration of mercurous ion formed as the oxidation product of mercury at the anode surface. It was of interest to determine whether mercurous or mercuric salts are formed by anodic dissolution of mercury in liquid ammonia, and to investigate various anions as possible anodic depolarizers.

There is some evidence that mercurous ions disproportionate in liquid ammonia to give mercury and mercuric ions. For example, mercurous chloride,[6a] iodide[6b] and nitrite[6c] have been reported to react and darken in liquid ammonia. Various mercuric salts, such as the iodide,[7a] bromide,[7b,c] nitrate,[7d] cyanide,[6c] cyanate[7e] and thiocyanate[7e] are soluble while the sulfate,[7d] metaborate[7f] and various base salts[7b,c,d] are insoluble. The fact that ammonobasic salts are generally precipitated in solutions containing amide ion is concordant with the large shift of anode potential previously observed upon the addition of sodamide.[3] Of the common anions, only the sulfate ion would appear to be useful as an anodic depolarizer for polarographic work. Unfortunately, its use is precluded by the insolubility of all of its common salts, including even ammonium sulfate.

To determine whether a reversible oxidation of mercury occurs at a dropping mercury anode, a determination of the slope of the anodic current–voltage curve would be desirable. Thus Kolthoff and Miller[8] showed that in water solution mercurous ions are reversibly produced at the anode in the absence of depolarizing ions. In the present work, it was found that a reliable value for the slope of the anodic curve could not be obtained using a single compartment cell with saturated tetrabutylammonium iodide as the electrolyte, because of the absence of a cathodic depolarizer for the mercury pool.

Therefore, the anodic oxidation product of mercury was prepared by electrolysis in a divided cell, and identified by chemical tests to be the mercuric ion. A cathodic current–voltage curve of the solution in the anode compartment established the reversible behavior of the mercury–mercuric ion electrode.

To determine variations in the potential of a mercury pool anode, it was convenient to employ the thallous ion as a "pilot ion" as is commonly done in aqueous solution.[9] The reduction of thallous ion was shown to be reversible, and therefore its half-wave potential served as a convenient reference point for potential measurements.

Experimental

The apparatus differed in several details from that described previously.[3] A drawing of the single-compartment cell is shown in Fig. 1. A side arm attached to the top part of the cell provided space for open sample capsules with sealed-in pieces of soft iron wire. The capsules, supported by means of Alnico magnets, could be added in sequence to the sealed cells by removing the magnets.

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[1] Abstracted from a thesis presented by Carlyle E. Shoemaker in partial fulfillment of the requirements for the Ph.D. Degree in the Graduate College of the University of Illinois, 1949.

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[3] H. A. Laitinen and C. J. Nyman, THIS JOURNAL, **70**, 2241 3002 (1948).

[4] V. A. Pleskov and A. M. Monosson, *Acta Physicochim., U. R. S. S.*, **1**, 871 (1935).

[5] I. M. Kolthoff and J. J. Lingane, "Polarography," Interscience Publishers, Inc., New York, N. Y., 1941, pp. 322 *et seq.*

[6] (a) W. Blitz and C. Man, *Z. anorg. allgem. Chem.*, **148**, 170 (1925); (b) C. A. Kraus and M. F. Kurtz, THIS JOURNAL, **47**, 43 (1925); (c) G. Gore, *Proc. Roy. Soc.* (*London*), **20**, 441 (1872).

[7] (a) W. Blitz and W. Fischer, *Z. anorg. allgem. Chem.*, **124**, 230 (1927); (b) F. F. Fitzgerald, THIS JOURNAL, **29**, 656 (1907); (c) E. C. Franklin, *ibid.*, **27**, 820 (1905), *Z. anorg. allgem. Chem.*, **46**, 1 (1905); (d) F. Friedricks, THIS JOURNAL, **35**, 1866 (1913), *Z. anorg. allgem. Chem.*, **84**, 373 (1924); (e) E. C. Franklin and C. A. Kraus, *Am. Chem. J.*, **20**, 820 (1898); (f) E. C. Franklin and C. A. Kraus, *ibid.*, **21**, 1 (1899).

[8] I. M. Kolthoff and C. S. Miller, THIS JOURNAL, **63**, 1405, 2732 (1941).

[9] H. Hohn, "Chemische Analysen mit dem Polarographen," J. Springer, Berlin, 1937.

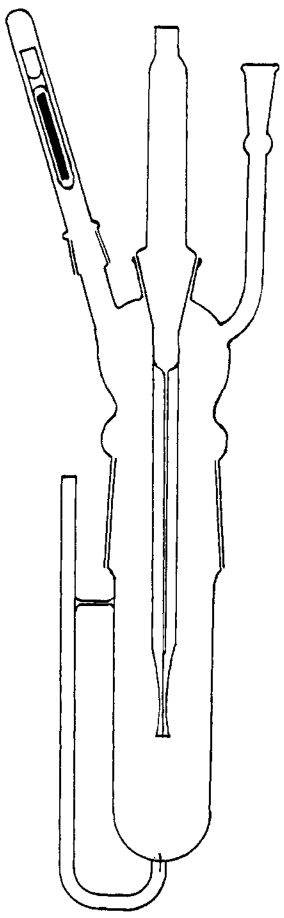

Fig. 1.—Single-compartment cell.

The divided cell was in the form of an H-cell with a sintered glass disk separator. One half of the cell, with the same provision for adding capsules as described above, was used for the dropping mercury electrode. The two compartments were connected above the liquid ammonia level by 6-mm. tubing provided with a stopcock raised above the level of the cooling reservoir.

The dropping electrode capillary was modified somewhat from the usual form to minimize the danger of clogging during the freezing and melting of the mercury which is necessary in condensing ammonia into the cell. It was made by drawing out a length of 0.5-mm. Pyrex capillary tubing, but instead of cutting it at the narrowest portion it was cut about one-half inch below this point to provide a somewhat larger and tapering exit. This form of capillary gave considerably less trouble in service, and the short constricted portion was easily cleaned. The open circuit drop time was 4.3 seconds in liquid ammonia at −36° with a pressure of 65 cm. The mass rate of flow of mercury at the same temperature was 0.623 mg. sec.$^{-1}$.

Gaseous ammonia was drawn directly from a tank of liquid ammonia through a reducing valve, and introduced into the cell after purification as previously described. All experiments were carried out at −36 ± 0.2° using the thermostat previously described. A Model XXI Sargent polarograph was used for the measurements, with a student type potentiometer for checking the voltage readings.

A solution of thallous sulfate was prepared by treating reprecipitated thallous hydroxide with dilute sulfuric acid and sulfur dioxide. Thallous chloride, precipitated by the addition of hydrochloric acid, was washed by filtration. Thallous nitrate was available as a C. P. Eimer and Amend product. Both salts were dried at 110° for several hours. Tetrabutylammonium iodide was prepared as described previously.[10]

Results and Discussion

To establish the oxidation state of anodically dissolved mercury, an electrolysis experiment was carried out in the divided cell, using mercury pool electrodes with an electrolyte of 0.1 *N* potassium nitrate in liquid ammonia. After the passage of 0.2 ampere of current for thirty minutes, a sample of solution was withdrawn from the anode compartment and allowed to evaporate to dryness. The residue was soluble in dilute hydrochloric acid. Upon the addition of ammonium hydroxide to the acid solution, a white precipitate of $HgNH_2Cl$ was formed. Another portion of the solution, upon treatment with potassium iodide, gave a red precipitate of mercuric iodide, soluble in excess potassium iodide. The chemical tests clearly indicated the formation of mercuric ion and the absence of mercurous ion.

To determine the equation of the cathodic current–voltage curve of mercuric ion, a similar electrolysis experiment was carried out in the divided cell. After the passage of about 30 milliamperes of current for a period of one hundred and ten seconds, an appreciable cathodic current could be detected polarographically using the dropping mercury electrode in the anode compartment. The current–voltage curve (Fig. 2), starting at an applied e. m. f. of zero, was a smooth curve without an indication of a maximum. A plot of applied potential *versus* log ($i_d - i$) gave a straight line (Fig. 2) with a reciprocal slope of 0.0250 as compared with the theoretical value of 2.3 $RT/2F$ or 0.0245 for a reversible two-electron process at −36°. It is concluded that the mercury–mercuric ion electrode behaves essentially reversibly at the dropping electrode.

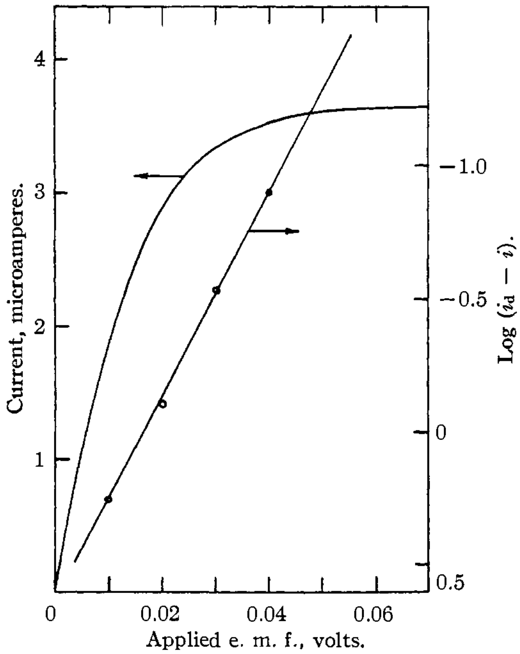

Fig. 2.—Cathodic reduction of mercuric ion in 0.1 *M* KNO_3.

A series of experiments was carried out with thallous ion as the pilot ion to determine the effect of composition of the solution on the mercury pool anode potential. The first group of experiments, which were run before an effective maximum suppressor for thallium was found, gave curves of the type shown in Fig. 3, with distinct maxima. Because of the presence of maxima, exact significance cannot be attached to the half-wave potentials listed in Table I. However, it is

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[10] H. A. Laitinen and S. Wawzonek, THIS JOURNAL, 64, 1765 (1942).

evident that the anode potential was relatively unaffected by the presence of nitrate, chloride, iodide or ammonium ions.

TABLE I

HALF-WAVE POTENTIAL OF THALLIUM *vs.* MERCURY POOL ANODE

Thallous chloride present in 3 to 5 × 10^{-4} *M* concentration; no maximum suppressor.

Additional electrolytes	$-E_{1/2}$, volts
0.1 *M* KNO_3	0.177
.1 *M* KNO_3, 0.005 *M* KI	.181
.1 *M* KI	.181
.1 *M* KNO_3, 0.0071 *M* NH_4NO_3	.183
.1 *M* KNO_3, 0.0927 *M* NH_4NO_3	.188
.1 *M* NH_4Cl	.195

In another set of experiments, summarized in Table II, a trace of methylcellulose was used as a maximum suppressor. The anode potential was calculated with reference to the lead–0.1 *N* lead nitrate electrode, using the previously determined value[3] of the anode potential in saturated tetrabutylammonium iodide as a basis. The anode potential was unaffected by iodide or ammonium ion concentration, but became increasingly positive with increasing mercuric ion concentration. The calculated values of the normal potential of the mercury–mercuric ion electrode are in agreement with the measured value of 0.421 volt observed at −50° by Pleskov and Monosson.[11]

TABLE II

HALF-WAVE POTENTIAL OF THALLIUM AND POTENTIAL OF MERCURY POOL ANODE[a]

Added electrolyte, *M* × 10^4	$-E_{1/2}$, volt	*E* anode, volt	E^0 Hg, Hg^{++}, volt
None	0.151, 0.159	0.30, 0.30	
NH_3NO_3, 4.36	0.161	0.31	
KI, 11.2	.158	.31	
HgI_2, 0.46	.195	.35	0.44
HgI_2, 1.03	0.197, 0.198	.35	.44
HgI_2, 1.03[b]	0.198		
Hg^{++}, 3.4[c]	0.226	.38	.45

[a] All solutions saturated with tetrabutylammonium iodide except where noted. Thallous nitrate present in 3 to 5 × 10^{-4} *M* concentration. Methylcellulose added as maximum suppressor. [b] Plus H_2O, 2.78 × 10^{-3} *M*. [c] Plus KNO_3, 0.1 *M*, no tetrabutylammonium iodide present; Hg^{++} by electrolysis.

It is concluded that the concentration of mercuric ion is the only potential determining factor at a mercury pool anode in the presence of nitrate, chloride, iodide and nitrate ions. The fact that the anode potential is independent of ammonium ion concentration implies that solvolysis of the ammoniated mercuric ion to form species such as $HgNH_2^+$ must occur only to a very limited extent. This observation is in accord with the very slight degree of auto-ionization of liquid ammonia.[12] Even traces of water had no detectable effect, showing that mercuric oxide or hydroxy cations do not form under these conditions.

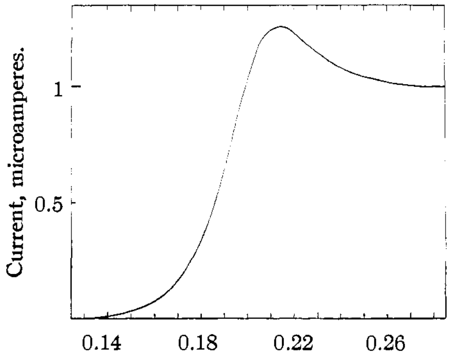

Fig. 3.—Polarogram of 2.89 × 10^{-4} *M* TlCl in 0.005 *M* KI, 0.1 *M* KNO_3.

For practical work, it is recommended that no mercuric salts be added, but that successive polarograms be run until the observed half-wave potential is constant. The small amount of mercuric ion formed at the anode during the recording of three polarograms was generally sufficient to stabilize the anode potential within 10 millivolts for the recording of ten to fifteen additional curves.

Summary

1. An improved type of dropping mercury electrode and electrolysis cell has been designed for polarographic measurements in liquid ammonia.

2. Mercuric ion was established as the anodic oxidation product of mercury in liquid ammonia. The mercury–mercuric ion electrode behaves reversibly in liquid ammonia.

3. The potential of a mercury pool anode was found to be independent of the concentration of nitrate, chloride, iodide or ammonium ions in solution. The potential was dependent only on the concentration of mercuric ion.

URBANA, ILL. RECEIVED JUNE 25, 1949

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(11) V. A. Pleskov and A. M. Monosson, *J. Phys. Chem.* (*U. S. S. R.*), **4**, 696 (1933).

(12) V. A. Pleskov and A. M. Monosson, *Acta Physicochim. U. R. S. S.*, **1**, 713 (1935).