responsible for the optical interaction and the exchange reaction is then assumed to be present at very low concentration), or the colored complex is not the activated complex for the exchange.

As a result of the lack of accurate knowledge concerning the nature of the ions in solution, it seems rather futile to attempt to decide definitely on the mechanism of the exchange reaction at present.

Further experiments designed to obtain more information about the nature of the antimony ions are planned.

Summary

1. A method has been developed for the separation of antimony(V) from antimony(III) by means of an ether extraction from hydrochloric acid solution.

2. A study of the rate of the exchange reaction between antimony(III) and antimony(V) shows that the rate law at 25.0°, with hydrogen ion concentrations from 4.7 *f* to 6.1 *f*, chloride ion concentration from 5.4 *f* to 6.1 *f*, antimony(III) concentrations from 0.0008 *f* to 0.040 *f*, antimony (V) concentrations from 0.0008 *f* to 0.0040 *f* and Na^+ concentrations from 0.0 *f* to 0.8 *f* is $R = (8.8 \pm 0.9) \times 10^{-11} (\mathrm{Sb(III)})^{0.6} (\mathrm{Sb(V)})^{1.1} (\mathrm{H}^+)^4 (\mathrm{Cl}^-)^9$ mole × $\text{liter}^{-1} \times \text{hr.}^{-1}$.

3. In the same ranges of concentrations the experimental activation energy is 27 ± 2 kcal./mole (measurement made at 9.8, 25.0 and 34.6°).

4. In 12.0 *f* hydrochloric acid at 25.0° the half-time for exchange is 36.2 minutes with an antimony(III) concentration of 0.0235 *f* and an antimony(V) concentration of 0.0198 *f*.

ST. LOUIS, MO. RECEIVED MAY 31, 1949

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE STATE COLLEGE OF WASHINGTON]

Polarography of Calcium, Strontium and Barium in Liquid Ammonia

BY C. J. NYMAN

The polarographic characteristics of several ions in liquid ammonia have been previously reported.[1] The present paper deals with the reduction of calcium, strontium and barium salts in this solvent.

Experimental

The electrolysis cells and apparatus for preparing the anhydrous liquid ammonia solutions have been described previously.[1] The cell with the internal reference electrode was used in all cases.

The dropping mercury electrode had the following characteristics in a saturated solution (0.021 *M*) of tetraethylammonium iodide in liquid ammonia at −36°. At a pressure of 20 cm., the drop time *t* was 5.1 sec. (open circuit) and the mass of mercury *m* flowing through the capillary was 1.184 mg./sec.

A Fisher Elecdropode, calibrated in the usual manner, was used in this investigation. All applied potentials were checked by means of a student type potentiometer.

The ammonia, barium nitrate and strontium nitrate were C. P. materials of commerce. Calcium iodide was prepared in the following way: 3 g. of calcium hydroxide was made into a slurry with 100 cc. of water, and then ammonium iodide was added until all the calcium hydroxide dissolved. The solution was filtered, and an additional 15 g. of ammonium iodide was added. The solution was evaporated almost to dryness on a hot-plate, and the resulting paste was transferred to porcelain boats. These were placed in a Pyrex combustion tube and heated by means of a tube furnace. A stream of dry hydrogen was used to sweep the water vapor and excess ammonium iodide from the region of the boats. The temperature was raised slowly to about 150° and held for two hours, when it was increased to 400° for two hours. The material was allowed to cool with the stream of hydrogen still passing through the tube. On analysis, the calcium iodide contained less than 0.5% impurity. The purification of the tetraalkylammonium salts has been described previously.[1]

Data and Discussion

Figure 1 shows typical polarograms obtained on electrolysis of calcium iodide solutions when using tetraethylammonium iodide as indifferent electrolyte. A maximum was observed even with low concentrations of calcium ion, and it was only partially suppressed by traces of methyl red. Higher concentrations of methyl red did not completely eliminate the maximum. A similar behavior was exhibited by the strontium ion (see Fig. 2), but the barium ion did not show a maximum when using tetraethylammonium iodide as the indifferent electrolyte (see curve II, Fig. 3). With tetrapropylammonium iodide, barium exhibits a maximum which is not suppressed by either methyl red or methyl cellulose (see curve I, Fig. 3).

TABLE I

DIFFUSION CURRENTS OF CALCIUM, STRONTIUM AND BARIUM IN LIQUID AMMONIA AT −36°

Ion	*C*	*D*	$m^{2/3}t^{1/6}$	i_d, microamp. Calcd.	i_d, microamp. Obs.	% Δ
Ca	0.38	1.91×10^{-5}	1.019	2.05	2.0	−2.5
Ca	.82		1.019	4.4	4.5	+2
Sr	.37	1.94×10^{-5}	1.180	2.32	2.39	+3
Sr	.52		1.180	3.28	3.27	...
Sr	.78		1.185	4.94	5.21	+6
Ba	.43	1.77×10^{-5}	1.249	2.72	2.65	−3
Ba	.63		1.249	4.00	3.90	−3

The diffusion currents for various concentrations of the alkaline earth metal ions, as measured in liquid ammonia at −36°, are recorded in Table I. Tetraethylammonium iodide served

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[1] For previous papers, see H. A. Laitinen and C. J. Nyman, THIS JOURNAL, **70**, 2241, 3002 (1948).

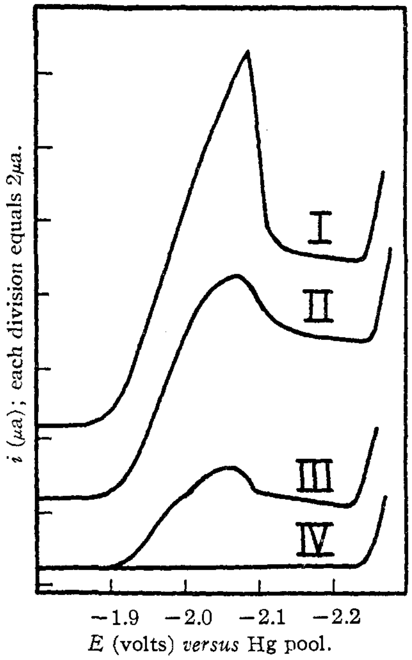

Fig. 1.—Polarograms of calcium iodide in saturated tetraethylammonium iodide: curve I, 8.2 × 10^{-4} *M*; curve II, 8.2 × 10^{-4} *M* plus a trace of methyl red; curve III, 3.8 × 10^{-4} *M* plus a trace of methyl red; curve IV, saturated solution of tetraethylammonium iodide.

as the supporting electrolyte. Theoretical values were calculated by means of the Ilkovic equation[2,3]

$$i_d = 605nCD^{1/2}m^{2/3}t^{1/6}$$

which relates the diffusion current i_d (microamperes) of an ion to n, the number of faradays of electricity required per mole of electrode reaction, to its concentration C (millimoles per liter), to its ionic diffusion coefficient D (sq. cm./sec.), and to the capillary characteristics m (mg./sec.) and t (sec.). The ionic diffusion coefficient D can be evaluated by means of the expression[4,5]

$$D = RT\lambda^0/zF^2$$

where R is 8.317 volt-coulombs per degree, T is the absolute temperature, λ^0 is the equivalent conductance of the ion at infinite dilution (ohm^{-1}-sq. cm.-equiv.$^{-1}$), z is the charge of ion, and F is 96,500 coulombs. Most of these terms are experimental quantities which can be easily evaluated. Gurjanowa and Pleskov[6] reported the equivalent ionic conductance at −40° of calcium, strontium and barium at infinite dilution as 180, 183 and 167 ohm^{-1}-sq. cm.-equiv.$^{-1}$, respectively.

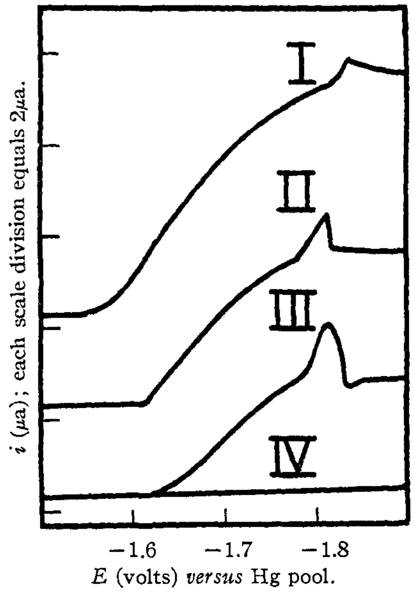

Fig. 2.—Polarograms of strontium nitrate in saturated tetraethylammonium iodide: curve I, 7.8 × 10^{-4} *M* plus a trace of methyl red; curve II, 5.2 × 10^{-4} *M* plus a trace of methyl red; curve III, 3.7 × 10^{-4} *M*; curve IV, saturated solution of tetraethylammonium iodide.

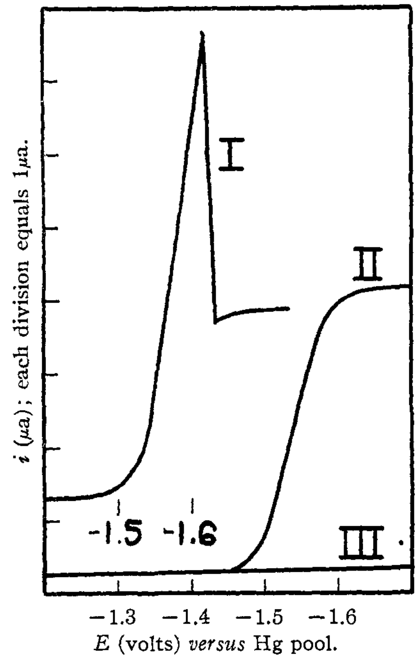

Fig. 3.—Polarograms of barium nitrate: curve I, 4.3 × 10^{-4} *M* in saturated tetrapropylammonium iodide; curve II, 6.3 × 10^{-4} *M* in saturated tetraethylammonium iodide; curve III, saturated solution of tetraethylammonium iodide.

As can be seen, the agreement between the observed and calculated values of i_d is good, and it is considerably better than that observed in the case of the alkali metal ions[1] where the ob-

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(2) D. Ilkovic, *Coll. Czech. Chem. Commun.*, **6**, 498 (1934).

(3) D. MacGillavry and E. K. Rideal, *Rec. trav. chim.*, **56**, 1013 (1937).

(4) W. Nernst, *Z. physik. Chem.*, **2**, 613 (1888).

(5) I. M. Kolthoff and J. J. Lingane, THIS JOURNAL, **61**, 825 (1939).

(6) E. N. Gurjanowa and V. A. Pleskov, *Acta Physicochim. U. R. S. S.*, **5**, 509 (1936).

served values were higher by 10%. This is attributed to the fact that the migration current has been markedly reduced by the higher relative concentration of indifferent electrolyte. The solubility of tetraethylammonium iodide, which was used in this investigation, is about four times as great as that of tetrabutylammonium iodide, which was used in the investigation of the alkali metal ions.

TABLE II

$E_{1/2}$ IN LIQUID AMMONIA AT $-36°$ *versus* MERCURY POOL

Ion	C. mmole/l.	$E_{1/2}$, volts	Slope of $E_{d.e.}$ vs. log $\left(\frac{i_d - i}{i}\right)$
Ca	0.38	−1.96	0.058
Ca	.82	−1.96	.044
Sr	.37	−1.69	.061
Sr	.52	−1.68	.078
Sr	.78	−1.67	.117
Ba	.58	−1.54	.033
Ba	.63	−1.54	.040

Since the shape of a polarographic reduction wave, when the metal is soluble in mercury, is given by the expression[7]

$$E_{d.e.} = E_{1/2} + \frac{2.303RT}{nF} \log \frac{(i_d - i)}{i}$$

the slope of a plot of $E_{d.e.}$ *versus* log $(i_d - i)/i$ can be used as a test for reversibility. $E_{d.e.}$ is the potential of the dropping mercury electrode; $E_{1/2}$ is the half-wave potential; i_d is the diffusion current; and i is the current flowing at a potential $E_{d.e.}$. A reversible two-electron reduction would give a slope of 0.024.

In Table II are recorded values for the half-wave potentials of calcium, strontium and barium in liquid ammonia at $-36°$ and also the slope of $E_{d.e.}$ *vs.* log $(i_d - i)/i$. The approach of the reduction to reversibility is not so close in the case of the alkaline earth ions as it is in the case of the alkali metal ions.[1] There is a parallel behavior between these ions and the alkali metal ions in that the largest ion is the most readily reduced to the amalgam. Insufficient data are available to calculate theoretical values of the half-wave potentials.

Summary

The diffusion currents of calcium, strontium and barium ions were measured and found to agree with those calculated by the Ilkovic equation.

The half-wave potentials were determined, and the reduction was found to be less reversible than in the case of the alkali metal ions.

PULLMAN, WASH. RECEIVED JULY 26, 1949

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[7] J. Heyrovsky and D. Ilkovic, *Coll. Czech. Chem. Commun.*, **7**, 198 (1935).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF PURDUE UNIVERSITY AND THE PURDUE RESEARCH FOUNDATION]

Polarographic Behavior of Organic Compounds. I. The Maleate and Fumarate Species

BY PHILIP J. ELVING* AND CHARLES TEITELBAUM

Although extensive polarographic investigations of maleic and fumaric acids have been carried out, there was felt to be a need for a thorough study of the acids with a more careful control of the factors affecting polarographic reduction.

Insufficient attention was paid in much of the previous work[1] to such factors as buffering, electrolyte concentration, capillary characteristics, temperature control and concentration. The most thorough previous work is that of Vopicka,[1c] although the concentrations he used were somewhat high, capillary characteristics were not given, buffering at the ends of the *p*H range studied was not satisfactory, no measurements were made between *p*H 5.3 and 9.0, and no temperature control was attempted. He developed an equation to express the effect of *p*H on half-wave potential. Herasymenko[1e] interpreted Vopicka's results on the basis of a new equation, which gave slightly better agreement with the experimental results. The only previous work on the calculation of the "*n*" values (apparent electron change per molecule reduced) is that of Furman and Bricker[1k] for maleic acid where values of 1.17 and 1.22 were obtained. No clear relationship between diffusion current and *p*H has been established; Vopicka[1c] indicates a straight line relation between half-wave potential, $E_{0.5}$, and *p*H. No previous report has been found of the appearance of double waves in buffered solution. No previously reported polarographic investigation of the esters has been located.

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[1] (a) Herasymenko, *Z. Elektrochem.*, **34**, 74 (1928); (b) Schwaer, *Chem. Listy*, **26**, 485 (1932); (c) Vopicka, *Coll. Czechoslav. Chem. Commun.*, **8**, 349 (1936); (d) Semerano and Bettinelli, *Gazz. chim. ital.*, **66**, 744 (1936); (e) Herasymenko, *Coll. Czechoslav. Chem. Commun.*, **9**, 104 (1937); (f) Miolati, *Mem. accad. Italia, Classe. sci. fis. mat. nat.*, **8**, 215 (1937); (g) Semerano and Bettinelli, *ibid.*, **8**, 255 (1937); (h) Miolati and Semerano, *Ricerca sci.*, **8**, II, 243 (1937); (i) Semarano and Rao, *Mikrochemie*, **23**, 9 (1937); (j) Semerano, *ibid.*, **24**, 10 (1938); (k) Furman and Bricker, THIS JOURNAL, **64**, 666 (1942); (l) Clark and Knopf, ACS, Abstracts of Papers, Meeting in Print, p. 3L, Sept., 1945; (m) Warshowsky, Elving and Mandel, *Anal. Chem.*, **19**, 161 (1947).