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Polarography in N,N'-Dimethylformamide. I. Alkali Metal Ions, Alkaline Earth Metal Ions and Certain Transition Metal Ions

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The polarography of the alkali metal and alkaline earth metal ions and cobalt(II), copper(II), nickel and zinc ions in N,N'-dimethylformamide has been studied, and the following half-wave potentials (*vs.* mercury pool) were determined: Li −1.81, Na −1.53, K −1.55, Ca −1.84, Sr −1.68, Ba −1.49, Co −1.32, Cu −0.15, Ni −1.06 and Zn −1.12 v. The supporting electrolyte for the alkali metal ions and the alkaline earth metal ions was 0.1 *M* tetrabutylammonium iodide and that for the transition metals was 0.2 *M* sodium perchlorate. Rubidium and cesium ions gave curves with maxima that could not be suppressed. The diffusion current constants of the ions studied were from 60 to 70% of the values reported in water and approximately twice those reported in acetonitrile.

N,N'-Dimethylformamide is an interesting solvent for polarographic studies. It has a high dielectric constant (36.7 at 25°), a convenient liquid range (freezing point − 63°, boiling point 153°), a relatively low viscosity (0.802 cp. at 25°), a low vapor pressure (3.7 mm. at 25°), and its solutions have a low electrical resistance. Moreover, with dimethylformamide as the solvent and tetrabutylammonium iodide as the supporting electrolyte, a negative potential of −2.4 volt *versus* the mercury pool can be obtained. Thus, well-defined waves for lithium, sodium and potassium ions and the alkaline earth metal ions can be obtained in this solvent, a condition which is not always the case with water as the solvent.

Perchlorates, in general, are soluble in dimethylformamide; iodides of the alkali metals and alkaline earth metals are very soluble; chlorides of the alkali metals and the alkaline earth metals are sparingly soluble, except lithium chloride which is soluble to an extent that it can be used as a supporting electrolyte in the solvent. All nitrates are soluble in dimethylformamide but decompose on standing.

Edsberg, Eichlin and Garis[2] studied the polarography of the anthraquinone–anthrahydroquinone system in N,N'-dimethylformamide as a solvent. Berkey[3] studied the polarographic behavior of a number of aromatic olefins and quinones in dimethylformamide while Wawzonek,[4] *et al.*, studied quinones and hydroquinones. The behavior of aromatic olefins and hydrocarbons in dimethylformamide has been reported by Wawzonek, Berkey, Blaha and Runner.[5] Prior to this investigation, there appears to be only one reference to the use of dimethylformamide in the polarography of inorganic salts. Findies and DeVries[6] studied the polarography of potassium tetraphenylborate-(III) in dimethylformamide as a method for the analysis of potassium.

This paper deals with the polarography of the alkali metal ions, the alkaline earth metal ions, as well as the four other metal ions: cobalt, copper, nickel and zinc.

Experimental

Instrumentation and Procedure.—All polarograms were obtained using a Leeds and Northrup recording "Electro-Chemograph." The electromotive force recorded by the instrument was checked with a Leeds and Northrup student type potentiometer. All diffusion currents were corrected for residual current which never exceeded 1.5 μ amp. for any potential at which the diffusion current was measured. Since the resistance of the cell with either tetrabutylammonium iodide or sodium perchlorate as the supporting electrolyte was low, the potentials were not corrected for "*iR* drop" (did not exceed 6 millivolts in the most extreme case) across the electrolysis cell. The cathode was a dropping mercury electrode and the anode a mercury pool. The half-wave potentials were measured against the mercury pool as the non-polarized electrode.

Maxima in the polarograms occasionally were observed, especially at higher concentrations of the reducible ions. Rubidium and cesium ions gave maxima that persisted even at concentrations as low as could be measured polarographically. These maxima could not be suppressed by any substances used for this purpose in water systems.

The capillaries were made of Corning marine barometer tubing which has a capillary of 28.4-micron radius and were prepared 10 cm. in length. Three different capillaries were constructed for this study and their characteristics, "*m*" and "*t*" established. Capillary 1 (open circuit): m = 2.22 mg./sec. and t = 4.2 sec. for h = 33.5 cm.; capillary 2 (open circuit): m = 1.48 mg./sec. and t = 5.1 sec. for h = 33.5 cm.; capillary 3 (open circuit): m = 1.42 mg./sec. and t = 5.2 sec. for h = 33.5 cm.

The polarographic cell used in this work was a Sargent Cell No. 29373. Since it has been found[6] that the temperature coefficient of the diffusion current in dimethylformamide is rather large, a temperature control was critical. The cell was immersed in a water-bath at a temperature of 25 ± 0.2°. The electrolysis solutions were deaerated by bubbling tank nitrogen, obtained from the National Cylinder Company, through them.

Materials.—The N,N'-dimethylformamide obtained from The Matheson Company, Inc., was used as the solvent. It has been reported[6] that there is no measurable difference between the polarograms obtained with this solvent which was dried by distillation over calcium hydride and the commercial grade (boiling point 152–154°). It was found in this work that a water concentration of 3 ml. in 25 ml. of dimethylformamide did not change the decomposition potentials of the supporting electrolyte. Two supporting electrolytes were used in this study. Tetrabutylammonium iodide, obtained from Matheson Coleman and Bell Division of The Matheson Company, Inc., was purified by recrystallization from ethyl acetate according to the directions of Laitinen and Wawzonek.[7] It was then dried at 60° in a vacuum oven at 27 mm. pressure. A solution of tetrabutylammonium iodide in dimethylformamide decomposes slowly on standing and the impurity current becomes appreciable after several weeks. Therefore, freshly prepared electrolyte solutions were used for all measurements made in this

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[1] Taken in part from a thesis submitted by Rasmia Al-Urfali to the Graduate School of the University of Cincinnati in partial fulfillment of the requirements for the Master of Science degree, June, 1958.

[2] R. L. Edsberg, D. Eichlin and J. J. Garis, *Anal. Chem.*, **25**, 798 (1953).

[3] R. Berkey, *Dissertation Abst.*, **15**, 953 (1955).

[4] S. Wawzonek, R. Berkey, E. Blaha and M. E. Runner, *J. Electrochem. Soc*, **103**, 456 (1956).

[5] S. Wawzonek, E. W. Blaha, R. Berkey and M. E. Runner, *ibid.*, **102**, 235 (1955).

[6] A. Findies and T. DeVries, *Anal. Chem.*, **28**, 209 (1956).

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

study. The decomposition potential of a 0.1 *M* solution of tetrabutylammonium iodide in dimethylformamide at 25° is −2.4 v. *vs.* a mercury pool.

Anhydrous sodium perchlorate was found to be quite soluble in dimethylformamide at 25°. It was used as the non-complexing, supporting electrolyte for the study of cobalt(II), copper(II), nickel and zinc ions. Anhydrous sodium perchlorate of "reagent" quality purchased from G. Frederick Smith Chemical Company was used without further purification. The decomposition potential of a 0.2 *M* solution of sodium perchlorate in dimethylformamide is −1.6 v. *vs.* a mercury pool.

Sodium iodide, potassium iodide, rubidium iodide, cesium chloride and lithium chloride were used for the polarograms of the alkali metal ions. Solutions were prepared from "reagent" quality salts which were dried at 60° *in vacuo* at 27 mm. pressure. With the exception of cesium chloride, all salts were readily soluble in the solvent. The highest concentration of cesium chloride that could be prepared was approximately four millimolar.

The anhydrous barium and strontium perchlorates, and calcium perchlorate (hydrate), as obtained from The G. Frederick Smith Company, were used without further purification. Solutions of calcium ions also were prepared from anhydrous calcium chloride. Solutions of barium and strontium perchlorates and calcium chloride were prepared from samples dried at 100° in a vacuum oven at 27 mm. pressure. The calcium perchlorate solutions were prepared from samples dried in a current of dry air and dissolved as the hydrate.

Cobalt, copper, nickel and zinc perchlorates (hydrates) obtained from the G. Frederick Smith Company were used without further purification. Solutions were prepared from samples dried in a current of dry air and dissolved as the hydrates.

Results and Discussion

Polarography of the Alkali Metal Ions.—Well-defined waves were obtained for lithium, sodium and potassium while rubidium and cesium always gave maxima in the polarograms even at concentrations as low as could be measured polarographically. Lithium and sodium ions gave maxima at concentrations greater than 3 millimolar. The supporting electrolyte in all cases was decinormal tetrabutylammonium iodide. Different concentrations (1-3 millimolar) of the electro-reducible ions were used and the diffusion current was proportional to the concentration of the ion. The half-wave potentials of the ions remained constant with concentration over the range tested. It should be noted that the lithium ion gives a well-defined wave and that the reduction is reversible. In acetonitrile the reduction of lithium has been reported[8] as reversibly incomplete as is also the case for this ion in water.

The half-wave potentials of sodium, potassium, rubidium and cesium are closely grouped as in aqueous solution. Also, the order of reducibility of these ions is the same as in water.[9] The lithium wave is sufficiently separated from the other alkali metal ions so as to afford a means of analysis of this ion in the presence of any one or all of the others. It is difficult to compare half-wave potentials secured in different solvents. Also, where different reference electrodes are involved, the $E_{1/2}$ values cannot be expected to be the same or even to be directly related in any absolute sense. Discussion of the reasons for this last statement may be found elsewhere.[10] Relative comparisons for a series of cations do have significance, however. The half-wave potentials of the alkali metal ions are more positive than those obtained in water and more negative than those obtained in acetonitrile.[8,11,12] It may be inferred from these results that dimethylformamide has a more basic character than acetonitrile and a less basic character than water. Data on the alkali metal ions are to be found in Table I.

TABLE I

POLAROGRAPHIC CHARACTERISTICS OF THE ALKALI METAL IONS, ALKALINE EARTH METAL IONS, COBALT(II), COPPER(II), NICKEL AND ZINC IN N,N′-DIMETHYLFORMAMIDE

Salt	Supporting electrolyte	Concn. mmole/l.	I_d	$-E_{1/2}$ v. *vs.* Hg. Pool	D, cm.²/sec. × 10^5	$\frac{0.059}{n}$
LiCl	Bu_4NI[a]	4	1.09	1.81	0.32	0.062
NaI	Bu_4NI	2	1.61	1.53	.70	.062
KI	Bu_4NI	2	1.63	1.55	.72	.069
RbI	Bu_4NI	2	1.68[b]	1.52[b]	.77	Maximum
CsCl	Bu_4NI	2	1.98[b]	1.53[b]	1.06	Maximum
$Ba(ClO_4)_2$	Bu_4NI	2	2.36	1.49	0.38	0.043
$Sr(ClO_4)_2$	Bu_4NI	2	2.41	1.68	.39	.059
$Ca(ClO_4)_2 \cdot 6H_2O$	Bu_4NI	4	2.10	1.84	.29	.076
$CaCl_2$	Bu_4NI	2	1.96	1.78	.25	...
$Co(ClO_4)_2 \cdot 6H_2O$	$NaClO_4$	2	2.88	1.32	.57	.116
$Cu(ClO_4)_2 \cdot 6H_2O$	$NaClO_4$	2	2.13	0.15	.31	.049
$Ni(ClO_4)_2 \cdot 6H_2O$	$NaClO_4$	2	2.59	1.06	.46	.105
$Zn(ClO_4)_2 \cdot 6H_2O$	$NaClO_4$	2	2.24	1.12	.34	.048

[a] Bu_4NI is tetrabutylammonium iodide. [b] Values are only approximate.

Polarography of the Alkaline Earth Metal Ions.—The polarograms of barium, strontium and calcium perchlorates in dimethylformamide with 0.1 *M* tetrabutylammonium iodide as the supporting electrolyte are given in Fig. 1. As can be seen from the figure, the half-wave potentials of these ions are sufficiently separated from each other so that any ion may be determined in the presence of the others.

The barium wave shows a reversible reduction and the waves for calcium and strontium show a behavior which is not far from reversibility. The order of magnitude of the half-wave potentials of these ions is the same as that found in aqueous solution (*i.e.*, Ca > Sr > Ba). However, the half-wave potentials for a given ion are shifted to more positive values in dimethylformamide than in water.[15] The separation of the half-wave potentials of these ions in dimethylformamide is more pronounced than in acetonitrile[8,12,14] thus making the analysis of one in the presence of the others much easier in the former solvent. The polarographic characteristics of these ions are given in Table I.

Polarography of Cobalt, Copper, Nickel and Zinc Ions.—The polarographic data on cobalt(II), copper(II), nickel and zinc with decinormal sodium perchlorate as the supporting electrolyte are given in Table I. Polarograms of these four ions are well-defined and are comparable in many respects to those obtained in aqueous solutions. The reduction in aqueous solution of nickel(II) and cobalt(II)

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[8] I. M. Kolthoff and J. F. Coetzee, THIS JOURNAL, **79**, 870 (1957).

[9] G. W. G. Milner, "The Principles and Applications of Polarography," Longmans, Green and Co., New York, N. Y., 1957, pp. 185–192.

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

[11] S. Wawzonek and M. E. Runner, *J. Electrochem. Soc.*, **99**, 457 (1952).

[12] A. I. Popov and D. H. Geske, THIS JOURNAL, **79**, 2074 (1957).

ions at the dropping electrode requires a large overvoltage[13] with the result that highly irreversible waves are obtained at much more negative potentials than would be predicted from the reversible standard potential of the metal–metal ion couples. The same appears to be the case in the reduction of nickel(II) and cobalt(II) in dimethylformamide. The reduction waves for these ions are well-defined but the reduction is definitely irreversible as can be seen by the values of 0.059/*n* in Table I. The half-wave potentials of cobalt(II) and nickel(II) in dimethylformamide are almost the same as those obtained in water.[13] These facts indicate that the $Co(DMF)_n^{+2}$ ion and the $Ni(DMF)_n^{+2}$ ion are as irreversibly reduced as the aquo cobalt(II) and aquo nickel(II) ions. It has been reported[14] that nickel is reduced reversibly in acetonitrile while cobalt deviates only slightly from reversibility. However, Popov and Geske[12] report two reducible species in nickel perchlorate solutions in acetonitrile but the height of the individual waves was not reproducible.

TABLE II

DIFFUSION CURRENT CONSTANTS OF METAL IONS IN DIFFERENT SOLVENTS

Ion	I_d in water (ref. 15)	I_d in DMF (present work)	I_d in CH_3CN (ref. 8, 14)
Lithium		1.09	2.56
Sodium		1.61	3.16
Potassium		1.63	3.38
Rubidium		1.68[a]	3.25
Cesium		1.98[a]	. .
Calcium	3.39	2.10	4.61
Strontium	3.44	2.41	5.43
Barium	3.57	2.36	5.37
Cobalt(II)	. .	2.88	4.26
Copper(II)	3.24	2.18	2.37 2.37 } 2 Waves
Nickel	3.54	2.59	4.04
Zinc	3.42	2.24	4.18

[a] Approximate values.

Copper(II) gave a one-step reduction wave showing that copper(I) is as unstable in dimethylformamide as it is in water. Zinc ions give a well-defined, reversible wave. It should be pointed out that a zinc nitrate solution does not give a reproducible polarographic wave. This can be explained by the fact that nitrates decompose in dimethylformamide.

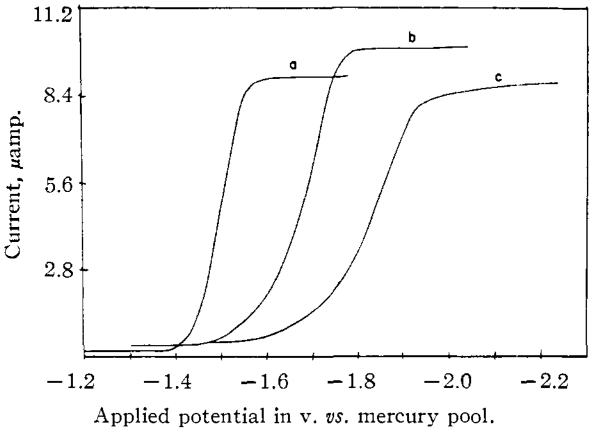

Fig. 1.—Polarography of alkaline earth metal ions in dimethylformamide: (a) 2×10^{-3} *M* $Ba(ClO_4)_2$; ˙(b) 2×10^{-3} *M* $Sr(ClO_4)_2$; (c) 2×10^{-3} *M* $Ca(ClO_4)_2$. Decinormal tetrabutylammonium iodide was the supporting electrolyte.

Diffusion Current Constants.—The diffusion current constants reported in Table I were calculated using values for "*t*" which were taken at the decomposition potential of the particular ion. It is interesting to compare the diffusion current constants of the twelve ions reported in this paper with the constants obtained for these ions in other solvents. Values of I_d for these ions in different solvents are summarized in Table II.

From Table **II** it can be seen that the diffusion current constants for the ions in dimethylformamide are from 60 to 70% of the values obtained in water. This difference can be attributed mainly to the smaller diffusion coefficients of these ions in dimethylformamide than in water. The two factors that would have most influence on the diffusion coefficients in these solutions are viscosity difference and difference in the size of the solvated species. The effect of the difference in viscosity is almost negligible because the viscosities of dimethylformamide (0.802 cp. at 25°) and water (0.8437 cp. at 25°) are nearly equal. Therefore, the decreased diffusion coefficient may be attributed to the larger solvated ions in the dimethylformamide; thus these ions diffuse more slowly than hydrated ions. On comparison of the diffusion current constants obtained in acetonitrile with those that were obtained in dimethylformamide, it can be seen that most values are twice those obtained in dimethylformamide. In this case the difference in viscosity is certainly an important factor (acetonitrile 0.345 cp. at 25°) while difference in the size of the solvated electroreducible ion will also contribute to the variation.

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(13) I. M. Kolthoff and J. J. Lingane, "Polarography," Vol. 2, Interscience Publishers, New York, N. Y., 1952, pp. 480–486.

(14) I. M. Kolthoff and J. F. Coetzee, THIS JOURNAL, **79**, 1852 (1957).

(15) I. M. Kolthoff and J. J. Lingane, "Polarography," Vol. 2, Interscience Publishers, New York, N. Y., 1952, pp. 431–433 and pp. 487–504.