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N-Methylacetamide as a Polarographic Solvent

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Two methods, both of which require an unusual amount of care, are described for the preparation of polarographically pure N-methylacetamide (NMA). The polarographic range in such a purified solvent extends from +0.35 to −2.7 volts (*vs.* s.c.e.) using 0.1 *M* $(C_2H_5)_4NClO_4$ as supporting electrolyte. The polarographic reduction potentials of thallium(I) and of copper(II) are of the same order of magnitude as those in water. As far as reduction of cations (except hydrogen ion) is concerned, NMA appears to behave like water as a solvent. From acid–base studies to be reported in a subsequent paper, we conclude that NMA is a weaker acid than water, and in that respect resembles acetonitrile and dimethyl sulfoxide. In solvents which are poor proton donors, complicated polarographic waves may be expected in the reduction of compounds (mainly organic) which require two electrons and the participation of protons. The unequal height of the two waves in the reduction of oxygen in NMA probably is accounted for on this basis. From an analytical viewpoint, it can be concluded that NMA as a polarographic medium has no advantages over water and several other solvents.

Introduction

Polarographic studies in non-aqueous media generally have been confined to solvents with a lower dielectric constant than water. The present study is an exploratory polarographic study in N-methylacetamide (NMA) which has a dielectric constant about twice as large as that of water (Table I). Some physical properties of NMA which are of interest in polarography are listed in Table I.

TABLE I

PHYSICAL PROPERTIES OF N-METHYLACETAMIDE[1]

Dielectric constant	165.5 at 40°
Viscosity (centipoise)	3.019 at 40°
Density (g./ml.)	0.9421 at 40°
Melting point	29.5°
Boiling point	206°
Conductivity (mho/cm.)	1–3 × 10^{-7} at 40°

French and Glover[2] and especially Dawson and co-workers[1,3–5] studied the conductances of a great number of strong electrolytes in NMA at temperatures of 35 and 45°, and at 30, 40, 50, and 60°, respectively, and concluded that they were completely dissociated. Dawson's studies allowed interesting conclusions to be drawn concerning the character of solvation of small inorganic cations, *e.g.* potassium, which seems to be determined mainly by an ion–dipole interaction.

Mizushima, *et al.*,[6] determined the structure of NMA from Raman, infrared, and ultraviolet spectra, concluding that the NMA molecule takes only the *trans* form and that through intermolecular hydrogen bonds these molecules form a "liquid polymer" or chain-like structure in the liquid state. Measurements by Leader and Gormley[7] of the dielectric constants of monomethylamides substantiate the results of Mizushima. On the basis of its structure, NMA may be expected to have marked basic properties, and indeed Dawson found that hydrochloric and picric acids are completely dissociated at concentrations less than 0.01 *M*.

In our investigation of this solvent, very much time has been spent in efforts to obtain a polarographically "pure" solvent and in studies of its stability on storage. The preparation of "pure" solvent is difficult. For this reason, and also because of detailed studies on the correction for *iR* drop, progress in polarographic work has been slow and of an exploratory nature. It is confined to the polarography of copper(II), thallium(I), oxygen, methyl red, and perchloric, sulfuric, hydrochloric, and acetic acids.

It could be concluded that the characteristics observed in the reduction of inorganic cations in NMA are very similar to those in water, indicating

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(1) L. R. Dawson, P. G. Sears, and R. H. Graves, *J. Am. Chem. Soc.*, **77**, 1986 (1955).

(2) C. M. French and K. H. Glover, *Trans. Faraday Soc.*, **51**, 1427 (1955).

(3) L. R. Dawson, E. D. Wilhoit, and P. G. Sears, *J. Am. Chem. Soc.*, **78**, 1569 (1956).

(4) L. R. Dawson, E. D. Wilhoit, R. R. Holmes, and P. G. Sears, *ibid.*, **79**, 3004 (1957).

(5) L. R. Dawson, G. R. Lester, and P. G. Sears, *ibid.*, **80**, 4233 (1958).

(6) S. Mizushima, T. Simanouti, S. Nagakura, K. Kuratani, M. Tsuboi, H. Baba, and O. Fujioka, *ibid.*, **72**, 3490 (1950).

(7) G. R. Leader and J. F. Gormley, *ibid.*, **73**, 5731 (1951).

that both solvents are very similar as far as their basic properties are concerned. This has been confirmed by specific acid–base studies to be described in a subsequent paper and which allowed the conclusion that NMA is a slightly weaker base than water. The polarographic behavior of oxygen indicated that NMA is a considerably weaker acid (proton donor) than water and in this respect resembles acetonitrile[8] and dimethyl sulfoxide.[9]

From an analytical viewpoint, NMA as a polarographic medium appears to have no advantages over water, and our studies have been discontinued From a theoretical viewpoint, NMA as a solvent would be of interest in polarographic studies of organic compounds which require hydrogen ions in their reduction.

Experimental

Instruments.—Polarographic measurements were made with the Leeds and Northrup Electrochemograph-Type E. The recording galvanometer of this instrument has a full scale response time of 1 sec. Therefore, when the galvanometer is not damped and the drop time of the dropping mercury electrode (d.m.e.) is not less than 3 sec., the instrument is capable of recording true maximum current during the life of each mercury drop. All polarograms were recorded in this way. The importance of this use of maximum rather than average current is pointed out in the section of this paper dealing with correction of the applied e.m.f. for cell *iR* drop.

Electrical resistances of the polarographic cell were measured using a simple A.C. Wheatstone conductance bridge manufactured by the Industrial Instruments Corporation of Jersey City, N. J. Balance of the bridge was indicated by a maximum opening of an "electronic eye" vacuum tube. The leads from the bridge were connected across the cell, one to the d.m.e. reservoir and the other to the reference electrode contact. To obtain values of the minimum cell resistance, *i.e.*, the cell resistance at maximum drop size, the bridge was adjusted until the maximum opening of the eye coincided with the drop fall. A more accurate determination of the minimum cell resistance involving extrapolation of a linear plot of cell resistance *vs.* time$^{-1/3}$ during the drop growth, although investigated and found suitable, was not necessary for these polarographic measurements.

Polarographic Cell.—The polarographic cell compartment used is shown in Fig. 1. This cell, requiring 10 ml. of solution, is equipped with separate side arms for the reference electrode salt bridge and for the passage of deaerating nitrogen. The fine sintered glass disk separating the d.m.e. compartment from the salt bridge side arm prevents contamination of the solution in the d.m.e. compartment by the salt bridge constituents. The side arm contains the same solution as used in the d.m.e. compartment. The T-stopcock allows nitrogen to be passed over the surface of the solution after deaeration and while measurements are being made.

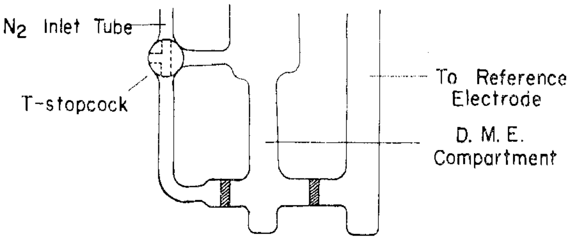

Fig. 1.—The polarographic cell.

The reference electrode used in all polarographic studies was an aqueous saturated calomel electrode (s.c.e.) equipped with a salt bridge approximately 20 cm. long and plugged at the end with agar saturated with potassium chloride.

Later in this work we found it possible to use a silver–silver chloride electrode as a non-aqueous reference electrode by using a silver electrode in NMA saturated with both sodium chloride and silver chloride. The potential of this reference electrode was shown to be stable and reproducible.

The d.m.e. capillary used in all polarographic measurements was characterized according to the methods described by Müller,[10] who suggests two constants characteristic of the capillary. These are: (1) the "capillary constant", *K*, and (2) the radius of the capillary orifice, *r*. The capillary constant, *K*, is equal to $P/m = 8\eta l/d\pi r^4$, where *P* is the pressure of mercury in cm., *m* is the mass of mercury flowing in mg. per sec., η and *d* are viscosity and density, respectively, of mercury at the operating temperature, *l* is the length of the capillary, and *r* is the radius of the capillary.

Since *P* and *m* are experimental quantities, there is no difficulty in obtaining *K*. For the d.m.e. used throughout this work the value of *K* was 70.9.

The radius of the capillary was determined by three different methods: (1) direct microscopic observation; (2) calculation from *K* using known values of η, *l*, and *d;* and (3) measurement of the electrical resistance of the capillary filled with mercury using the known specific resistance of mercury. These three methods all gave a value of 28 microns for the radius, *r*, of the d.m.e. capillary.

Temperature.—Since NMA freezes at 29.5°, all polarographic measurements were carried out using a cell in a 30° thermostatic water bath. The temperature was held constant within 0.1° or better.

Chemicals.—The supporting electrolyte chosen for all polarographic measurements was tetraethylammonium perchlorate ($(C_2H_5)_4NClO_4$). It was prepared with nearly quantitative yield by dropping cold, concentrated (70%) perchloric acid with stirring into a cold, concentrated aqueous solution of tetraethylammonium bromide, the latter being commercially available (Eastman Kodak). The precipitated $(C_2H_5)_4NClO_4$ was recrystallized twice from water, the final supernatant and wash liquids having been tested and found free of bromide. The final product is stable to shock and also can be dried in an oven at 110°

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(8) J. F. Coetzee and I. M. Kolthoff, *ibid.*, **79**, 6110 (1957).

(9) T. B. Reddy and I. M. Kolthoff, *J. Electrochem. Soc.*, in press.

(10) O. Müller, "The Polarographic Method of Analysis," 2nd ed., Chemical Education Publishing Co., Easton, Pa., 1951, pp. 183–184.

without danger. Such a product is water-free and not hygroscopic.

Other perchlorate salts used in this work were obtained from the G. Frederick Smith Chemical Company, Columbus, Ohio, and were recrystallized from water, dried at a suitable (safe) temperature in a vacuum oven, and stored in a vacuum desiccator charged with anhydrous magnesium perchlorate.

The remaining chemicals used were all of analytical reagent grade.

Solvent.—Commercially available NMA is not sufficiently pure for polarographic studies. At best it contains both unreacted methylamine and acetic acid. Such impure solvent shows a cathodic polarographic discharge in 0.1 *M* $(C_2H_5)_4NClO_4$ beginning at about −1.7 volts (*vs.* aqueous s.c.e.) depending upon the amount of acetic acid present.

Dawson and co-workers[1] prepared NMA by allowing aqueous methylamine to react with glacial acetic acid and purified the product by distillation followed by several fractional freezing cycles. The purification procedure described by French and Glover[2] involving treatment with phosphorus pentoxide and subsequent vacuum distillation was found to be ineffective when the crude solvent was prepared by Dawson's method.

Since a large volume of solvent was required in our work, we have studied various methods of purification. Two alternate methods were developed, and on the basis of both polarographic and conductance data it is concluded that the solvent obtained by these two methods is at least of equal purity to that obtained by Dawson. Since the two methods both require more than an ordinary amount of care, they are described here in some detail.

For both purification procedures the crude product was obtained by allowing an excess of glacial acetic acid to react with 40% aqueous methylamine under reflux for 12 to 15 hr. The reaction flask then was fitted with a 6-in. fractionating column, distilling head, and condenser, and distillation was continued until the vapor temperature reached 130°, indicating that all water and much of the excess acetic acid had been removed. It was observed (universal indicator paper) that the *p*H of the distillate changed during the course of this initial distillation. It was acidic at first, when the temperature was still near 100°, then became basic when the temperature rose to 105°, and finally became acidic again when the temperature rose above 105°. Apparently in the initial stages much acetic acid distils along with the water, giving way to the distillation of unreacted methylamine (or methylammonium acetate) as the temperature rises. When the concentration of these drops to a low level, the distillate becomes acidic again by distillation of the large excess of acetic acid.

The crude product at this stage appears to be contaminated not only with acetic acid but also with methylamine. In spite of the excess acetic acid and the high temperature, some methylamine remains, probably in the form of methylammonium acetate from which water apparently is not easily split out.

Purification Procedure 1.—In this procedure the crude product, contaminated only by acetic acid and methylamine, was fractionated under nitrogen at atmospheric pressure using an 18-in. heated column packed with porcelain saddles. The temperature during this fractionation rose only gradually to 204°, all fractions up to this temperature containing too much acetic acid to be used in the steps to follow.

The fraction boiling at 204–206°, the major fraction, was found to contain three impurities: acetic acid, methylamine, and a third impurity of unknown composition which is formed even in pure solvent when NMA is heated to its boiling point. This unidentified impurity (impurity "X") imparts to the solvent a peculiar amine-like odor which is easily distinguished from methylamine. A polarogram run on a solution of $(C_2H_5)_4NClO_4$ supporting electrolyte in solvent containing only this impurity shows a cathodic discharge in the region −2.2 volts. The three impurities exist only in relatively small amounts and can be removed in the following way.

Impurity "X" is removed first by extraction with several portions of petroleum ether. Water must be added to effect a separation of phases, however, and this water, along with dissolved petroleum ether, is removed from the solvent, now freed of impurity "X," by ordinary distillation at atmospheric pressure, care being taken not to allow the temperature to rise above 130°. When the water and petroleum ether are nearly completely removed, distillation is discontinued and the solvent is cooled to room temperature.

Approximately 10 ml. of concentrated sulfuric acid per liter of solvent are added and this mixture is vacuum distilled (boiling point approximately 80° at 3–5 mm.). This step serves to remove methylamine from the solvent by retaining it as the sulfate in the distillation flask. During this vacuum distillation the remaining small amounts of water and petroleum ether also distil and, being much more volatile than the NMA, usually collect in the Dry Ice–acetone-cooled trap between the system and the vacuum pump. If much water and petroleum ether are present, it is advisable to repeat this vacuum distillation with concentrated sulfuric acid before proceeding to the next step, for the hydrolysis of NMA in aqueous solution is acid catalyzed.[11] The distillate at this point contains only NMA, a small amount of acetic acid, and an even smaller amount of water.

All of the acetic acid and most of the water are removed by adding freshly ground calcium oxide to this distillate and allowing the mixture to stand for several hours with occasional shaking. This mixture then is filtered rapidly through a coarse sintered glass filter (the filtrate is still cloudy due to incomplete removal of the finely divided calcium oxide) into the distillation flask and vacuum distilled. Since most of the remaining traces of water distil during the initial stages, the vacuum distillation is discontinued after about 1% of the solvent has distilled and the receiver is replaced by a fresh dry one. The product from this final vacuum distillation is "pure" (tests for purity described below).

Several points are not immediately obvious from the above description of this purification procedure. First, omission of the extraction step will not alter the effectiveness of the other steps in the purification procedure, but the final product still will contain impurity "X."

Second, all traces of unreacted methylamine must be removed from the solvent before calcium oxide is added be-

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[11] K. Heyns and W. v. Bebenburg, *Ann.*, **595**, 55 (1955).

cause the decomposition of NMA in basic medium is autocatalytic with respect to methylamine. Therefore, vacuum distillation with sulfuric acid must precede treatment with calcium oxide.

Third, NMA boiled at atmospheric pressure with calcium oxide rapidly decomposes with the liberation of ammonia and methylamine.

Fourth, it is odd that methylamine and acetic acid are not more nearly completely removed by fractionation at atmospheric pressure. On the basis of their relative boiling points, one would expect these substances to distil completely during the first stages of the fractionation. Such is not the case, however. Even the fraction boiling at 202–204° contains too much acetic acid to be carried through the purification procedure described. This difficult removal of acetic acid and methylamine may be due to the formation of the salt, methylammonium acetate, which does not distil at the lower temperatures. At the boiling point of NMA, 206°, this salt may distil by dissociating into methylamine and acetic acid and recombining in the distillate.

Purification Procedure 2.—In this procedure the temperature is never allowed to exceed 130° and consequently no impurity "X" is formed. The temperature during the distillation of water and acetic acid from the crude solvent is allowed to reach 130° very slowly so that as much acetic acid as possible can be removed. At this stage the crude solvent is contaminated by relatively large amounts of methylamine, acetic acid, and water.

Concentrated sulfuric acid is added to the crude solvent at room temperature and the mixture is vacuum distilled. As in the first procedure this results in complete removal of methylamine.

Too much acetic acid remains in the solvent to be removed by the calcium oxide treatment without the precipitation of large amounts of gelatinous calcium acetate. Instead, potassium carbonate is added and the mixture is allowed to stand for several hours with intermittent shaking. When it is certain that neutralization is complete and that potassium carbonate is present in excess, the mixture is filtered into the distillation flask and vacuum distilled. A large amount of potassium acetate will have been formed during the neutralization, and although potassium acetate is more soluble than calcium acetate, it will eventually begin to precipitate in the flask during the course of the vacuum distillation. The distillation then must be discontinued and the mixture cooled to room temperature and filtered. Potassium acetate is not gelatinous, and the filtration poses no serious problem. The filtrate can be vacuum distilled as before.

At this point the vacuum distillate contains no impurities other than a relatively large amount of water (from the neutralization of acetic acid with potassium carbonate —$K_2CO_3 + HAc = KHCO_3 + KAc; 2KHCO_3 \rightarrow K_2CO_3 + H_2O + CO_2$). The presence of acetic acid (indicating incomplete neutralization) can be detected polarographically by the appearance of a cathodic discharge in the region -1.7 to -1.9 volts. An anodic wave at a potential less positive than $+0.35$ volt indicates the presence of methylamine and another vacuum distillation from sulfuric acid is necessary.

If the solvent is "pure" by these polarographic standards, the water is removed by shaking the solvent with calcium oxide and vacuum distilling. Tests of purity indicate that the final product from this purification procedure is identical to that obtained by the first procedure.

Tests for Purity. Stability on Storage.—Three tests were used to determine the degree of purity of the solvent prepared and purified as described above. They are: (1) the polarographic range determined with 0.1 *M* $(C_2H_5)_4NClO_4$ supporting electrolyte is between $+0.35$ and -2.75 volts; (2) the water content determined by Karl Fischer titration is less than 0.01 *M*; and (3) the specific conductance is less than 3×10^{-7} mho/cm., and usually of the order of 1×10^{-7} mho/cm.

In addition to these three tests, the freezing point was determined and found to be 29.5°. The "pure" solvent from both purification procedures had no detectable odor.

Prolonged storage (one to two months) of the pure solvent at a temperature of 40 to 50° and in the presence of air results in the formation of an impurity which is reducible at the d.m.e., the reduction wave beginning at approximately -0.2 volt. Presumably this impurity is the result of slow air-oxidation, and therefore its formation might be prevented by storing the solvent under nitrogen. The impurity is easily removed, however, by a single vacuum distillation, the impurity remaining in the distillation flask.

Polarographic Procedure.—Solutions for polarographic analysis were made up in 10-ml. volumetric flasks. Solid $(C_2H_5)_4NClO_4$ was weighed out to make a 0.1 *M* solution. The substances to be analyzed were added either by weight or by dilution of an aliquot of a more concentrated solution using a Gilmont plunger-displacement type ultramicroburet of total capacity 1.0 or 0.1 ml.

Solutions for polarographic analysis were deaerated using pure dry nitrogen obtained from the Linde Air Products Company. It required no further purification. Deaeration of NMA solutions is quite rapid, requiring only 10 to 15 min. of bubbling with nitrogen.

Reported polarographic data are all corrected for residual current.

Correction for *iR* Drops.—Polarography in non-aqueous solutions frequently is complicated by the fact that in many cases electrical resistances of the cell solutions are very high, resulting in distortion of the current–voltage curves. Such is the case with NMA solutions. Conductances of electrolytes in NMA are approximately one tenth as high as the corresponding aqueous conductances.

Correction for *iR* drops would be a simple matter if it were not for the fact that the current and cell resistance, and therefore also the mercury drop potential, are changing with time during the growth of a mercury drop. Only the external circuit resistances are constant, and since they can be measured easily and accurately, they are easy to correct for.

The average value of the current generally is used in plotting current–voltage curves primarily because it is easier to obtain a galvanometer whose average deflection accurately represents the average current than it is to obtain a galvanometer of sufficiently rapid response to indicate accurately the true maximum current.

Employing the average current makes it necessary to use the corresponding average cell resistance in calculating the average *iR* drop correction for the polarographic cell. The difficulty lies in determining this average value for the cell resistance.

An exact expression for this correction on points of a polarographic wave is difficult to find. For a completely depolarized electrode Ilkovic[12] derived the average resistance of the cell, $\bar{R}_c$, as 4/3 $R_{\min}$, where $R_{\min}$ is the minimum cell resistance at maximum drop size. In the absence of an external resistance the average current $\bar{i} = E_a/(4/3\ R_{\min})$. (For a brief treatment see ref. 13.) The situation in the presence of an external resistance is more complicated and has been dealt with by Brdicka.[14] For a completely polarized electrode it can be derived[15] that in the absence of an external resistance, $\bar{R}_c = 7/5\ R_{\min}$.

The situation is more involved for points on a wave without a maximum. In the first place it must be realized that the cell resistance is composed of a true internal resistance of the mercury drop and a very thin layer in its immediate neighborhood[16] which varies greatly during the growth of the drop and a resistance of a column of liquid between the drop and the reference electrode which does not vary during the growth of the drop and which behaves as an external resistance.

In addition, the resistances of the mercury in the d.m.e. capillary and the s.c.e. behave as external resistances. With our cell these two resistances were 83 and 318 ohms, respectively, and negligibly small. However, the resistance of the liquid in the cell was appreciable—several thousand ohms.

Because of these complications it was decided to measure $i_{\max}$ and $R_{\min}$ so that the iR correction was known when the current was recorded at its maximum value. When applied to points on the wave this correction is still approximate because the diffusion layer during the growth of the drop is established at a varying and not constant potential. The correction for this effect is difficult to evaluate and has been neglected.

Results

Electrocapillary Curves.—The electrocapillary curves for mercury in NMA using three different supporting electrolytes, $(C_2H_5)_4NClO_4$, KCl, and KI are shown in Fig. 2. The height of the mercury column, P, was 57.0 cm. for these and all subsequent measurements.

The electrocapillary maximum in 0.1 M $(C_2H_5)_4NClO_4$ supporting electrolyte is found at −0.20 volt (*vs.* s.c.e.), approximately 0.35 volt more positive than in water (−0.55 volt). Iodide in a concentration of 0.1 M is strongly electrocapillary active and displaces the electrocapillary maximum to −0.60 volt. It is desorbed at approximately − 0.7 volt. Chloride ion at a concentration of 0.1 M also is capillary active and displaces the electrocapillary maximum to −0.35 volt. It is desorbed at approximately −0.5 volt.

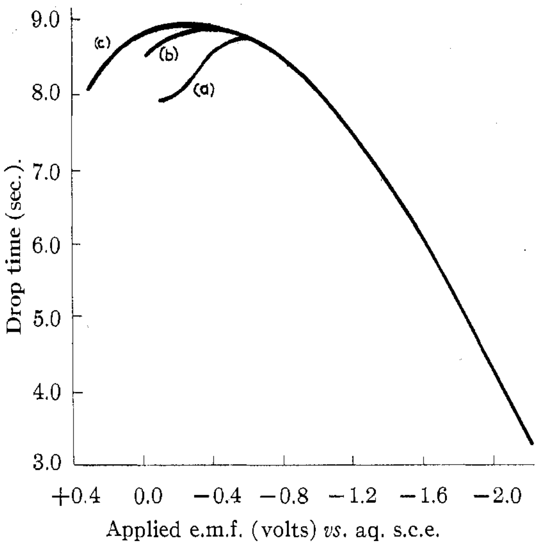

Fig. 2.—Electrocapillary curves of mercury in NMA: (a) 0.1 M KI, (b) 0.1 M KCl, (c) 0.1 M $(C_2H_5)_4NClO_4$.

The electrocapillary curves are similar in shape to those observed in aqueous solution, and the effect of various anions on the potential and height of the electrocapillary maximum is likewise similar. Because of an unknown liquid junction potential no exact comparison of the electrocapillary maximum potentials in both solvents is possible.

Polarographic Range. Residual Current.—The limiting range of polarography in 0.1 M $(C_2H_5)_4NClO_4$ in NMA is between +0.35 volt (anodic dissolution of mercury) and −2.7 volts. The residual current in such a solution is very small —approximately 0.4 μamp. at −2.7 volts and smaller at less negative potentials. The plot of i_{res} *vs.* E_a appears normal.

Depolarization Potentials.—For orientation purposes "depolarization potentials" for several cations and anions using 0.1 M $(C_2H_5)_4NClO_4$ as supporting electrolyte were determined and these are reported in Table II. For comparison the corresponding values in water also are tabulated. Concentrations of the solutions were between 0.01 and 0.1 M, too great to give a diffusion limited polarographic wave.

Polarography of Oxygen.—Figure 3 shows the polarographic reduction wave for an air-saturated NMA solution containing 0.1 M $(C_2H_5)_4NClO_4$. Two waves of unequal height without maxima are clearly distinguished, the height of the first wave being 7.5 μamp. and that of the second 12.4 μamp. Evidently oxygen is considerably more soluble in NMA than in water.

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[12] D. Ilkovic, *Collection Czechoslov. Chem. Communs.*, **4**, 480 (1932).

[13] I. M. Kolthoff and J. J. Lingane, "Polarography," 2nd ed., Vol. I, Interscience Publishers, New York, N. Y., 1952, pp. 182–3.

[14] R. Brdicka, *Collection Czechoslov. Chem. Communs.*, **8**, 419 (1936).

[15] L. A. Knecht, Ph.D. Thesis, University of Minnesota, 1959.

[16] I. M. Kolthoff, J. C. Marshall, and S. L. Gupta, *J. Electroanal. Chem.*, in press.

Table II

Depolarization Potentials (*vs.* s.c.e.) of Some Cations and Anions in NMA

Ion	NMA	H_2O
ClO_4^-	0.35[a]	0.45
Cl^- (anodic)	0.00	0.20
Br^- (anodic)	−0.15	0.05
I^- (anodic)	−0.40	−0.20
H^+ (str. acid)[b]	−1.53 ($E_{1/2}$)	−1.58 ($E_{1/2}$)
HAc	−1.70	−1.80
NH_4^+	−1.85	−2.05
Ca^{++}	−2.00[c]	−2.2
Na^+	−2.10	−2.1
K^+	−2.10	−2.1
Mg^{++}	−2.40	−2.2
$(C_2H_5)_4N^+$	−2.75	−2.4

[a] Dissolution of mercury in the absence of reactive anions. [b] 0.001 N. [c] Solvent of questionable purity leaves some doubt as to the accuracy of this value.

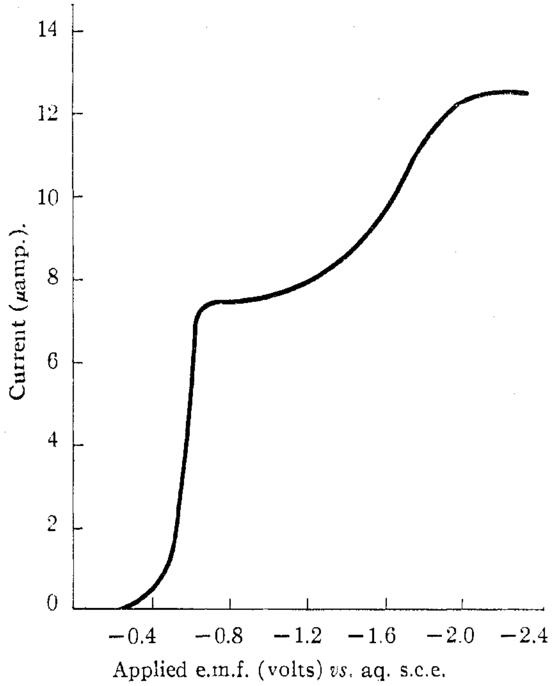

Fig. 3.—Polarogram of air-saturated NMA.

Analysis of the first wave, after correcting for cell iR drop, by the log plot showed a nonlinear slope from which it is apparent that the reduction is not reversible. The half-wave potential for the first reduction step, taken from this log plot, is −0.54 volt. From the drawn-out nature of the second wave it is apparent that the second reduction step is even less reversible than the first.

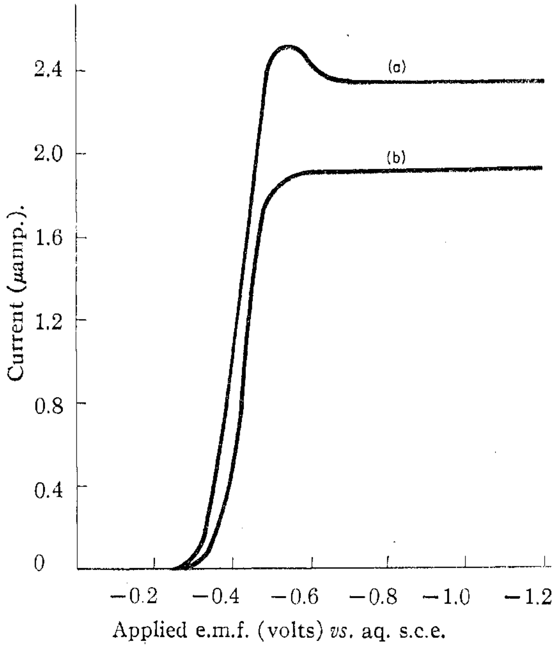

Fig. 4.—Polarograms of thallium(I) in NMA: (a) no methyl red, (b) <0.01% methyl red added.

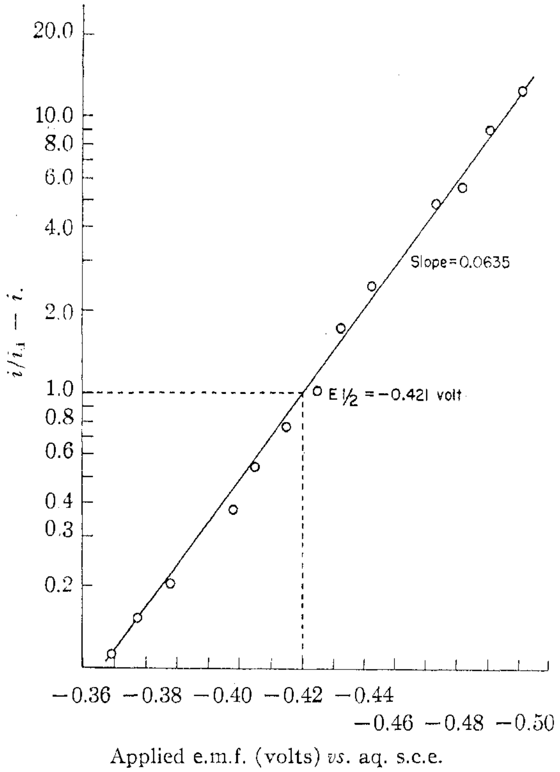

Fig. 5.—Log plot analysis of thallium(I) in NMA.

Polarography of Thallium(I).—Polarograms of 0.001 M thallium(I) nitrate solution in NMA are shown in Fig. 4. In the absence of a maximum suppressor, a small rounded maximum is observed (curve "a"). Making the solution 0.0004 M in methyl red (approximately 0.01%) resulted in a suppression of this maximum but also in a depression of the diffusion current (curve "b").

A log plot analysis of curve "b," after correction for cell iR drop (Fig. 5), is linear and shows a slope of 0.0635 (theoretical value for reversible reaction 0.0601 at 30°).

$E_{1/2}$ is -0.421 volt, and the diffusion current constant, calculated for curve "a" (without maximum suppressor), is 1.53. Camphor, thymol, and gelatin were not effective in suppressing this maximum, perhaps because of insolubility in the case of gelatin.

Polarography of Copper.—Cupric perchlorate, recrystallized from water and dried in a vacuum desiccator over anhydrous magnesium perchlorate, was weighed rapidly into a 10-ml. volumetric flask and dissolved in NMA. The blue solid was assumed to be the hexahydrate. The 0.1 *M* stock solution prepared in this way has the same blue color observed in aqueous cupric solutions (see Discussion).

Using a Gilmont plunger-displacement type microburet, enough of this 0.1 *M* stock solution was added to the NMA solution containing the supporting electrolyte in the polarographic cell to make a 0.002 *M* solution. Polarograms of this solution with varying amounts of methyl red (in NMA) added as a maximum suppressor are shown in Fig. 6.

The log plot analysis of the wave on which the maximum has been completely suppressed and which has been corrected for cell *iR* drop yields a straight line of slope 0.0633. The half-wave potential is $+0.069$ volt, and the diffusion current constant is 1.77. This slope indicates a one-electron reduction, but from a comparison of heights of diffusion currents for the same concentration on waves which have been separated by complexation (*v.i.*) it appears that the reduction taking place is that of cupric to metallic copper (copper amalgam). This conclusion is strengthened by the fact that no second reduction wave is observed out to -2.7 volts. Kolthoff and Okinaka[17] have studied the reduction of aquo–cupric ion in aqueous solutions and found it to be slightly irreversible. The degree of reversibility of the same reaction in NMA may be less than that in water.

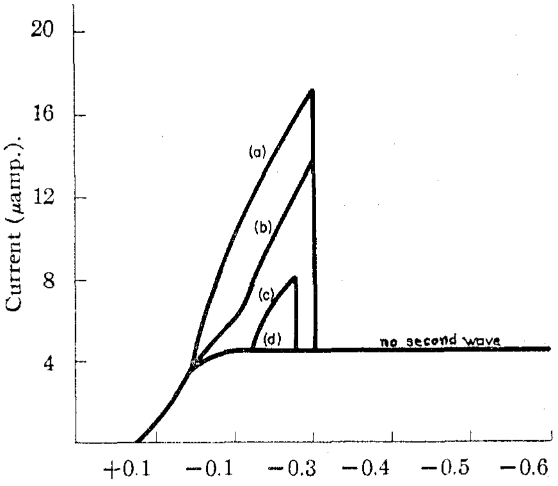

Fig. 6.—Polarographic reduction wave of 0.002 *M* $Cu(ClO_4)_2 \cdot 6H_2O$ in NMA: (a) no methyl red, (b) 0.002% methyl red, (c) 0.006% methyl red, (d) 0.01% methyl red.

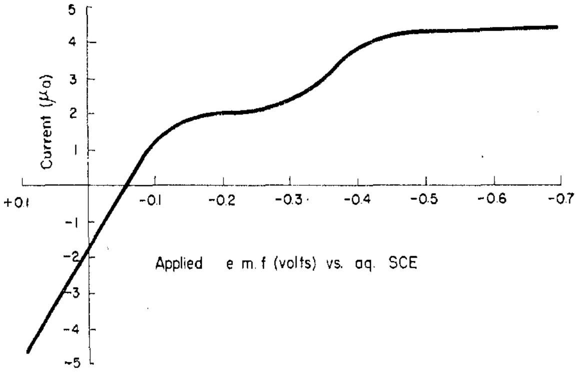

Fig. 7.—Polarogram of cupric ion with NH_3 in NMA.

The polarographic wave of cupric ion in NMA can be split into two waves of equal height by adding to the solution a complexing agent such as ammonia (Fig. 7) or chloride ion. The polarograms of the solutions with these two complexing agents are nearly identical. The first and second waves are of equal height if correction is made for the reduction current of methyl red itself (*v.i.*).

Since with both ammonia and chloride the first wave rises from the anodic dissolution current and the second wave is affected by the simultaneous reduction of methyl red or an impurity in the methyl red, the waves could not be analyzed by the log plot. Nevertheless, it is obvious that the ammonia and chloride both form stronger complexes with cuprous ion than with cupric ion, resulting in the appearance of two waves.

$E_{1/2}$ for the first wave is -0.10 volt, and $E_{1/2}$ for the second wave is -0.37 volt under the specified experimental conditions.

By comparing wave heights in Fig. 6 and 7 it is obvious that the single reduction step in perchlorate medium corresponds to the reduction of cupric ion to copper amalgam.

It is interesting to note that the depression of the limiting (diffusion) current of the thallium(I) wave by methyl red does not occur with copper.

Polarography of Methyl Red.—The unusual polarographic behavior of methyl red indicator

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[17] I. M. Kolthoff and Y. Okinaka, *J. Am. Chem. Soc.*, **83**, 47 (1961).

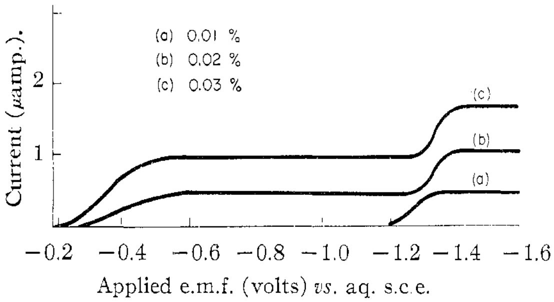

Fig. 8.—Polarograms of methyl red in NMA: (a) 0.01%, (b) 0.02%, (c) 0.03%.

(commercial, unpurified) dissolved in NMA containing only $(C_2H_5)_4NClO_4$ supporting electrolyte is shown in Fig. 8. At concentrations below 0.0005 *M*, a single polarographic wave is observed with a half-wave potential approximately −1.27 volts. The color of solutions of this concentration is yellow, presumably due to the basic form of the indicator. At higher concentrations the color becomes red-orange indicating the probable presence of both acidic and basic forms of the indicator, and two polarographic waves are observed, the first, presumably due to reduction of the acid form, at about −0.36 volt, and the second again at −1.27 volts. The further addition of methyl red increases the height of both waves proportionately, *i.e.*, the height of the polarographic waves is proportional to concentration.

Discussion

The polarographic behavior of the depolarizers studied in NMA does not differ greatly from that observed for the same substances in aqueous solution (see Table II). The decomposition potentials for the reduction of the alkali metals, ammonium, and magnesium ions occur in the same order in NMA and water. Only the decomposition potential of calcium is out of order, and this may be due to impurity in the solvent used in that measurement. The half-wave potentials of thallium(I) and copper(II) ions also fit into this order. The conclusion is that as far as reduction of cations (with the exception of hydrogen ion) is concerned, NMA behaves as a water-like solvent.

The anodic depolarization potentials in the presence of chloride and iodide are 0.2 volt more negative than in water (the effect of an unknown liquid junction potential cannot be considered). This difference is accounted for in part by the fact that the anodic dissolution wave of mercury occurs at a potential which apparently is 0.1 volt less positive in NMA than in water.

The polarographic reduction of oxygen in NMA occurs at a potential considerably more negative (first wave −0.54 volt) than the corresponding wave in aqueous solution (first wave −0.05 volt). Furthermore, the two waves of oxygen are not of equal height, i_{d_2} being only 65% as high as i_{d_1}. Coetzee[8] and Reddy[9] have found similar behavior of oxygen in the solvents acetonitrile (AN) and dimethyl sulfoxide (DMSO), respectively. Half-wave potentials and diffusion current ratios for oxygen in these solvents are listed in Table III.

TABLE III
POLAROGRAPHIC DATA FOR OXYGEN IN VARIOUS SOLVENTS

	Solvent			
	H_2O	NMA	DMSO	AN
$E_{1/2}$ (first wave)	−0.05	−0.52	−0.72	−0.75
$E_{1/2}$ (second wave)	−0.9	−1.6	−1.13	−1.4 to −2.2[a]
Ratio i_{d_2}/i_{d_1}	2.00	1.65	1.53	1.6

[a] Depends on supporting electrolyte used.

The behavior of oxygen in these solvents is accounted for by their weakly acidic properties as compared to water.[18,19] From acid–base studies it is concluded that NMA is also a considerably weaker acid than water.

The maxima on the polarograms of 0.002 *M* cupric perchlorate using varying amounts of methyl red have a peculiar appearance. Unlike ordinary maxima which rise nearly linearly along the rising portion of the polarographic wave, these maxima seem to originate only after the potential reaches −0.05 volt. This suggests the formation of a film of cuprous perchlorate adsorbed on the mercury surface; however this was not investigated further. Similar polarographic waves of cupric reduction were found[17] in aqueous solution in the presence of chloride ion.

It already has been mentioned that solutions of cupric perchlorate hexahydrate in NMA exhibit the same blue color that exists in aqueous cupric solutions, the color being due to the aquo–cupric ion. On the other hand, anhydrous cupric sulfate dissolves in NMA to produce a brilliant green solution, the color presumably being due to the cupric ion solvated with NMA. If water is added to this green solution, the blue color gradually displaces the green. The reverse is not true, *i.e.*, the blue solution of cupric perchlorate hexahydrate in NMA does not turn green, even on prolonged

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(18) P. H. Given and M. E. Peover, *J. Chem. Soc.*, 385 (1960).

(19) G. J. Hoijtink, J. v. Schooten, E. de Boer, and W. Y. Aalbersberg, *Rec. trav. chim.*, **73**, 355 (1954).

standing. Apparently water has a greater affinity for cupric ions than NMA does. Heating the blue solution to 206° does effect a color change from blue to green, supposedly with the expulsion of water and replacement by NMA in the coördination sphere. However, the green solution prepared in this way rapidly turns yellow and finally brown as cupric is reduced (by solvent oxidation) to finely divided metallic copper (observed under the microscope in reflected light). If the intermediate yellow brown solution is cooled rapidly to room temperature and exposed to air (oxygen), some of the green color gradually returns, indicating air-oxidation to cupric ion. Preliminary attempts to investigate polarographically these green to brown solutions as well as air-free solutions of cuprous salts yielded inconclusive results, and further study must be carried out before the observed phenomena can be interpreted.

The polarographic behavior of methyl red was investigated only in a superficial way in connection with its effect on the reduction waves of copper. Further studies in NMA solutions buffered at various acidities should be carried out to verify the assumption that the two waves are due to basic and acidic forms of the indicator.

In Table IV the Walden product, $D\eta \times 10^6$, for thallium(I) and cupric ions in NMA is compared with that in water. D was calculated from the diffusion current constant: $D = (I_d/706\ n)^2$. Dawson observed that the Walden product in NMA is generally lower than it is in water. The data of Table IV confirm this observation.

TABLE IV

POLAROGRAPHIC DATA AND WALDEN PRODUCTS FOR Tl^+ AND Cu^{++} IN WATER AND IN N-METHYLACETAMIDE

		Tl^+	Cu^{++}
$E_{1/2}$	H_2O	−0.46	+0.04
	NMA	−0.42	+0.069
I_d	H_2O	2.7	3.23
	NMA	1.53	1.77
$D\eta \times 10^6$	H_2O	7.2	20
	NMA	6.1	18.3

The addition of water in amounts up to 5% does not affect significantly the polarographic behavior of the depolarizers studied, substantiating the conclusion that NMA behaves as a water-like solvent in the reduction of cations. In greater amounts, the diffusion currents increase as would be expected as conductances increase with increasing amounts of water.

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