

TABLE II

Solution		Wet solid		Solid phase
% Sr-(NO ₃) ₂	% Ca-(NO ₃) ₂	% Sr-(NO ₃) ₂	% Ca-(NO ₃) ₂	
25° Isotherm				
44.50	Sr(NO ₃) ₂ ·4H ₂ O
32.30	12.23	{ 58.90 4.21 55.80 6.00 }		Sr(NO ₃) ₂ ·4H ₂ O
27.70	17.60	84.40 4.53		Sr(NO ₃) ₂
19.90	25.90	82.80 6.09		Sr(NO ₃) ₂
9.25	39.15	80.00 8.70		Sr(NO ₃) ₂
6.54	44.00	78.05 10.56		Sr(NO ₃) ₂
4.85	46.80	76.55 11.46		Sr(NO ₃) ₂
4.71	47.05	78.10 10.76		Sr(NO ₃) ₂
4.58	48.10	77.80 11.06		Sr(NO ₃) ₂
3.15	51.00	75.40 12.85		Sr(NO ₃) ₂
1.55	56.10	{ 58.50 28.80 66.20 20.60 }		Ca(NO ₃) ₂ ·4H ₂ O + Sr(NO ₃) ₂
..	57.20			Ca(NO ₃) ₂ ·4H ₂ O
60° Isotherm				
48.25	...			Sr(NO ₃) ₂
15.42	33.04	78.50 8.69		Sr(NO ₃) ₂
4.20	51.00			
0.14	70.20	64.45 24.85		Sr(NO ₃) ₂
0.084	76.00			
0.07	76.98	{ 59.70 32.10 2.60 84.80 }		Ca(NO ₃) ₂ + Sr(NO ₃) ₂
..	77.15			Ca(NO ₃) ₂

hydrrous salt as solid phases in equilibrium with the solutions. The appearance of anhydrous salt was checked by obtaining it in each of two tubes, one prepared at room temperature and the other at 100°. The composition of the solution in equilibrium with both forms was not determined. The 60° isotherm shows only the anhydrous salts present as solid phases. The calcium nitrate branch of the curve is so short that no investigation was made and the solid phase is considered to be that reported by the previous workers.

Summary

The 25° and 60° isotherms for the system Ca(NO₃)₂-Sr(NO₃)₂-H₂O have been determined. From these it follows that the solid phases at 25° are: Sr(NO₃)₂·4H₂O, Sr(NO₃)₂ and Ca(NO₃)₂·4H₂O; at 60°, Sr(NO₃)₂ and Ca(NO₃)₂.

SEATTLE, WASHINGTON RECEIVED DECEMBER 22, 1941

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF PURDUE UNIVERSITY]

The Dropping Mercury Electrode in Acetic Acid. I. Discontinuous Current-Voltage Curves¹

BY G. BRYANT BACHMAN AND MELVIN J. ASTLE²

Phenomena associated with the dropping mercury electrode have been investigated extensively in aqueous solutions, but not much has been published concerning this electrode in non-aqueous solvents. This is not surprising since analytical conditions in such solvents are not ideal and do not compare favorably in most respects with those in water. Current-voltage curves in organic solvents are generally smaller in amplitude. This follows from Ilkovic's equation³ for the diffusion current, $i_d = 0.627nFD^{1/2}Cm^{2/3}t^{1/3}$, where i is the diffusion current, n the number of electrons involved in the reduction, F the faraday, D the diffusion coefficient of the ion or molecule being reduced, C its concentration, and m and t are the rate (in g. sec.⁻¹) and time of formation, respectively, of the mercury drop. Kolthoff and Lingane⁴ have shown that for a given capillary, at a given pressure on the dropping mercury, and at a

constant temperature, m is practically independent of the medium. Since the drop time is proportional to the interfacial tension, t will vary with the medium, but since i_d is proportional only to the sixth root of t , large variations in the drop time will produce only small changes in the magnitude of the diffusion current. It follows, therefore, that in going from aqueous to non-aqueous systems, variations in current will result almost entirely from changes in the diffusion coefficient D . The diffusion coefficients for reducible ions are, in general, smaller in non-aqueous systems than in water, and therefore the wave heights are also smaller in non-aqueous systems. This has been established experimentally on a qualitative basis by Perachio and Meloche,⁵ who studied the diffusion currents of various alkali ions in alcohol-water, ethylene glycol-water and glycerol-water mixtures and found them to be smaller in these systems than in water. At present there are not sufficient data on diffusion coefficients to make possible quantitative predictions concerning wave heights in non-aqueous systems.

(1) Presented before the Physical and Inorganic Division at the St. Louis meeting of the American Chemical Society, April 8-12, 1941. From the Ph.D. thesis of Melvin J. Astle.

(2) Present address, University of Kentucky, Lexington, Kentucky.

(3) Ilkovic, *J. Chim. Phys.*, **35**, 129 (1938).

(4) Kolthoff and Lingane, *Chem. Rev.*, **24**, 1 (1939).

(5) Perachio and Meloche, *THIS JOURNAL*, **60**, 1770 (1938).

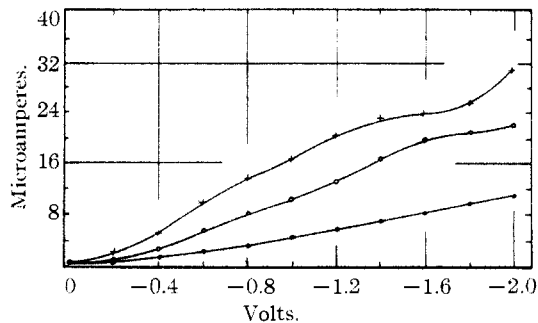


Fig. 1.—Current-voltage curves in glacial acetic acid: $\bullet\text{---}\bullet$, 0.1 *M* sodium acetate; +---+ , 0.5 *M* sodium acetate; $\text{---}\circ\text{---}$, 0.5 *M* lithium chloride.

It is obvious that ordinary routine analyses for the determinations of inorganic cations are best conducted in water solutions where curve heights are at a maximum and irregularities at a minimum. However, for theoretical reasons, where water-insoluble organic substances are concerned, and in special cases where anhydrous conditions are desired, it would be advantageous to be able to employ non-aqueous solvents in the polarographic procedure. We have chosen acetic acid as the first solvent to investigate because it readily dissolves many inorganic salts, it has a moderately high dielectric constant for an organic liquid, and there is considerable interest in reactions occurring in it. Previous work in this system is limited to that of MacGillavry,⁶ who obtained current-voltage curves for a single electrolyte in this solvent. He reports that the curve for sodium acetate is essentially a straight line between zero and -6.0 volts at low concentrations of the salt, and that it contains two inflections at higher concentrations. He suggests that the first inflection is caused by the reduction of mercurous ion while the second is caused by the reduction of the sodium ion. MacGillavry also makes the statement that oxygen maxima do not occur in anhydrous acetic acid solutions and that degassing has no effect on the curves.

We have been able to obtain curves (similar to those of MacGillavry) by plotting current against applied voltage in dilute and in concentrated solutions, for sodium acetate, and also for ammonium acetate and lithium chloride (Fig. 1). We have shown, however, that the first inflection to which he refers cannot be caused by mercurous ion, since it disappears completely on thoroughly degassing the solution (Fig. 2). Far from being without effect, degassing (removal of dissolved

(6) MacGillavry, *Trans. Faraday Soc.*, **32**, 1447 (1936).

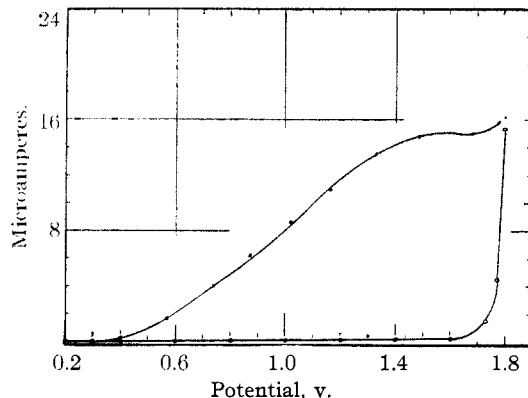


Fig. 2.—The effect of degassing on the current-potential curve for 0.24 molar ammonium acetate in acetic acid: $\bullet\text{---}\bullet$, before degassing; $\text{---}\circ\text{---}$, degassed for four hours.

oxygen) leads to marked modifications in the curves. This is evident in Fig. 3 in which the presence of dissolved oxygen is seen completely to obscure the curve of a 1.2×10^{-3} molar zinc acetate solution. In Fig. 2 and subsequent curves, correction is made for the *IR* drop, which is large for acetic acid solutions, and this corrected potential is plotted against the current passed through the cell.

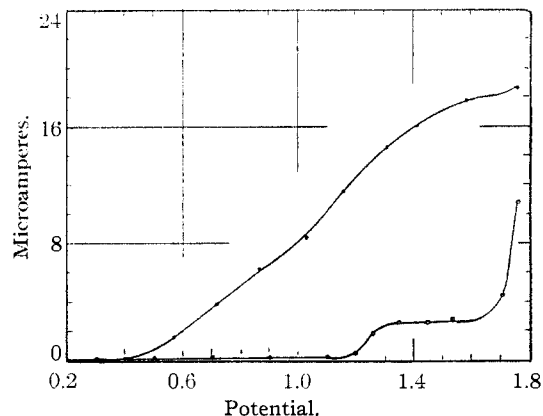


Fig. 3.—The effect of degassing on the current-potential curve for Zn^{++} ion in glacial acetic acid (0.25 molar ammonium acetate, 1.2×10^{-3} molar zinc acetate): $\bullet\text{---}\bullet$, before degassing; $\text{---}\circ\text{---}$, degassed for four hours.

In general, certain metallic ions may be determined normally in acetic acid solutions, while others cannot. The ions studied include Pb^{++} , Cd^{++} , Zn^{++} , Co^{++} , Cr^{+++} , Sb^{+++} , Ni^{++} , Cu^{++} , Fe^{+++} , Hg^{++} , Pb^{++++} . Of these the first seven ions (through Ni^{++}) give normal S-shaped curves in which the current rise occurs at a potential somewhat higher than it is in water, is smaller in magnitude than it is in water, but is proportional in magnitude to the concentration of the reducible

ion. These curves are easily obscured by oxygen even when the ions are present in relatively high concentrations. Interestingly enough, gelatine, methyl cellulose, and various dyes frequently used to eliminate oxygen maxima in aqueous solutions, do not seem to have much effect in preventing oxygen disturbances with these ions. The curves in Fig. 3 are typical of ions of this group.

In Table I are shown comparisons between the wave heights and the half wave reduction potentials in water and in acetic acid for those ions giving normal reduction curves. The supporting electrolyte was 0.25 *M* ammonium acetate in each case. The wave heights are obviously higher in water than those in acetic acid and the ratio is about 1.5 to 1.6. Data could not be obtained for Al^{+++} and Cr^{+++} because of interference from the H^+ ion wave which appears at about -1.7 volts in degassed solutions. The early appearance of the hydrogen wave is a disadvantage in applying the polarographic method to acetic acid solutions.

TABLE I

WAVE HEIGHTS AND HALF-WAVE POTENTIALS OF CERTAIN IONS IN ACETIC ACID

Concentration of ion is 0.001 molar. Supporting electrolyte is 0.25 molar ammonium acetate in each case.

Ion	Wave heights ^a		Ratio $\text{H}_2\text{O}/\text{HOAc}$	Half-wave potentials	
	H_2O	HOAc		H_2O	HOAc ^b
Pb^{++}	3.92	2.24	1.75	-0.48	-0.70
Cd^{++}	3.52	2.24	1.57	-0.59	-0.83
Zn^{++}	3.52	2.22	1.60	-1.05	-1.25
Co^{++}	3.44	2.16	1.59	-1.25	-1.35
Ni^{++}	3.32	2.22	1.50	-1.05	-1.15

^a In microamperes. The value of $m^2/3s^{1/2}$ for the capillary was 1.1 $\text{mg.}^{2/3} \text{sec.}^{-1/2}$. ^b These potentials were measured against a chloranil electrode with acetic acid as solvent and were converted to the potentials corresponding to the saturated calomel electrode.⁷ The potentials given for water and acetic acid solutions are both against the saturated calomel electrode in water solutions and are therefore comparable.

One property which all of the above normal ions possess in common is that they show reduction potentials (half-wave potentials) more negative than -0.3 volt. The importance of this characteristic is further indicated by the fact that the ions reduced at potentials more positive than -0.3 volt also behave alike in many respects. The cations Cu^{++} , Fe^{+++} , Hg^{++} and Pb^{++++} give highly abnormal reduction curves characterized by large initial slopes and by a discontinuous drop to lower levels. Following the discontinuity the current curve rises somewhat less sharply until

(7) Conant; Small and Taylor, *THIS JOURNAL*, **47**, 1050 (1925).

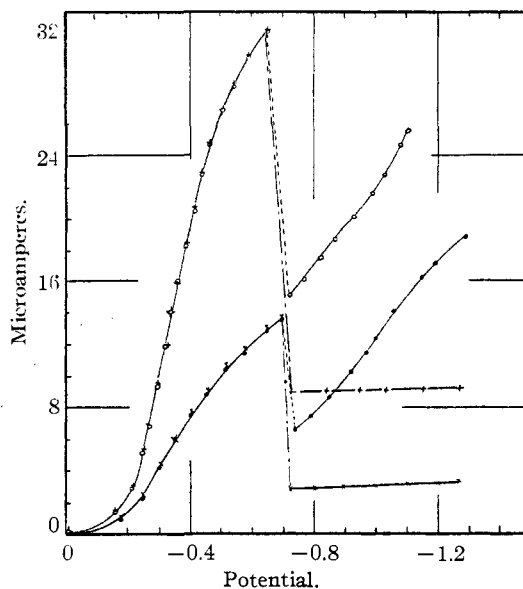


Fig. 4.—The effect of degassing on acetic acid solution of ammonium acetate and copper acetate: 0.20 molar NH_4OAc , 0.001 molar Cu^{++} , before degassing, $\bullet\text{---}\bullet$; after degassing, $\text{---}\times\text{---}$; 0.20 molar NH_4OAc , 0.004 molar Cu^{++} , before degassing, $\circ\text{---}\circ$; after degassing, $\text{---}+\text{---}$.

the reduction potential of H^+ is reached. Degassing with these ions does not cause the normal S-shaped curve to appear. In fact, it does not alter the first part of the curve appreciably, but may greatly increase the magnitude of the discontinuity. These effects are seen in the curves of Fig. 4, which are for Cu^{++} , but which are quite typical of all of the ions of this group. A hysteresis effect is observed in the current-voltage curves. By careful manipulation of the voltage it is possible to follow either curve for some distance to the left or right of the initial position of discontinuity. The overlapping may amount to as much as 0.5 volt and is greater the lower the concentration of the supporting electrolyte. This suggests that the resistance of the cell may be a factor in the overlapping, and this has been found to be the case. The resistance of the cell amounts to 28,000 ohms for a solution 0.2 molar in ammonium acetate and 0.001 molar in copper acetate. When correction is made for the IR drop of the cell the overlapping disappears and the curves become discontinuous at about -0.7 volt (Fig. 4). The curves are still discontinuous on the descending side, and with a little care a potential may be found at which the galvanometer swings to a point on the lower curve, hesitates a fraction of a second, and then moves on to a point on the upper curve.

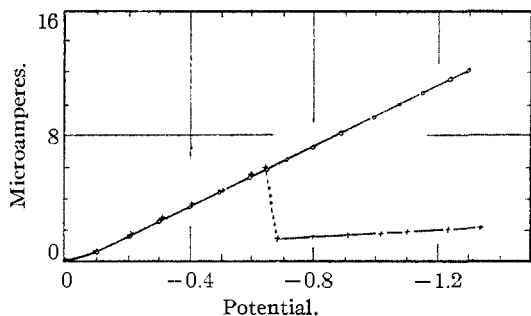


Fig. 5.—The effect of degassing an acetic acid solution 0.09 molar in ammonium acetate and 0.0012 molar in copper acetate; $\circ\text{---}\circ$, before degassing; $\text{---}\text{+---}$, degassed for two hours.

The nature of the maxima is affected by the concentration of the electrolytes and also by the presence of small amounts of water in the system. A certain minimum concentration of the supporting electrolyte seems to be necessary before the break is observed at all in solutions which have not been degassed. Thus with concentrations less than about 0.15 molar in sodium or ammonium acetate no break is observed and a continuous and more or less linear curve results (Fig. 5). Degassing causes the current following the discontinuity potential to shift to lower values, and the break appears.

After correction has been made for the *IR* drop

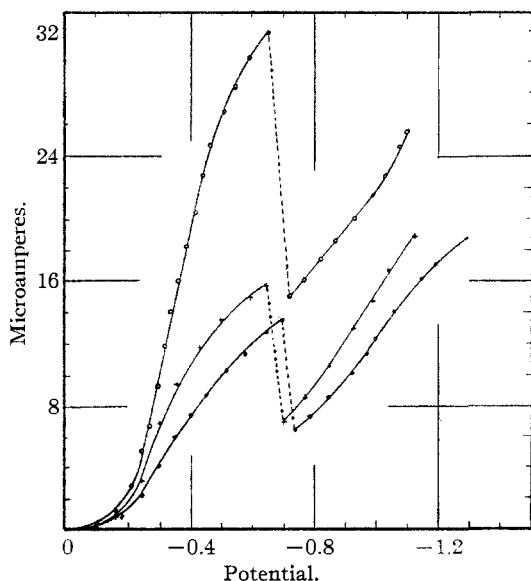


Fig. 6.—The effect of concentration of the supporting electrolyte and of the reducible ion on the discontinuous current-potential curves in acetic acid: $\text{---}\text{+---}$, 0.3 molar NH_4OAc , 0.001 molar Cu^{++} ; $\text{---}\bullet\text{---}\bullet$, 0.2 molar NH_4OAc , 0.001 molar Cu^{++} ; $\circ\text{---}\circ$, 0.2 molar NH_4OAc , 0.004 molar Cu^{++} .

of the cell, the apparent change in the discontinuity potential, caused by changes in the concentration of the supporting electrolyte and of the reducible substance, disappears and the curves all become discontinuous at about -0.7 volt (Fig. 6). The magnitude of the discontinuity is increased by increases in the concentration of either the supporting electrolyte or the reducible ions.

The addition of small amounts of water to solutions in which the supporting electrolyte concentration is too small to permit the discontinuity to appear (without degassing) causes the curves to become discontinuous. This is probably caused by a lowering of the resistance. Further addition of water augments the break and causes the curves to become discontinuous at the nor-

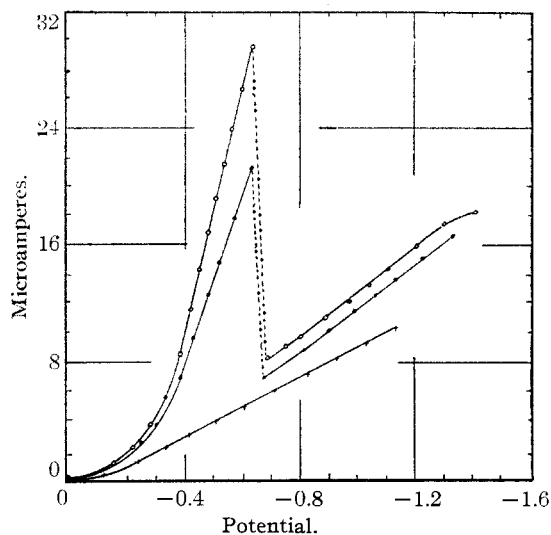


Fig. 7.—Current-potential curves for 0.1 molar ammonium acetate, 0.0012 molar copper acetate in: $\text{---}\text{+---}$, glacial acetic acid; $\text{---}\bullet\text{---}\bullet$, 6.9 mole per cent. water added; $\circ\text{---}\circ$, 13.4 mole per cent. water added.

mal potential. From Fig. 7 it may be seen that a solution 0.1 molar in ammonium acetate and 1.2×10^{-3} molar in copper acetate has the discontinuity obscured by the presence of oxygen but that the addition of water (6.9 mole per cent.) causes the curve to become discontinuous. A larger amount of water (13.4 mole per cent.) increases the magnitude of the break. Still further addition of water gives a curve (Fig. 8) which is discontinuous but which exhibits a rounded maximum of the type frequently observed in aqueous solutions. It is to be noted that when the curves do become discontinuous, they always do so on the more negative side of the maximum.

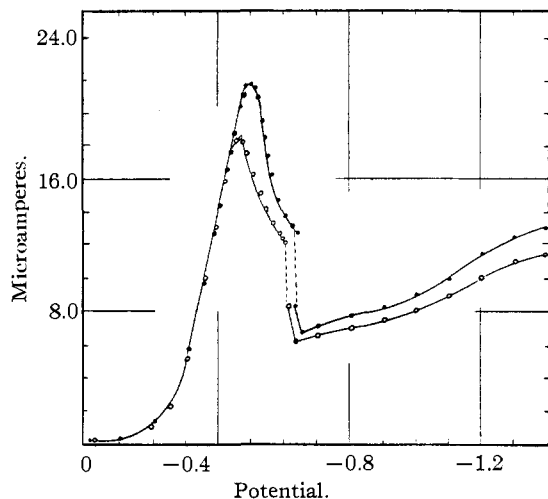


Fig. 8.—Current-potential curves for 0.1 molar ammonium acetate and 0.0012 molar copper acetate in aqueous acetic acid: —●—●—, 28.4 mole per cent. water; —○—○—, 36.8 mole per cent. water.

As the amounts of water are increased, the heights of the maxima become progressively lower. This effect continues until the medium contains 50 mole per cent. water, at which point a reversal occurs and the maxima become progressively higher again. From Fig. 9 it may be seen that the maxima heights not only go through a minimum at 50 mole per cent. water but also through an inflection point at 65 mole per cent. water. These points are apparently dependent upon the solvent composition only and not upon the concentration of supporting electrolyte. Furthermore, the heights of the maxima at the minimum point are the same for different concentrations of electrolyte. All of the above facts indicate that the effects noted depend on some prop-

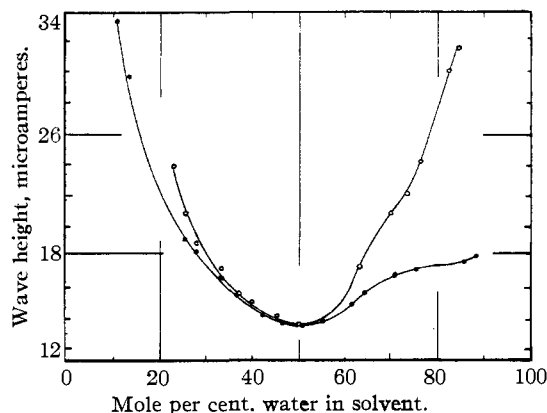


Fig. 9.—The effect of adding water to the system ammonium acetate-copper acetate-acetic acid: —●—●—, 0.25 molar NH_4OAc , 1.2×10^{-3} molar $\text{Cu}(\text{OAc})_2$; —○—○—, 0.10 molar NH_4OAc , 1.2×10^{-3} molar $\text{Cu}(\text{OAc})_2$.

erty of acetic acid-water mixtures which varies in the same manner as the maximum heights. Actually the fluidity of such mixtures varies in a strikingly similar manner. In Fig. 10 are plotted the heights of the maxima along with the fluidity data obtained by other investigators.⁸ It is obvious that these curves show much the same characteristics except for the inflection point. This inflection may be caused by the ammonium acetate whose influence is doubtless appreciable at the concentrations employed. The reciprocal density of acetic acid-water mixtures also passes through a minimum at 50 mole per cent. water.⁹ This composition corresponds to that of the ortho acid $\text{CH}_3\text{C}(\text{OH})_3$.

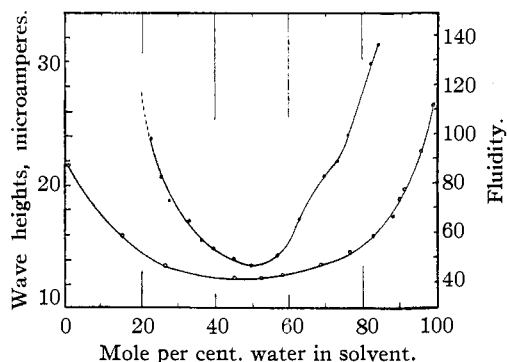


Fig. 10.—The relationship between fluidity and the heights of the maxima in current-potential curves for water-acetic acid mixtures: —○—○—, fluidity; —●—●—, maxima heights in 0.1 molar ammonium acetate, 0.0012 molar Cu^{++} solutions.

Since the occurrence of discontinuities with inorganic ions depends on the reduction potential of the ion, it might be expected that the same effect would be observed with organic materials. A substance like quinhydrone, whose reduction potential is not high (half wave potential -0.02 in water at pH 3.9),¹⁰ would be expected to give discontinuous electrolysis curves. Actually this was the case and curves having the same appearance as those obtained with Cu^{++} resulted from the electrolysis of a solution of quinhydrone in 0.25 molar ammonium acetate. On the other hand, benzil and benzoin with half-wave potentials of -0.6 and -1.2 volts, respectively, in 0.25 molar ammonium acetate give smooth S-shaped curves. Wave heights for these compounds were found to be directly proportional to the concentration.

(8) Bingham, White, Thomas and Caldwell, *Z. physik. Chem.*, **83**, 641 (1913).

(9) "International Critical Tables," 1928, Vol. III, p. 123.

(10) Hohn, "Chemische Analysen mit dem Polarographen," Verlag Julius Springer, Berlin, 1937.

Wave heights in acetic acid solutions are appreciably affected by the concentrations of the supporting electrolyte, just as they are in water solutions. In all cases a slight increase in wave height occurs with a decrease in concentration of supporting electrolyte between 1 molar and 0.25 molar. When the concentration of supporting electrolyte becomes less than this amount a more pronounced effect is noted (Fig. 11). This suggests that for best results the concentration of supporting electrolyte should be maintained constant at some molarity which is 0.25 or more. We have found 0.25 molar ammonium acetate quite satisfactory in most cases. The limiting factor in acetic acid is the reduction potential of H^+ rather than of the supporting cation.

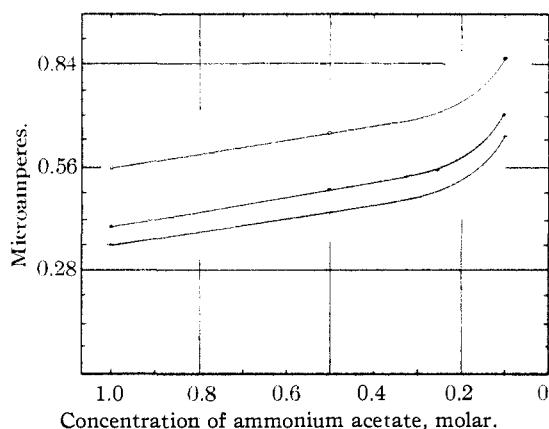


Fig. 11.—The effect of the supporting electrolyte concentration on the wave height: $\bullet\text{---}\bullet$, $2.5 \times 10^{-4} M$ cadmium acetate; $++$, $2.5 \times 10^{-4} M$ benzoin; $\text{---}\text{O}\text{---}$, $2.5 \times 10^{-4} M$ benzil.

Our conclusions concerning the application of the dropping mercury electrode to acetic acid solutions may be summarized as follows: (a) Organic and inorganic ions and molecules which can be determined satisfactorily in aqueous solutions can also be determined satisfactorily in acetic acid solutions provided their half-wave potentials lie between the approximate values of -0.3 and -1.4 volt. (b) Substances whose half-wave reduction potentials lie at more positive values than about -0.3 volt give discontinuous current-voltage curves and cannot be determined polarographically in the usual fashion even with the addition of maximum suppressing agents. Those whose half wave reduction potentials lie at more negative potentials than -1.4 volts encountered interference from the H^+ reduction wave which begins to appear at this voltage. (c) Oxygen

interferes strongly with the determination of such substances as can be determined and influences the nature of the curves in all cases. Degassing is an important preliminary to determinations conducted in acetic acid at all concentrations of the reducible material. (d) The addition of water in amounts at least as great as 5 mole per cent. does not alter any of the above conclusions although it does bring about certain changes. (e) Minimum concentrations of supporting electrolyte of about 0.25 molar are recommended. Below this concentration the wave heights become increasingly variable with changes in concentration of the supporting electrolyte. (f) For a given reducible substance the half-wave reduction potential in acetic acid is somewhat greater than in water and the wave height corresponding to a given concentration is much lower. In the cases observed the ratio of the wave height in water to the wave height in acetic acid was about 1.60.

Experimental

Apparatus and Materials.—The current-voltage curves were obtained with the aid of the Eledropode manufactured by the Fisher Scientific Company. This instrument is manually operated and is admirably suited for studies of this type because of its flexibility and simplicity of operation. Curves were obtained by plotting the maximum swing of the galvanometer against the applied voltage across the cell.

The capillary of the dropping mercury electrode had an internal diameter of 0.03 mm. and a dropping rate of 4 seconds per drop in a 0.25 molar ammonium acetate solution in glacial acetic acid with a mercury height of 70 cm. The value of $m^{2/3}t^{1/6}$ was $1.1 \text{ mg.}^{2/3} \text{ sec.}^{-1/6}$.

Degassing was accomplished with natural gas taken from the laboratory tap. This was stored over a copper sulfate solution, passed through a Jones reductor,¹¹ a column of Drierite, and finally bubbled through a sample of the cell solution before entering the cell itself. This method was found to be quite satisfactory, very convenient, and free of the expense attached to the rental of cylinders of other gases over extended periods of time.

Unless otherwise noted the acetic acid used in all experiments was the "99.5%" acid supplied by the J. T. Baker Chemical Company. Since the curves with this acid closely approximated the curves obtained by MacGillavry⁶ with a specially purified acid, no further efforts were made to refine the commercial product. The cations studied were employed in the form of their acetates, or as with Fe^{+++} and Bi^{+++} ions, as their chlorides. The salts, with the exception of ammonium acetate, were dried at 110° for at least twenty-four hours. Ammonium acetate, which decomposes at this temperature, was recrystallized from acetic acid. The anhydrous salts, or more often solutions of the salts in acetic acid, were added directly to the cell solution. The organic chemicals used were East-

(11) Stone and Hume, *Ind. Eng. Chem., Anal. Ed.*, **11**, 598 (1939).

man Kodak Co. grade. The purity of all of the above substances was further tested by determining their current-voltage curves at high sensitivity. The absence of irregularities indicated the absence of more than very small traces of interfering electroreducible impurities.

Summary

The dropping mercury electrode has been applied to determinations of electroreducible substances in anhydrous acetic acid. It has been

found that such substances with half wave reduction potentials lying between about -0.3 and -1.4 volts may be determined normally, while other substances give discontinuous curves or are interfered with by the hydrogen ion curve and cannot be determined polarographically. Dissolved oxygen exerts a marked influence on current-voltage curves in acetic acid.

LAFAYETTE, INDIANA RECEIVED NOVEMBER 17, 1941

[CONTRIBUTION FROM THE PARKE, DAVIS & COMPANY RESEARCH LABORATORIES AND THE AVERY LABORATORY OF CHEMISTRY OF THE UNIVERSITY OF NEBRASKA]

Derivatives of 4-Amino-6-methoxyquinaldine*

BY WALTER F. HOLCOMB AND CLIFF S. HAMILTON

Magidson¹ has described several 6-methoxyquinolines substituted in the four position by dialkylaminoalkylamino groups which exhibited considerable antiplasmodial action whereas the corresponding quinaldines, particularly 4- γ -diethylaminopropylamino - 6 - methoxyquinaldine, were reported by Krichevskii² to be void of anti-malarial activity. Since the chemical characterization of the above diethylaminopropyl derivative was not published, this product was prepared and when tested for its action in avian malaria was found to have a noticeable effect.³ Kermack⁴ has prepared 6-methoxy-4-piperazinoquinaldine and the corresponding piperidino derivative but the activity of these compounds has not yet been published. In view of the apparent discrepancy regarding the activity of basically substituted aliphatic quinaldines, and the lack of information on the heterocyclic substituted compounds of the above type, it was deemed advisable to prepare a representative series of these drugs for antimalarial studies.

γ -Diethylaminopropylamine has been prepared by Shriner⁵ through the Gabriel phthalimide type of synthesis and γ -morpholinepropylamine has been prepared by Utermohlen⁶ in a similar manner. Both of these compounds were readily obtained

in about double the previous yields by hydrogenation of the corresponding nitriles using Raney nickel catalyst. β -Diethylaminopropionitrile⁷ is available commercially and β -morpholinepropionitrile was obtained by the reaction of acrylonitrile⁷ with morpholine at 50° . The preparation of higher homologs of the series by this method, such as γ -di-*n*-butylaminopropylamine⁸ and γ -di-*n*-amylaminopropylamine, indicates that this reaction is quite general.

Condensation of γ -diethylaminopropylamine and γ -morpholinepropylamine with 4-chloro-6-methoxyquinaldine proceeded quite well at 175° yielding the corresponding substituted quinaldine, but with 4-amino-1-diethylaminopentane it was necessary to resort to a sealed tube reaction at 225° .

Attempts to condense 2-aminopyridine directly with 4-chloro-6-methoxyquinaldine gave unsatisfactory results, but 3-aminopyridine reacted readily to give rather poor yields of the expected β -pyridylaminoquinaldine.

Morpholine reacted very readily with the above chloroquinaldine at 140° giving good yields of the desired morpholine compound. 8-Aminoquinoline, 8-amino-6-methoxyquinoline, thionine, and 5-aminoindazole condensed easily with 4-chloro-6-methoxyquinaldine at about 170° and fair yields of these substituted derivatives were obtained.

Experimental

β -Di-*n*-amylaminopropionitrile.—A well mixed solution of 15.9 g. (0.3 mole) of acrylonitrile and 47.1 g. (0.3 mole)

* Presented before the Organic Division of the American Chemical Society, Memphis, April 20-24, 1942.

(1) Magidson and Rubtsov, *J. Gen. Chem.* (U. S. S. R.), **7**, 1896 (1937) [*C. A.*, **32**, 564 (1938)].

(2) Krichevskii, Shternberg and Halperin, *J. Microbiol., Epidemiol., and Immunobiol.* (U. S. S. R.), **14**, 642 (1935) [*C. A.*, **30**, 4218 (1936)].

(3) A. L. Tatum, University of Wisconsin, private communication.

(4) Kermack and Smith, *J. Chem. Soc.*, 1356 (1930).

(5) Shriner and Hickey, *THIS JOURNAL*, **61**, 888 (1939).

(6) Utermohlen and Hamilton, *ibid.*, **63**, 156 (1941).

(7) Röhm and Haas Company, Philadelphia, Pa.

(8) U. S. Patent 1,992,615; *C. A.*, **29**, 2548 (1935).