[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY, UNIVERSITY OF MINNESOTA]

Polarography in Acetonitrile. III. Brønsted Acids. Amperometric Titration of Amines with Perchloric Acid. Oxygen

BY J. F. COETZEE AND I. M. KOLTHOFF

RECEIVED JUNE 12, 1957

Acetonitrile is a strongly differentiating solvent as regards the strength of acids and bases dissolved in it. The polarography of selected uncharged, cationic and anionic acids was studied in acetonitrile as solvent, and it was found that there is a much wider spread in the reduction potentials of acids of different intrinsic strength in acetonitrile than in water. Generally well-defined but incompletely reversible waves were obtained. The following "half-wave potentials" (for 1 millimolar solutions) were determined at the dropping mercury electrode *versus* the aqueous saturated calomel electrode: perchloric acid −0.70, hydrobromic −0.90, 2,5-dichloroanilinium ion −1.00, hydrochloric −1.06, *p*-toluenesulfonic −1.20, sulfuric −1.20, 2,5-diethylanilinium ion −1.43, fluorovaleric *ca.* −1.5, oxalic −1.55, phosphoric −1.75, benzoic −2.1 and acetic acid −2.3 volts. These acids all give incompletely reversible waves, and a quantitative comparison of acid strengths on the basis of relative half-wave potentials is impossible. Considering that the overpotential of hydrogen on mercury may vary from acid to acid, the order of the half-wave potentials is not necessarily the order of the acid strengths. Nevertheless the order of the half-wave potentials found agrees well with the order of the strengths of some of these acids in other differentiating solvents, such as acetic acid. Perchloric acid is a typical strong electrolyte in acetonitrile (shown conductometrically), while hydrogen chloride is not. Sulfuric, oxalic and phosphoric acids behave polarographically as monobasic acids in acetonitrile. Ammonia and certain aliphatic and aromatic amines give well-defined anodic waves at the dropping mercury electrode in acetonitrile as solvent. Tribenzylamine and urea were titrated amperometrically with perchloric acid. An exploratory study of the polarography of oxygen was made and attention is drawn to several unexplained phenomena.

Two previous papers[1,2] dealt with the polarography and solid electrode voltammetry of various cations and anions in acetonitrile as solvent. It was shown that the polarographic properties of most of these ions in acetonitrile as solvent can be correlated with the fact that the solvation energies of cations and especially anions are usually much lower in acetonitrile than in water. Two exceptional cases were discussed, namely, those of silver and cuprous copper ions, which interact in a more or less specific manner with acetonitrile.

The present paper deals mainly with the polarography of various Brønsted acids in acetonitrile as solvent. As an analytical application of the polarographic data obtained, the amperometric titration of amines with perchloric acid is discussed. Finally results of exploratory experiments on the polarography of oxygen are included.

The polarography of perchloric acid in acetonitrile as solvent has been studied by Vlček.[3,4] Streuli[5] titrated various amines in acetonitrile as solvent with coulometrically generated hydrogen ion. The results of the above authors will be discussed in conjunction with those presented in this paper.

Strength of Acids and Bases in Acetonitrile as Solvent.—There is considerable experimental evidence that acetonitrile is an amphoteric solvent with much weaker basic properties than water and even weaker acidic properties.

That acetonitrile can act as a base is evident from the fact that it forms solvates with numerous Lewis acids, such as BF_3, $AlCl_3$, etc. (see Part I, references 3, 4 and 5). The basic properties of acetonitrile can logically be ascribed to the presence of an unshared electron pair on the nitrogen atom of its molecule. Acetonitrile is however a much weaker base than water; this is evident from the relative strength of various acids in acetonitrile as determined colorimetrically[6] and conductometrically,[7] as well as from the fact that sulfuric acid can be titrated as a monobasic acid in acetonitrile.[8] Kilpatrick and Kilpatrick[6] already have determined colorimetrically the relative acid strengths of a number of Brønsted acids on the basis on the equilibrium: $HA + CH_3CN \rightleftarrows CH_3CNH^+ + A^-$, and were able to make the following generalizations: (a) for carboxylic (not hydroxy-carboxylic) acids and picric acid: $pK_{CH_3CN} = pK_{H_2O} + 4.4$; (b) for hydroxy-carboxylic acids and dinitrophenols: $pK_{CH_3CN} = pK_{H_2O} + 3.0$; (c) for cationic acids of the amine type: $pK_{CH_3CN} = 0.47\,pK_{H_2O} + 2.2$ It is evident that acids belonging to the first two types are considerably weaker in acetonitrile than in water, and that in acetonitirle as solvent cationic acids are relatively strong as compared to uncharged ones. The effect of the charge type of the acid is accounted for by the relatively low dielectric constant of acetonitrile as compared to water. The polarographic data reported in this paper are in qualitative agreement with those of Kilpatrick and Kilpatrick.

That acetonitrile can act as an acid is evident from measurements of the conductivity of a number of amines dissolved in it. However, the acidic properties of acetonitrile are extremely weak. Thus Usanovich and Dulova found that the equivalent conductivity of piperidine (pK 2.8 in water) is only of the order of 10^{-6} ohm^{-1} cm.^{2} equiv.$^{-1}$ in acetonitrile, which is much lower than the value which they found for acetic acid in the same solvent. In order to account for the acidic properties of acetonitrile, it is necessary to assume that it can act as a Lewis acid by accepting electrons from donor substances. Further evidence for the postulate that the acidic properties of aceto-

---

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

[2] I. M. Kolthoff and J. F. Coetzee, *ibid.*, **79**, 1852 (1957).

[3] A. A. Vlček, *Chem. Listy*, **48**, 1741 (1954); *C. A.*, **49**, 5158 (1955).

[4] A. A. Vlček, *Collection Czechoslov. Chem. Communs.*, **20**, 636 (1955).

[5] C. A. Streuli, *Anal. Chem.*, **28**, 130 (1956).

[6] M. Kilpatrick, Jr., and M. L. Kilpatrick, *Chem. Revs.*, **13**, 131 (1933).

[7] M. Usanovich and V. Dulova, *J. Gen. Chem.* (*U.S.S.R.*), **16**, 1978 (1946); *C. A.*, **41**, 6795 (1947).

[8] F. E. Critchfield and J. B. Johnson, *Anal. Chem.*, **26**, 1803 (1954).

[9] M. Usanovich and V. Dulova, *J. Gen. Chem.* (*U.S.S.R.*), **17**, 669 (1947); *C. A.*, **42**, 519 (1948).

nitrile are much weaker than those of water comes from the fact that mixtures of amines, which are such weak bases in water that they cannot be titrated differentially, can be titrated in this manner with perchloric acid in acetonitrile as solvent.[10]

Experimental

The solvent and supporting electrolytes were purified as described before.[1] The polarographic cell was the same as that used previously, and polarograms were recorded in the same manner. Likewise all potentials reported in this paper refer to the aqueous saturated calomel electrode. Abbreviations and symbols, as well as the sign convention, are the same as used before. Polarograms were recorded at 25.0 ± 0.5°.

Compounds Used for Polarographic Analysis.—All compounds used were of ordinary reagent quality, with the following exceptions: the fluorovaleric acid was a technical grade sample obtained from the Minnesota Mining Co.; dichloroanilinium perchlorate and diethylanilinium perchlorate were prepared from perchloric acid and the respective bases in glacial acetic acid as solvent, followed by recrystallization from the same solvent; a solution of tetraethylammonium bioxalate in acetonitrile was prepared by half-neutralizing oxalic acid with tetraethylammonium hydroxide in acetonitrile as solvent.

Preparation of Solutions of Perchloric Acid in Acetonitrile.—An anhydrous 1 M solution of perchloric acid in *acetic acid* as solvent was prepared by heating a solution of 71% aqueous perchloric acid in glacial acetic acid with the amount of acetic anhydride required to remove the water present (water present in acetic acid determined by Karl Fischer titration). This stock solution of anhydrous perchloric acid was standardized by titration against potassium hydrogen phthalate in acetic acid as solvent, using crystal violet as indicator. Standard solutions of perchloric acid in acetonitrile were then prepared from this stock solution. The acetic acid introduced does not interfere with the polarographic wave of perchloric acid, because acetic acid is an extremely weak acid in acetonitrile as solvent and its reduction wave occurs at a much more negative potential than that of perchloric acid; likewise the measured conductivity of such a solution of perchloric acid in acetonitrile requires no correction for the presence of the small concentration of acetic acid introduced.

The acetonitrile contained 1.3×10^{-3} M water (determined by Karl Fischer titration). In order to determine whether this quantity of water would affect the polarographic wave and/or the conductivity of perchloric acid in acetonitrile as solvent, a 10^{-3} M solution of 71% aqueous perchloric acid in acetonitrile was heated to 70° with the amount of acetic anhydride required to remove all the water present. The resultant solution contained less water than could be determined by Karl Fischer titration (less than about 10^{-4} M), and its polarographic wave and conductance were identical to those of a 10^{-3} M perchloric acid solution containing 1.3×10^{-3} M water, as prepared by adding the stock solution of perchloric acid in anhydrous acetic acid to acetonitrile containing 1.3×10^{-3} M water. Due to the risk of hydrolysis setting in when acetonitrile is heated with water in the presence of perchloric acid, this treatment was subsequently omitted, and the polarographic and conductometric data presented in this paper were obtained with solutions prepared by adding anhydrous perchloric acid in acetic acid to acetonitrile containing 1.3×10^{-3} M water.

Conductance Measurements.—Conductances were measured at 25.00 ± 0.02°, using an Industrial Instruments Inc. no. RC-1B conductance bridge and a conductance cell with a cell constant of 0.1409. The solvent had a conductivity of 1.1×10^{-7} ohm^{-1} cm.$^{-1}$. Measured conductances were corrected for the contribution of the solvent, which never exceeded 2% of the total.

Results and Discussion

I. Brønsted Acids. Conductivity of Perchloric Acid in Acetonitrile as Solvent.

—Conductivities were measured as described before. The results are presented in Table I.

TABLE I

CONDUCTIVITY OF FRESHLY PREPARED SOLUTIONS OF PERCHLORIC ACID IN ACETONITRILE

Normality N	$10^3N^{1/2}$	Resistance R, ohms	$\Lambda_v = 140.9/NR^a$
1×10^{-2}	100.0	100.3	140.4
3×10^{-3}	54.77	292.9	160.3
1×10^{-3}	31.62	826.4	170.5
3×10^{-4}	17.32	2656	176.8
1×10^{-4}	10.00	7820	180.1
5×10^{-5}	7.071	15520	181.6

[a] Cell constant = 140.9×10^{-3}.

Plotting Λ_v as a function of $N^1/_2$ gives a straight line which on extrapolation cuts the Λ_v-axis at $\Lambda_o = 184.5$. Perchloric acid therefore behaves as a typical strong electrolyte in acetonitrile as solvent. The conductivities of freshly prepared solutions remained constant for at least a day.

Accepting Walden and Birr's[11] value of 104.5 for the equivalent conductivity at infinite dilution of the perchlorate ion in acetonitrile as solvent,[12] the corresponding value for the solvated proton will be 80.0. Furthermore, the transport number of the perchlorate ion in a solution of perchloric acid in acetonitrile will be given by 104.5/184.5 = 0.57 (*vide infra*).

Polarography of Perchloric Acid.—Solutions of perchloric acid in acetonitrile were prepared as described before. Decinormal tetraethylammonium perchlorate served as supporting electrolyte. Well-defined though incompletely reversible waves were obtained (slope = 0.135 for a millimolar solution). The diffusion current was found proportional to concentration over a wide range (tested 0.5 to 5.0 millimolar).

The "half-wave potential" (−0.70 volt for a millimolar solution) is much less negative than in aqueous solution (−1.58 volts). This can be attributed in part to the fact that the solvation energy of the proton will be much lower in acetonitrile than in water, thereby making the solvated proton CH_3CNH^+ a "super-acid" in acetonitrile as solvent. However, the difference in the "half-wave potentials" of the solvated proton in acetonitrile and in water is far greater than can be accounted for by the difference in basic strength of the two solvents.[6] Evidently the hydrogen over-potential on mercury must be far smaller in acetonitrile than in water. Vlček[3,4] arrived at the same conclusion; by measuring the difference Δ in the half-wave potentials of potassium and the solvated proton in acetonitrile solutions containing varying concentrations of water, and by extrapolating Δ to zero concentration of water, Vlček concluded that the hydrogen overpotential on mercury is about 0.8 volt smaller

---

[10] J. S. Fritz, *Anal. Chem.*, **25**, 407 (1953).

[11] P. Walden and E. J. Birr, *Z. physik. Chem.*, **144**, 269 (1929).

[12] Walden and his co-workers found that in various ionizing solvents, including water and acetonitrile, the product of the viscosity of the solvent and the equivalent conductivity at infinite dilution of the electrolyte tetraethylammonium picrate, has a constant value of 0.563. By writing this product as the sum of the corresponding products for the individual ions: $\Lambda_0\eta = (\lambda_0^c + \lambda_0^a)\eta = 0.563$, and by substituting the value $\lambda_0^a\eta = 0.267$ determined for the picrate ion in *aqueous* solution, Walden and Birr calculated values for the two individual ionic conductivities in acetonitrile as solvent. The feasibility of this calculation is in question, because the solvation of individual ions usually is different in two solvents, and the constancy of the product $\Lambda_0\eta$ in the two solvents may therefore be coincidental.

in acetonitrile than in water. However, the accuracy of Vlček's calculation is in question, because it is based on Pleskov's[13] potentiometrically determined value for the standard potential of the H_2-H^+ couple in acetonitrile as solvent, which in turn depends on the erroneous assumption that hydrogen chloride behaves as a strong electrolyte in acetonitrile (*vide infra*).

The effect of water on the polarographic wave of perchloric acid in acetonitrile as solvent is illustrated by Fig. 1. As in the instances of other cations which are strongly coordinated with water in aqueous solution,[2] addition of water causes a rapid shift of the wave to more negative potentials. As before, this can be attributed in part to formation of the hydronium ion H_3O^+. However, for the reasons mentioned before, the overpotential of hydrogen on mercury must also increase rapidly when water is added.

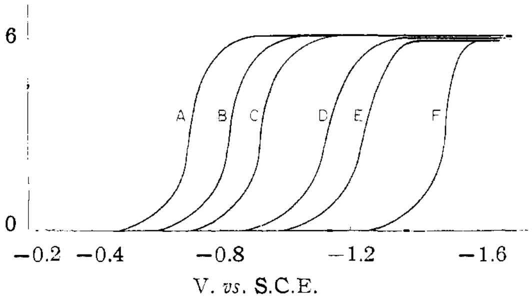

Fig. 1.—10^{-3} *M* $HClO_4$ in 0.1 *M* Et_4NClO_4: A, no water added; B, C, D, E and F, 0.01, 0.1, 1.0, 3.0 and 10 *M* water added.

The diffusion current of the solvated proton is virtually unaffected by the addition of up to 2% of water (*vide* Fig. 1). Evidently the species CH_3CNH^+ and H_3O^+ must have very similar diffusion coefficients in acetonitrile, and neither has the abnormally high mobility which is characteristic of the hydronium ion in water. At concentrations of water higher than about 5% (v./v.), the diffusion current gradually decreases, undoubtedly as a result of the increasing viscosity of the solution.

Limiting Current and Diffusion Coefficient of the Solvated Proton.—From the approximate relation of Heyrovsky and Ilkovic: $i_d/i_l = t_-$ for the polarographic reduction of a cation, the ratio of the diffusion current i_d, given by a solution of perchloric acid in acetonitrile, to its limiting current i_l, should be equal to the transport number of the perchlorate ion in the solution (0.57, as calculated before). This ratio was determined experimentally for a 1.5 millimolar solution of perchloric acid in acetonitrile, using an internal mercury pool as anode; decinormal tetraethylammonium perchlorate served as supporting electrolyte for the measurement of diffusion current. The observed ratio was 0.56; its excellent agreement with the calculated value is no doubt partly fortuitous in view of the fact that the relation $i_d/i_l = t_-$ is based on the approximations that the diffusion component of the limiting current is independent of the presence of supporting electrolyte and that the Ilkovic equation is correct. Moreover, Walden and Birr's method of calculating individual ionic conductivities is open to criticism.

Using the Nernst expression for the relation between the diffusion coefficient D_0 and the equivalent conductivity λ_0 of an ion at infinite dilution: $D_0 = RT\ \lambda_0/ZF^2$, where R = 8.32 volt-coulombs per degree, Z = charge of the ion and F = 96,500 coulombs, the diffusion coefficient at infinite dilution can be calculated for the solvated proton in acetonitrile by substituting $\lambda_0 = 80.0$ (*vide supra*), giving a value of $D_0 = 2.13 \times 10^{-4}$ cm.^{2} sec.$^{-1}$. The Ilkovic equation: $I_d = 605\ nD^{1/2}$, where $I_d = i_d/Cm^{2/3}\ t^{1/6}$, involves the diffusion coefficient D of the electroactive species in the presence of supporting electrolyte, and not at infinite dilution. Nevertheless an approximate value can be obtained for the diffusion current constant I_d by substituting the D_0-value calculated above into the Ilkovic equation. A value of 2.79 is obtained, which, in view of the uncertainties in the values of D and especially λ_0, is in fair agreement with the experimentally determined value of 3.04 (*vide* Table I).

Polarography of Selected Brønsted Acids.—Acids belonging to the following general types were studied: (a) Uncharged monobasic acids; in addition to perchloric acid, the following: hydrobromic hydrochloric, *p*-toluenesulfonic, fluorovaleric ($C_5F_{11}COOH$), benzoic and acetic acids (b) Uncharged polybasic acids: sulfuric, oxalic and phosphoric acids. (c) Cationic acids: 2,5-diethylanilinium perchlorate and 2,5-dichloroanilinium perchlorate. (d) Anionic acid: tetraethylammonium bioxalate.

Some of the results obtained are presented in Table II. In all instances decinormal tetraethylammonium perchlorate served as supporting electrolyte.

TABLE II

POLAROGRAPHY OF FRESHLY PREPARED SOLUTIONS OF BRØNSTED ACIDS IN ACETONITRILE

Acid	$-E_{1/2}$[e]	I_d
Perchloric	0.70	3.04
Hydrobromic[a]	0.90	[g]
2,5-Dichloroanilinium ion[b]	1.00	2.55
Hydrochloric[a]	1.06	[g]
p-Toluenesulfonic	1.20	2.47
Sulfuric	1.20	2.81
2,5-Diethylanilinium ion[c]	1.43	2.51
Fluorovaleric ($C_5F_{11}COOH$)	*ca.* 1.5[f]	*ca.* 2.7[f]
Oxalic	1.55	2.06
Phosphoric	1.75[f]	1.47
Benzoic	2.1	1.95
Acetic	2.3	
Bioxalate ion[d]	No wave	..

[a] Solution prepared from dry gas. [b] Using 2,5-dichloroanilinium perchlorate. [c] Using 2,5-diethylanilinium perchlorate. [d] Using tetraethylammonium bioxalate solution. [e] For 1 millimolar solutions. [f] Very irreversible wave, drawn out over 0.3–0.4 volt. [g] Acid volatilized in nitrogen current.

The polarographic waves of these acids are all incompletely reversible (typical slopes for 10^{-3} *M* solutions: 2,5-dichloroanilinium ion 0.078, *p*-toluenesulfonic acid 0.095, perchloric acid 0.135).

---

[13] V. A. Pleskov, *J. Phys. Chem.* (*U.S.S.R.*), **22**, 351 (1948); *C. A.*, **42**, 6249 (1948).

Consequently the "half-wave potentials" reported have no exact thermodynamic significance. Nevertheless the waves are generally well-defined (with the exceptions noted in Table II), and diffusion currents are proportional to concentration over a wide range (generally tested for 0.5 to 5.0 millimolar).

The "discharge potentials" of a number of acids also were determined, because these may be of more exact significance than the "half-wave potentials" of the incompletely reversible polarographic waves. These discharge potentials (D.P.) refer to the potentials of the D.M.E. at which the current has reached 0.1 microamp, and are listed in Table III.

TABLE III

DISCHARGE POTENTIALS OF FRESHLY PREPARED SOLUTIONS OF BRØNSTED ACIDS AT D.M.E. IN ACETONITRILE

Acid	Molarity	−D.P.
Perchloric	0.1	0.37
	.01	.44
	.001	.50
Sulfuric	.05	.60
	.005	.69
	.0005	.77
2,5-Diethylanilinium ion	.1	1.05
Acetic	.1	1.9

Controlled potential electrolysis of perchloric and acetic acids, as well as of 2,5-dichloroanilinium perchlorate, carried out on the macro scale at the mercury pool cathode, showed that electrolysis of these acids in acetonitrile as solvent actually results in hydrogen evolution.

Relative Strengths of Brønsted Acids in Acetonitrile as Solvent.—In the light of the foregoing discussion on the acid–base properties of acetonitrile, it is evident that for a given acid the equilibrium: $HA + mCH_3CN \rightleftarrows H^+$ (solvated) $+ A^-$ (solvated) will be far less to the right than the analogous equilibrium in aqueous solution: $HA + nH_2O \rightleftarrows H^+$ (solvated) $+ A^-$ (solvated). Consequently acetonitrile acts as a strongly differentiating solvent for many acids which appear to have the same strength in a leveling solvent such as water.

Of the acids listed in Table II only perchloric acid behaves as a typical strong electrolyte in acetonitrile as solvent. The conductivity of a fresh 10^{-2} M solution of sulfuric or p-toluenesulfonic acid in acetonitrile is less than one-thirtieth of that of a perchloric acid solution of equal molarity in the same solvent. Hydrogen chloride and even hydrogen bromide can be quantitatively volatilized from its solution in acetonitrile by passing a current of nitrogen.

There is an extremely wide spread in the "half-wave potentials" listed in Table II (and in the discharge potentials of Table III). Thus the half-wave potentials of perchloric and acetic acids differ by 1.6 volts in acetonitrile, whereas in water this difference is less than 0.2 volt. The wide spread in the half-wave potentials of acids in acetonitrile can be attributed in part to the strongly differentiating nature of acetonitrile with respect to the relative strengths of acids dissolved in it. A quantitative comparison of acid strengths in acetonitrile on the basis of relative half-wave potentials is, however, impossible, due to the incompletely reversible nature of the polarographic waves obtained. As a matter of fact, it is impossible to state whether the reduction currents refer to those of the solvated proton or to those of the proton combined with an uncharged base (cationic acids) or with an anion. Nevertheless it is interesting to note that the order of the "half-wave potentials" in Table II agrees well with the order of acid strengths which has been determined for some of these substances in other differentiating solvents, such as acetic acid.

Sulfuric, oxalic and phosphoric acids behave as monobasic acids at the D.M.E. in acetonitrile as solvent. The bioxalate ion does not give a reduction wave at all. This indicates that anionic acids, as compared to uncharged ones, are extremely weak in acetonitrile. This phenomenon may perhaps be related to the extreme reluctance of acetonitrile to solvate polyvalent anions; thus salts with polyvalent anions (*e.g.*, sulfate) are extremely insoluble in acetonitrile.[1]

Solvolysis of Salts of Weak Bases.—Table IV illustrates the effect of 2,5-dichloroaniline on the polarographic wave of 2 millimolar 2,5-dichloroanilinium perchlorate in decinormal tetraethylammonium perchlorate as supporting electrolyte.

TABLE IV

EFFECT OF 2,5-DICHLOROANILINE ON POLAROGRAPHY OF 2,5-DICHLOROANILINIUM ION

Molarity of base added	$-E_{1/2}$	i_d
0	1.01	10.2
8×10^{-3}	1.00	10.0
4×10^{-2}	1.01	10.1
2×10^{-1}	1.02	10.0

The presence of even a hundred-fold excess of free base has no significant effect on either the half-wave potential or the diffusion current. The concentration of the solvated protons is greatly decreased by the free base and the constancy of the half-wave potential tends to indicate that the reduction corresponds to the reaction: $BH^+ + e^- \rightleftarrows B + {}^1/_2H_2$.

II. Amperometric Titration of Amines with Perchloric Acid. Anodic Waves of Amines in Acetonitrile as Solvent.—Ammonia and some of its derivatives, such as n-butylamine and aniline, give well-defined anodic waves at the D.M.E. in acetonitrile as solvent. Tribenzylamine gives a less well-defined wave, although a diffusion region is still obtained, while 1,3-diphenylguanidine gives a drawn-out wave without reaching a diffusion region. After this paper was written Nyman and Johnson[14] reported that ammonia and ethylenediamine give anodic waves with well-defined diffusion currents under specified conditions in aqueous medium. The anodic waves produced in acetonitrile as solvent may perhaps be attributed to formation of compounds of the type $HgNH_2ClO_4$, which must be remarkably stable in acetonitrile. The anodic dissolution potentials of the D.M.E. in millimolar solutions of these depolarizers, with decinormal sodium perchlorate as supporting elec-

---

[14] C. J. Nyman and B. A. Johnson, *Anal. Chem.*, **29**, 483 (1957).

trolyte, are as follows: tribenzylamine −0.05, *n*-butylamine +0.05, ammonia + 0.10 and aniline + 0.45 volt. (In the absence of depolarizing substances, anodic dissolution of mercury commences at + 0.60 volt in acetonitrile as solvent.) For these four substances the diffusion current was found proportional to concentration over the range tested (0.4 to 5.0 millimolar).

Table V illustrates the effect of water on the anodic wave of 0.4 millimolar *n*-butylamine with 0.2 *M* sodium perchlorate as supporting electrolyte. In anhydrous acetonitrile the capillary had the following characteristics: m = 1.08 mg.; *sec* and t = 5.0 sec., while I_d for *n*-butylamine was 3.3. Addition of water had virtually no effect on the potential at which the wave starts, but the diffusion current became smaller with increasing water concentration (as expected), and the wave actually became steeper. When 40% (v./v.) of water was present, the diffusion plateau became ill-defined.

Table V

Effect of Water on Polarography of *n*-Butylamine

Water added, % (v./v.)	$E_{1/2}$	i_d
0	0.19	1.80
0.4	.19	1.74
2.0	.17	1.55
8.0	.14	1.40
40.0	.12	1.25

Amperometric Titration of Amines.—In acetonitrile as solvent the reaction between the solvated proton and even extremely weak bases, such as tribenzylamine and urea, is far more nearly complete than in water: $CH_3CNH^+ + B \rightleftarrows BH^+ + CH_3CN$.

The end-point of the reaction may be detected potentiometrically. Fritz[10] used the glass electrode for this purpose, with perchloric acid in dioxane as titrant. Streuli[5] used the same indicator electrode, but the titrant was coulometrically generated hydrogen ion, produced at a platinium electrode by anodic oxidation of water in a 0.3% solution of water in acetonitrile: $2H_2O - 4e^- \rightleftarrows O_2 + 4H^+$. Streuli obtained good results with amines such as pyridine and triethylamine, while Fritz performed differential titrations on mixtures such as butylamine and pyridine, aniline and *o*-chloroaniline.

The end-point may also be detected amperometrically by making use of the polarographic wave of the solvated proton; the reaction product, the species BH^+, is reduced at a much more negative potential than the solvated proton, even for an extremely weak base (*vide* Table II). Alternatively, if the base gives an anodic wave with a well-defined diffusion plateau, this anodic wave may serve for the amperometric detection of the end-point. Table VI illustrates the amperometric titration of 6.82×10^{-5} mole of tribenzylamine, dissolved in approximately 20 ml. of acetonitrile. Decinormal sodium perchlorate served as supporting electrolyte, and 0.113 *M* perchloric acid in anhydrous acetic acid as titrant. The end-point was detected by both methods, namely, by measuring the anodic diffusion current of the amine at +0.5 volt as well as the cathodic diffusion current of perchloric acid at −1.1 volts. All diffusion currents were corrected for residual current. By plotting diffusion current (corrected for volume change) as a function of the volume of titrant added, a straight line was obtained for both series of measurements. The end-point, obtained in the conventional manner by extrapolation to the volume-axis, was found at 0.580 ml. for the titration at +0.5 volt and at 0.589 ml. for that at −1.1 volts. The theoretical titration value was 0.604 ml.; hence the titration errors were −4.0 and −2.5%, respectively.

Table VI

Amperometric Titration of Tribenzylamine with Perchloric Acid

Vol. $HClO_4$ added, ml.	i_d at +0.5 v.	i_d at −1.1 v.
0	34	0
0.150	25	0
.260	19	0
.411	10	0
.545	1.4	0
.568	0.4	0.1
.610	0.2	0.3
.656	0.1	1.31
.718	0	2.30
.878	0	5.12

Urea does not give an anodic wave which can be used for the amperometric titration of this substance. However, in spite of the fact that urea is an extremely weak base in water (*pK ca.* 14), it can be titrated with fair accuracy in acetonitrile by making use of the polarographic wave of perchloric acid. A solution of 6.67×10^{-5} mole of urea in approximately 20 ml. of acetonitrile was titrated with 0.113 *M* perchloric acid in anhydrous acetic acid. Decinormal sodium perchlorate served as supporting electrolyte. The amperometric titration was carried out at a potential of −0.90 volt. In the titration of urea the reduction waves of the two species CH_3CNH^+ and BH^+ are not completely separated, and selection of the proper cathode potential for the amperometric titration is somewhat critical. Even then the current does not remain negligible before the end-point, but it increases slowly during the titration. However, beyond the end-point the current increases much more rapidly, so that the end-point, given by the intersection of the two straight lines obtained, can be located with fair accuracy (±2%). From the results presented in Table VII the end-point was found at 0.62 ml., while the theoretical titration value was 0.590 ml. Hence the titration error was +5%.

Table VII

Amperometric Titration of Urea with Perchloric Acid

Vol. $HClO_4$ added, ml.	i_d at −0.90 v.	Vol. $HClO_4$ added, ml.	i_d at −0.90 v.
0	0	0.700	2.10
0.200	0.20	.800	3.40
.300	.35	.900	4.60
.400	.50	1.000	6.0
.500	.65	1.200	9.0
.600	1.00	1.400	11.8

It also should be possible to titrate mixtures of amines differentially by making use of the reduction waves of the titration products, namely, the species BH^+ (*vide* Table II).

The reduction potential of perchloric acid in acetonitrile is extremely sensitive to the presence of water, as described before. It is not to be expected that the reduction potentials of the species BH^+ will be affected by water to the same extent. Consequently the amperometric titration of amines by making use of the reduction waves of either perchloric acid or the species BH^+ probably will not be successful if more than a very small concentration of water is present (see Fig. 1). However, the anodic waves given by some of these bases will probably be suitable for their amperometric titration, even in the presence of relatively large concentrations of water (see Table V). Further study of this subject seems advisable.

III. Oxygen.—In aqueous solution oxygen gives two waves at the D.M.E., the first corresponding to its reduction to hydrogen peroxide: $O_2 + 2H^+ + 2e^- \rightarrow H_2O_2$ (acid solution), or $O_2 + 2H_2O + 2e^- \rightarrow H_2O_2 + 2OH^-$ (neutral or basic solution); the second wave corresponds to reduction of hydrogen peroxide to hydroxyl ion: $H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$ (acid solution), or $H_2O_2 + 2e^- \rightarrow 2OH^-$ (basic solution). In acetonitrile as solvent and with sodium perchlorate or potassium thiocyanate as supporting electrolyte, oxygen also gives two reduction waves, both occurring at much more negative potentials than in water (-0.75 and -1.4 volts, as compared to -0.05 and *ca.* -0.9 volt in water). The relatively negative reduction potential of oxygen in acetonitrile can be attributed to the fact that the acidic properties of acetonitrile are extremely weak; consequently a reaction of the type $O_2 + 2SH + 2e^- \rightarrow H_2O_2 + 2S^-$ (*vide supra*) will occur with much less ease in acetonitrile than in water. The subsequent reaction: $H_2O_2 + 2e^- \rightarrow 2OH^-$[15] also will occur with less ease in acetonitrile than in water, because at the same concentrations the activity of the hydroxyl ion as referred to water is much higher in the former solvent than in the latter.[2] Addition of a substance which is a stronger acid than acetonitrile should shift both waves to less negative potentials. This is indeed the case when water or benzoic acid is added to the solution; thus in the presence of 0.2 *M* benzoic acid the two waves were shifted to -0.38 and *ca.* -1.2 volts, respectively.

It seemed desirable to determine whether the two oxygen waves involve two electrons each. For this purpose the concentration of oxygen in an air-saturated decinormal solution of sodium perchlorate in acetonitrile was determined by injecting 5 ml. of such a solution into 120 ml. of 2.5×10^{-4} *M* aqueous ferrous pyrophosphate solution contained in a 130-ml. bottle closed with an air-tight rubber gasket. The excess of ferrous iron was then back-titrated in 0.2 *M* sulfuric acid medium with ceric sulfate (nitrogen atmosphere). The concentration of oxygen found was 1.6 ± 0.1 millimolar at 25°.

Determination of oxygen in acetonitrile by the iodometric method of Winkler[16] is less satisfactory, since hydrated manganese dioxide apparently is reduced (though relatively slowly) by acetonitrile, even when the reaction medium contains only 4% (v./v.) of acetonitrile as in the above experiment. The Winkler method gave a value of 1.4 ± 0.2 millimolar.

Assuming that the solvation, if any, of the oxygen molecule should not be radically different in acetonitrile and in water, Walden's rule may be applied for the calculation of an approximate diffusion coefficient of oxygen in acetonitrile as solvent. At 25° the viscosity of water is 0.894 cp., while that of acetonitrile is 0.345 cp. The diffusion coefficient of oxygen in aqueous solution is *ca.* 2.6×10^{-5} cm.^{2} sec.$^{-1}$. Hence from Walden's rule the diffusion coefficient of oxygen in acetonitrile should be $(0.894/0.345) \times 2.6 \times 10^{-5} = 6.7 \times 10^{-5}$ cm.^{2} sec.$^{-1}$. Substituting into the Ilkovic equation: $i_d = 25$ microamp. (observed for the first wave), $C = 1.6$ mmillimoles per liter, $D = 6.7 \times 10^{-5}$ cm.^{2} sec.$^{-1}$, $m = 1.08$ mg./sec., and $t = 6.0$ sec., the value of n for the first oxygen wave is found to be 2.2.

Several peculiar phenomena were observed: (a) In sodium perchlorate or potassium thiocyanate as supporting electrolyte the height of the second oxygen wave was found to decrease with increasing concentration of electrolyte, while the height of the first wave was virtually unaffected. (b) In tetraethylammonium perchlorate or bromide as supporting electrolyte the second oxygen wave occurred at a much more negative potential (-2.2 volts) than in sodium perchlorate or potassium thiocyanate as supporting electrolyte (-1.4 volts). Moreover, the height of the second wave (corrected for drop time) was only about 60% of that of the first. The positions and heights of both waves were virtually unaffected by changing the concentration of electrolyte from 5×10^{-3} to 10^{-1} *M*. Addition of water shifted both waves to more positive potentials (as expected), but the height of the second wave increased until at a water concentration of 10% (v./v.) the two waves were of equal height.

The present paper deals with the polarography of oxygen in acetonitrile in an exploratory manner, and further study of the peculiar phenomena observed seems desirable.

Acknowledgment.—The authors wish to express their appreciation to the Research Corporation for a grant in support of this work, and to Dr. Stanley Bruckenstein, University of Minnesota, who prepared a number of the compounds used in this study.

MINNEAPOLIS, MINNESOTA

---

[15] In acetonitrile, as in water, hydrogen peroxide is reduced at the same potential as that at which the second oxygen wave occurs. However, hydrogen peroxide solutions in acetonitrile are relatively unstable, and their polarographic waves are not completely reproducible, while the diffusion regions are quite erratic.

[16] L. W. Winkler, *Ber.*, **21**, 2843 (1888).