$K_1 = 1.5$ at 18° and $\mu = 3.5$ obtained by Peschanski.[4]

The thermodynamic formation constant for the mononitratothallium(III) complex K was estimated using the extended form of the Debye–Hückel equation as an estimate of the activity coefficients.

$$F = \log K_1 - 0.505\left(\Delta\sum_i z_i^2\right)\frac{\sqrt{\mu}}{1 + A\sqrt{\mu}} = \log K + B\mu \tag{18}$$

where $\Delta\sum_i z_i^2 = (2)^2 - (3)^2 - (1)^2 = -6$.

Following the suggestion of Guggenheim and Schindler,[9] A was first assumed to be unity and the function, $F = \log K_1 + (3.03\sqrt{\mu})/(1 + \sqrt{\mu})$ was plotted *vs.* μ. This resulted in a straight horizontal line; *i.e.*, $B = 0$, and led to an estimate of 170 l./mole for K. Additional values of A up to 2 were assumed and F plotted as before. The results obtained from these plots are given in Table IV. The only plot resulting in a straight line was that for $A = 1$; all others were concave upwards. The value of K, 170 ± 4 (standard deviation) given for $A = 1$ is the average value for antilog $(F_{A = 1})$. All other values of K were obtained by extrapolating plots of equation 18 to $\mu = 0$. It seems reasonable to suspect that K lies between 100 and 200, and because of the good agreement for $A = 1$, 170 is probably a rather good estimate.

Since values had been obtained for $(1 + \kappa_1/H)$ at the various ionic strengths, estimates were made for κ_1 as a function of μ. These estimates are included in Table III. It should be pointed out that Biedermann's work, from which $(1 + \kappa_1/H)$ was estimated, was done at 25° whereas our study was at 22° and these estimates do not include any correction for this discrepancy.

Table V displays some of the measured values of the association constants of complexes of nitrate with various cations. This table is not intended to be an exhaustive survey or a critical evaluation of nitrate association constants but rather only to indicate certain complexes which have been investigated and how the stability of the thallium(III) complex compares with the others. An extensive discussion of Table V does not appear to be justified since the data are too incomplete and their reliability is too uncertain. It seems evident, however, that a number of nitrate complexes do exist although as a general rule their stability is not very great. It appears that the mononitratothallium(III) ion possesses rather unusual stability.

Acknowledgment.—We are indebted to the U. S. Atomic Energy Commission for their support of this work.

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

Polarography in Acetonitrile.[1] I. Metal Ions which Have Comparable Polarographic Properties in Acetonitrile and in Water

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

RECEIVED AUGUST 31, 1956

Acetonitrile is a much weaker base than water. Consequently inorganic cations generally have lower solvation energies in acetonitrile than in water, except in those cases where there is specific interaction between the cation and acetonitrile. The half-wave potentials of cations which are reversibly reduced should, therefore, be less negative in acetonitrile than in water, and this is indeed the case. The polarography of the alkali and alkaline earth metal ions and ammonium ion in anhydrous acetonitrile has been studied, and the following half-wave potentials (*vs.* S.C.E.) were determined: Li −1.95, Na −1.85, K −1.94, Rb −1.95, NH_4 −1.83, Ca −1.82, Sr −1.76 and Ba −1.63 v. The alkali metal ions are reversibly reduced, with the exception of lithium, which shows a slight deviation. The half-wave potentials of cadmium (as the perchlorate) and zinc (as the nitrate) are about 0.3 v. less negative in acetonitrile than in water, the reduction of zinc being reversible. Zinc forms very stable complexes with halide ions in acetonitrile.

Acetonitrile is an interesting solvent for polarographic studies. It is a weaker base[2-8] and a much weaker acid[9,10] than water. Quite generally, therefore, cations and especially anions have lower solvation energies in acetonitrile than in water, except in those cases where there is specific interaction with the solvent (as with silver and cuprous copper ions). Thus most cations are reduced at considerably more positive[11] potentials in acetonitrile than in water, and anions which depolarize the dropping mercury electrode anodically do so at more negative potentials in acetonitrile than in water. Moreover, in water as solvent the most negative potential which can be attained at the dropping mercury electrode is approximately −2.3 v. *vs.* the saturated calomel electrode, whereas in the less acidic solvent acetonitrile the useful potential range can be extended to −2.8 v. (ignoring

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(1) From the Ph.D. thesis of J. F. Coetzee, University of Minnesota, 1955.

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(3) A. W. Laubengayer and D. S. Sears, THIS JOURNAL, **67**, 164 (1945).

(4) A. Hantzsch, *Ber.*, **64B**, 667 (1931).

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

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

(11) The sign convention used is the same as that in Kolthoff and Lingane, "Polarography," Interscience Publishers, Inc., New York, N. Y., 1952.

liquid junction potentials). Thus calcium and magnesium give well-defined waves in acetonitrile, but not in water. Magnesium amalgam reacts rapidly with water, but not rapidly with acetonitrile.

The favorable properties of acetonitrile as a solvent for voltammetric measurements are especially pronounced with rotated noble metal electrodes. The resistance of acetonitrile to electrolytic oxidation and reduction is reflected in the fact that in this solvent, with sodium perchlorate as supporting electrolyte, the useful potential range of the rotated platinum microelectrode extends from +1.8 to −1.5 v. *vs.* the saturated calomel electrode, as compared to the much narrower range of +1.1 to −1.1 v. attainable in water.

The dielectric constant of acetonitrile (38 at 25°) is sufficiently high to allow strong electrolyte behavior of salts like silver picrate and perchlorate, potassium picrate and quaternary ammonium picrates, perchlorates, nitrates, iodides, bromides and chlorides.[12-16] Salts like cerous nitrate[14] and aluminum chloride[17] are typical weak electrolytes in acetonitrile as solvent.

Acetonitrile possesses a convenient liquid range (freezing point −42,° boiling point 81°) and an advantageously low viscosity (0.345 cp. at 25°), but its vapor pressure is quite high (73 mm. at 20°). Solubilities of inorganic salts and strong bases are generally much less favorable in acetonitrile than in water.[2,12,18-20] The more soluble salt types in acetonitrile are perchlorates, iodides and thiocyanates; most nitrates are less soluble, while sulfates are generally insoluble.

Wawzonek and Runner[21] studied the polarography of a number of metal chlorides, iodides and perchlorates in acetonitrile as solvent, with decinormal solutions of tetrabutylammonium iodide and perchlorate as supporting electrolyte and the internal mercury pool as reference electrode. Wawzonek, *et al.*,[22] also studied the polarography of various aromatic hydrocarbons in acetonitrile as solvent. Their results will be discussed in conjunction with those of the present authors.

This paper deals with the polarography of the alkali and alkaline earth metal ions, as well as of cadmium and zinc ions. There is much similarity in the polarographic characteristics of these ions in acetonitrile and in water; however, cadmium and zinc form extremely stable halide complexes in acetonitrile.

Experimental

Purification and Storage of Solvent.—Matheson Coleman and Co. technical grade acetonitrile was purified by a method similar to that used by Wawzonek and Runner,[21] *viz.*, by shaking with a cold saturated aqueous solution of potassium hydroxide, followed by preliminary drying over anhydrous sodium carbonate and finally two or three distillations at 81.0 ± 0.5° from phosphorus pentoxide in an all-glass still. The distillate was stored in amber-colored bottles under an atmosphere of nitrogen, and was withdrawn as required by means of an all-glass siphon. The water content of the solvent, as determined by Karl Fischer titration,[23] was always less than 2 millimolar.

Supporting Electrolytes.—The majority of salts which are used as supporting electrolytes in aqueous solution are only very sparingly soluble in acetonitrile. Thus the chlorides and nitrates of sodium, potassium and ammonium are virtually insoluble in acetonitrile. The most useful supporting electrolytes in acetonitrile are sodium perchlorate, tetraethylammonium perchlorate and bromide and tetrabutylammonium iodide. G. F. Smith Company sodium perchlorate generally could be used without further purification; it was dried in a vacuum oven at 100°. Eastman Kodak Company tetraethylammonium bromide and tetrabutylammonium iodide were recrystallized from ethyl acetate and dried at 60° in a vacuum oven. Tetraethylammonium perchlorate is an extremely satisfactory supporting electrolyte in acetonitrile. It is not commercially available, but it is easily prepared and recrystallized; it shows no sign of decomposition when it is heated at 110°, and it is stable to moderate percussion; it is very soluble in acetonitrile (more than 1 *M* at 25°); it is only slightly hygroscopic; and it combines the advantages inherent in the use of a supporting electrolyte with tetraalkylammonium as the cation and perchlorate as the anion. It may be prepared by taking advantage of the fact that its solubility in water is considerably less than those of tetraethylammonium bromide and sodium (or hydrogen) perchlorate. A hot 1 *M* aqueous solution of tetraethylammonium bromide is added slowly and with stirring to an equivalent amount of a hot 0.1 *M* aqueous solution of sodium (or hydrogen) perchlorate. After cooling in ice-water the precipitate is filtered off on a buchner funnel and washed with ice-cold water until the wash-liquid is free from bromide. The salt is recrystallized from water and dried in a vacuum oven at 60°. The polarographic limits of decinormal solutions of a number of supporting electrolytes in acetonitrile as solvent are the following: sodium perchlorate +0.6 to −1.7, tetraethylammonium perchlorate +0.6 to −2.8, tetraethylammonium bromide −0.5 to −2.8, and tetrabutylammonium iodide −0.6 to −2.8 v. *vs.* the aqueous saturated calomel electrode.

Salts Used for Polarographic Analysis.—All metal perchlorates referred to in this paper were obtained from G. F. Smith Company. The perchlorates of lithium, ammonium, strontium and barium were dried at 60° in a vacuum oven at a few tenths of a millimeter of mercury pressure. Sodium perchlorate was dried *in vacuo* at 100°. Calcium and cadmium perchlorates and zinc nitrate were dried in a current of dry air and were dissolved as the hydrates. Consequently a certain amount of water was introduced into the electrolysis solution, apart from the 1-2 millimolar water already present in the solvent. However, deliberate addition of increasing amounts of water to acetonitrile solutions of a large number of metal salts had little effect on the half-wave potential or the diffusion current for water concentrations of less than about 0.1 *M*. Nevertheless, it is not unambiguously certain how removal of the last trace of water might affect the polarographic behavior of some of these ions.[24] Sodium, potassium and rubidium iodides and zinc chloride (anhydrous) were of ordinary reagent quality, and were dried *in vacuo* at 60°.

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[23] See *e.g.*, J. Mitchell and D. M. Smith, "Aquametry," Interscience Publishers, Inc., New York, N. Y., 1948, p. 127.

[24] Recrystallization of salts of these metals from those organic liquids in which they are soluble generally yields solvates of unknown composition. Direct solution of the metal oxide or carbonate in an acetonitrile solution of perchloric acid is impractical, because solutions of perchloric acid in acetonitrile are unstable, especially at higher temperatures; one of the reactions taking place is hydrolysis of acetonitrile to acetic acid and ammonium perchlorate.

The Polarographic Cell.—The dropping mercury electrode (hereafter designated by "D.M.E.") had the following characteristics in a 0.1 M solution of tetraethylammonium perchlorate in acetonitrile (open circuit): $m = 1.08$ mg./sec. and $t = 6.1$ sec. for $h = 50$ cm. The aqueous saturated calomel electrode ("S.C.E.") was used throughout as the reference electrode because all common reference electrodes with acetonitrile as solvent are unsuitable (*vide infra*); all potentials refer to the S.C.E. Accidental introduction of water from the S.C.E. into the electrolysis solution could be prevented completely (as shown by subsequent Karl Fischer titration) by using the following assembly: a conventional agar–potassium chloride salt bridge "A" dipped into a slightly wider glass tube "B" fitted with a sintered glass disk of fine porosity. Tube B contained just sufficient of an acetonitrile solution of the supporting electrolyte to make electrolytic contact with the gel in A. Tube B was dipped into the electrolysis solution, and the level of the acetonitrile solution was kept lower on the inside of B than on its outside, so that the pressure set up would counteract whatever undesirable transfer of water or potassium chloride could take place through the disk. With this assembly no detectable amount of water or potassium chloride passed into the electrolysis solution during the time required to complete a polarogram. Transfer of significant amounts of potassium chloride is in any event impossible, owing to the negligible solubility of this salt in acetonitrile. On prolonged immersion of the agar bridge in acetonitrile, a plug of solid potassium chloride forms at the end of the bridge, causing a significant increase in the resistance of the cell.

Reference Electrodes with Acetonitrile as Solvent.—Quite apart from the fact that the use of any internal reference electrode in any solvent suffers from certain intrinsic disadvantages,[25] mercury or silver reference electrodes are unsatisfactory in acetonitrile as solvent, because their potentials drift with time. A similar observation has been made with mercury–mercurous halide electrodes by Cruse, Goertz and Petermöller,[26] who were able to correlate this drift in potential with the formation of complexes of the type HgX_3M, accompanied by a shift in the disproportionation equilibrium of mercurous halides: $Hg_2X_2 \rightleftarrows Hg + HgX_2$ and $HgX_2 + MX \rightleftarrows [HgX_3]M$. A solid compound $HgBr_2{\cdot}(C_2H_5)_4NBr$ could actually be isolated. Silver halides are readily solubilized in acetonitrile solutions containing the corresponding halide ions.[27] Ulich and Spiegel[28] found that silver, thallium(I), mercury(I) and lead(II) halides, as well as silver and lead(II) thiocyanates, are all solubilized in acetonitrile solutions containing the corresponding anions.

The silver–silver ion electrode has a well-defined and constant potential in acetonitrile, and should be a useful reference electrode in this solvent; it has in fact been used as such by Pleskov.[18] However, the experimental difficulties in working with a liquid salt bridge are considerable.

Recording of Current-Voltage Curves.—Polarograms were obtained with a Leeds and Northrup recording "Electro-Chemograph," Type E. The electromotive force recorded by the instrument was checked with a Leeds and Northrup student type potentiometer. Currents recorded by the instrument were checked by measuring the potential drop across a precision resistor. All diffusion currents were corrected for residual current, which never exceeded 1.5 μamp. at any potential at which diffusion current was measured. All potentials were corrected for the "*IR*-drop" across the electrolysis cell. The resistance of the cell used, as measured with an "Industrial Instruments Inc." No. RC-1B conductance bridge, was 1170 ± 50 ohms with 0.1 M tetraethylammonium perchlorate or bromide as supporting electrolyte. For purposes of analysis of polarograms, the rising parts of waves were obtained by manual measurement. Maxima were occasionally observed, especially at higher concentrations of the electroactive species. They could not be suppressed with any of the substances used for this purpose in aqueous solution. The electrolysis solution could be deaerated completely within two or three minutes by passing Linde nitrogen through it by means of a sintered glass cylinder. Due to the high vapor pressure of acetonitrile (*ca.* 80 mm. at 25°), it is necessary to presaturate the nitrogen current with acetonitrile vapor; this was done by passing the nitrogen through a train of wash bottles fitted with sintered glass cylinders dipping into acetonitrile at 25 ± 2°. Polarograms were recorded at 25.0 ± 0.5°.

Results and Discussion

Polarography of the Alkali Metal Ions and Ammonium Ion.—For reasons given in the introductory section acetonitrile is well suited for polarographic studies of the more electronegative ions in particular. Well-defined waves were obtained for the reduction of lithium, sodium and ammonium ions in tetraethylammonium perchlorate as supporting electrolyte, and for the reduction of sodium, potassium and rubidium ions in tetrabutylammonium iodide as supporting electrolyte. The concentrations of these ions were varied from 0.2 to 2.0 millimolar, with a supporting electrolyte concentration of decinormal. In all instances, except that of ammonium ion[29] diffusion currents were proportional to concentration. The half-wave potentials of sodium, potassium and rubidium ions remained constant over the range tested. The half-wave potential of the sodium ion is the same in tetraethylammonium perchlorate as in tetrabutylammonium iodide as supporting electrolyte. Sodium, potassium and rubidium ions are reversibly reduced in the supporting electrolytes used. The reduction of lithium ion proceeds with incomplete reversibility in acetonitrile, as it does in water; nevertheless a well-defined diffusion plateau is obtained in acetonitrile, whereas in water the limiting current is erratic.[30]

Comparison of Observed Half-wave Potentials with those Calculated from Potentiometric Data.—For those metals which dissolve in mercury (*e.g.*, the alkali and alkaline earth metals), the polarographic half-wave potential is a function of the standard potential of the metal–metal ion couple, the solubility of the metal in mercury, and its free energy of amalgamation. Consequently the half-wave potentials of mercury-soluble metals can be calculated from their thermodynamic standard potentials, their solubilities in mercury, and their free energies of amalgamation,[31] or, more directly, from the standard potentials of the metla amalgams.[32]

The relation between the potential E_a of a metal amalgam electrode in a solution containing the corresponding metal ions, and the polarographic half-wave potential $E_{1/2}$, is given by the approximate[33] relation: $E_a = E_{1/2} + (RT/nF) \ln (C_{M}{}^{n+}/$

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(25) See *e.g.*, I. M. Kolthoff and J. J. Lingane, "Polarography," 2nd ed., Interscience Publishers, Inc., New York, N. Y., 1952, pp. 357–360.

(26) K. Cruse, E. P. Goertz and H. Petermöller, *Z. Elektrochem.*, **55**, 405 (1951).

(27) Cruse, *et al.*, did not observe any such solubilization of silver chloride in acetonitrile solutions of diethylammonium chloride; this may be attributed to the fact that diethylammonium chloride is quite a weak electrolyte in acetonitrile (see, *e.g.*, Walden and Birr, ref. 14). The authors found that silver chloride is readily soluble in an acetonitrile solution of tetraethylammonium chloride.

(28) H. Ulich and G. Spiegel, *Z. physik. Chem.*, **A177**, 103 (1936).

(29) The diffusion current of ammonium ion becomes erratic at concentrations above *ca.* 0.5 millimolar; it is possible that hydrogen evolution interferes here, as with certain cationic acids discussed in Part II of this series.

(30) E. S. Peracchio and V. W. Meloche, THIS JOURNAL, **60**, 1770 (1938).

(31) J. J. Lingane, *ibid.*, **61**, 2099 (1939).

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(33) Ignoring activity coefficients and the difference between the diffusion coefficients of the metal ions in solution and the metal in the mercury.

TABLE I

METAL IONS WHICH HAVE COMPARABLE POLAROGRAPHIC PROPERTIES IN ACETONITRILE AND IN WATER

Salt	Sup. el.	I_d[a]	Slope[b]	$(-E^{1}/_{2})_{\text{obsd.}}$	$(-E^{1}/_{2})_{\text{calcd.}}$	$(-E^{1}/_{2})_{\text{w.}}$	Δ[c]
$LiClO_4$	Et_4NClO_4	2.56	0.068	1.95	2.08	2.27	0.32
$NaClO_4$		3.22	.059	1.85	1.85	2.11	.26
NaI	Bu_4NI	3.16	.060	1.85	1.85	2.11	.26
KI		3.38	.059	1.94	1.94	2.13	.19
RbI		3.25	.061	1.95	1.95	2.03	.08
NH_4ClO_4	Et_4NClO_4	3.05	.068	1.83	..	2.05	.22
$Ca(ClO_4)_2 \cdot 6aq.$		4.61	.045	1.82	1.82	*ca.* 2.2	*ca.* 0.4
$Sr(ClO_4)_2$		5.43	.072	1.76	..	2.10	0.34
$Ba(ClO_4)_2$		5.37	.044	1.63	..	1.90	.27
$Cd(ClO_4)_2 \cdot 6aq.$	$NaClO_4$	4.30	.053	0.27	..	0.59	.32
$Zn(NO_3)_2 \cdot 6aq.$		4.18	.035	0.70	..	1.00	.30

[a] $I_d = i_d/Cm^{2/3}t^{1/6}$, where i_d is expressed in microamp., C in millimoles per liter, m in milligrams per second, t in seconds. [b] From analysis of waves obtained with 1 millimolar solutions. [c] Δ = (half-wave potential in acetonitrile) − (half-wave potential in water).

$C_{M(Hg)}$)), where $C_{M^{n+}}$ denotes the concentration of metal ions in the solution and $C_{M(Hg)}$ that of metal in the amalgam.

Pleskov[18] measured the potentials of several metal amalgams in 0.01 N solutions of the corresponding metal salts in acetonitrile as solvent, using as reference electrode the half-cell: Ag/0.01 normal $AgNO_3$ in acetonitrile. Pleskov concluded that the $Ca-Ca^{++}$, $Zn-Zn^{++}$ and $Cd-Cd^{++}$ couples are more noble in acetonitrile than in water (using as a basis of comparison the potential of the $Rb-Rb^{+}$ couple.)[34] Our polarographic results support this conclusion. The potential of Pleskov's Ag/Ag^{+} reference electrode is +0.29 v. *vs.* S.C.E. (This value naturally includes a liquid junction potential.)

In Table I observed half-wave potentials are compared to those calculated from Pleskov's potentiometric data by means of the above equation. The agreement between observed and calculated values is excellent for sodium, potassium and rubidium (as it is for calcium), but it is less satisfactory for lithium.

The relative values of the observed half-wave potentials listed in Table I are in satisfactory agreement with those obtained by Wawzonek and Runner,[21] who report the following half-wave potentials, all referred to the internal mercury pool in decinormal tetrabutylammonium iodide with acetonitrile as solvent: (a) with 0.1 M tetrabutylammonium perchlorate as supporting electrolyte: $LiClO_4$ −1.38, $KClO_4$ −1.34, $Zn(ClO_4)_2 \cdot 4aq$·−0.12, $Cd(ClO_4)_2 \cdot 4aq.$ +0.34; (b) with 0.1 M tetrabutylammonium iodide as supporting electrolyte: LiCl −1.42, RbCl −1.36, KI −1.34, NaI −1.25, CaI_2 −1.24 v.

Polarography of the Alkaline Earth Metal Ions.—In aqueous solution calcium gives a wave at very negative potentials (*ca.* −2.2 v.). This wave displays a pronounced maximum which is not easily suppressed, and it is unsuitable for analytical purposes. In acetonitrile as solvent the calcium wave is well-defined, although it is not completely reversible (Table I). On gradual addition of water to the electrolysis solution the "half-wave potential" is shifted to more and more negative values, until when 20% by volume of water has been added it reaches −2.1 v. With 20% of water the supporting electrolyte "discharges" at *ca.* −2.5 v., as compared to −2.8 v. with the anhydrous solvent. From the analytical point of view it is of interest to note that a well-defined diffusion current is obtained even in the presence of 20% by volume of water. The diffusion current is virtually unaffected by the addition of up to 5 or 6% of water, after which it slowly decreases, undoubtedly as a result of the increasing viscosity of the solution.

The observed "half-wave potential" of calcium agrees remarkably well (considering that the calcium wave is not completely reversible) with the value calculated from Pleskov's potentiometric data.

The strontium and barium waves are likewise well-defined in acetonitrile, though neither is completely reversible.

Polarography of Zinc and Cadium Ions.—With sodium or tetraethylammonium perchlorate as supporting electrolyte, zinc nitrate gives an almost reversible wave at −0.70 v., while zinc chloride gives a highly irreversible wave starting at approximately −1.2 v. In tetraethylammonium bromide as supporting electrolyte, zinc chloride gives an incompletely developed wave starting at an even more negative potential, and in agreement with Wawzonek and Runner[21] we find that with tetrabutylammonium iodide as supporting electrolyte no diffusion plateau is obtained before cathodic discharge of the supporting electrolyte sets in. Typical polarograms are given in Fig. 1.

Apparently zinc chloride is a very weak electrolyte in acetonitrile. Furthermore, in the presence of bromide and especially iodide ions zinc must form extremely stable complexes in acetonitrile. The relation between the equilibria of the two reactions

$$ZnCl_2 + aH_2O \rightleftarrows Zn(H_2O)_b^{++} + 2Cl(H_2O)_c^{-}$$

$$ZnCl_2 + dCH_3CN \rightleftarrows Zn(CH_3CN)_e^{++} + 2Cl(CH_3CN)_f^{-}$$

will depend on three factors: (a) the relative abilities of the two solvents to coördinate with the zinc ion, *i.e.*, the relative basic strengths of the two

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(34) This comparison depends upon the validity of the assumption that the $Rb-Rb^{+}$ couple will have approximately the same standard potential in acetonitrile and in water. Pleskov does not discuss his reasons for choosing this particular couple as a basis for comparison of electrode potentials in acetonitrile and in water; nevertheless, it is probably a fairly satisfactory choice, because, ignoring liquid junction potentials, the polarographic half-wave potentials of the rubidium ion in acetonitrile and in water differ by less than 0.1 v. (see Table I).

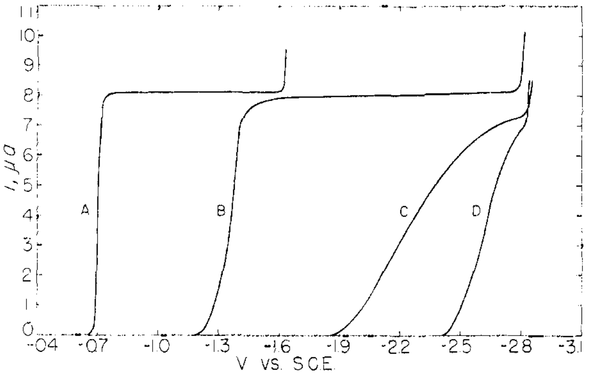

Fig. 1.—Polarography of zinc in acetonitrile: A, 10^{-3} *M* $Zn(NO_3)_2$ in 0.1 *M* $NaClO_4$; B, 10^{-3} *M* $ZnCl_2$ in 0.1 *M* Et_4NClO_4; C, 10^{-3} *M* $ZnCl_2$ in 0.1 *M* Et_4NBr; D, 10^{-3} *M* $ZnCl_2$ in 0.1 *M* Bu_4NI.

solvents; (b) the relative abilities of the two solvents to solvate the chloride ion, *i.e.*, the relative acidic strengths of the two solvents; (c) the relative abilities of the two solvents to support ionization, *i.e.*, the relative values of their dielectric constants. The dielectric constant of acetonitrile is considerably smaller than that of water, while its basic and especially its acidic properties are considerably weaker than those of water. Consequently the position of the second equilibrium should be much less to the right than that of the first. Unless there is specific interaction between the solvent and the cation (as with silver and cuprous copper ions) it is to be expected that quite generally metal complexes with anions (halides, thiocyanates, etc.) will be much more stable in acetonitrile than in water. In a subsequent paper several examples will be found which substantiate this conclusion.

Effect of the Size of Ions on the Relative Values of Their Half-wave Potentials in Acetonitrile and in Water.—On the basis of the foregoing it is also to be expected that the effect of the size of an ion on its solvation energy (and consequently on its absolute activity in the solvent) will be much greater in acetonitrile than in water. That this is indeed the case is evident from Table I. For example, the half-wave potential of the lithium ion is 0.32 v. more positive in acetonitrile than in water, while the difference for the larger rubidium ion is only 0.08 v. The same effect is found in the series calcium–strontium–barium.

Acknowledgment.—We wish to express our appreciation to the Research Corporation for a grant in support of this work.

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