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Polarography in Acetonitrile. II. Metal Ions Which Have Significantly Different Polarographic Properties in Acetonitrile and in Water. Anodic Waves. Voltammetry at Rotated Platinum Electrode

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Most metal ions have lower solvation energies in the relatively weak base acetonitrile than in the much stronger base water, and they are therefore reduced at more positive potentials in acetonitrile than in water. The difference between the half-wave potentials of a given cation in these two solvents is largest for those cations which are particularly strongly hydrated in aqueous solution. The reduction of certain cations (notably those of Co(II) and Ni(II)) at the dropping mercury electrode involves much smaller overvoltages in acetonitrile than in water. Silver and cuprous ions are exceptional in that they coördinate strongly with acetonitrile. Cupric copper is a comparatively powerful oxidizing agent in acetonitrile. The following cations are reversibly reduced at the dropping mercury electrode at the half-wave potentials (*vs.* aqueous S.C.E.) given: Ag +0.32, Cu(I) −0.36, Mn(II) −1.12, Ni(II) −0.33, Eu(III) → Eu(II) +0.15, Yb(III) → Yb(II) −0.57 and Sm(III) → Sm(II) −1.62. The reduction of Co(II) (−0.65) deviates slightly from reversibility. The following cations give well-defined but incompletely reversible waves: Fe(II) −1.0, Cr(II) −1.1, Be −1.6, Mg −1.8, Al −1.4, Y, La, Pr, Nd and Gd *ca.* −1.5, Eu(II) → Eu^0 and Yb(II) → Yb^0 −1.7. Under certain conditions the polarograms of "acidic" cations (*e.g.*, Be, Mg and the trivalent rare earth ions) show interfering solvolytic effects, which can be eliminated by adding a little water or acetic acid. Be, Mg and La can be electrodeposited as the amalgams by controlled potential electrolysis at the mercury pool cathode. Anodic depolarization of the dropping mercury electrode by thiocyanate and halide ions, and especially by hydroxyl ion, occurs at much more negative potentials in acetonitrile than in water. Rotated noble metal micro electrodes are particularly useful in acetonitrile as solvent in which their range of applicability extends both to more negative and positive potentials than in water. The following "half-wave potentials" were measured at the rotated platinum electrode: Ag +0.1, Cd −0.5, Zn −0.9, Cu(II) → Cu(I) +1.0, Cu(I) → Cu^0 −0.5, Cu(I) → Cu(II) +1.0, Fe(III) → Fe(II) +1.1, Fe(II) → Fe(III) +1.6, Hg(II) → Hg(I) +0.7 and Hg(I) → Hg^0 +0.5. Chloride, bromide and iodide ion each give two anodic waves at the rotated platinum electrode, attributed to successive formation of the trihalide ion and the free halogen.

The previous paper[1] dealt with those metal ions which have similar polarographic properties in acetonitrile and in water. Examples of such ions are those of the alkali and alkaline earth metals, and also of zinc and cadmium, provided no complexing anions are present. The latter two metals form very stable halide complexes in acetonitrile; this was related to the fact that acetonitrile is a weaker base and a much weaker acid than water.

The present paper deals mainly with those metal ions which have appreciably different polarographic properties in acetonitrile and in water. Anodic waves of halide and of hydroxyl ions at the DME are briefly discussed. Finally, several examples are given which illustrate the particularly favorable properties of acetonitrile for voltammetry with the rotated platinum micro-electrode.

Experimental

The solvent and supporting electrolytes were purified as described previously.[1] The polarographic cell was the same as that used before, 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. The temperature was 25°.

Salts Used for Polarographic Analysis.—Samples of yttrium, lanthanum, praseodymium, neodymium, samarium and gadolinium oxides were obtained from Dr. F. Spedding, Ames, Iowa. Europium and ytterbium oxides were obtained from Research Chemicals Inc., Burbank, Calif. The purity values of these samples were reported to be: Y_2O_3, La_2O_3 and Nd_2O_3 99.9%, Eu_2O_3 and Yb_2O_3 99.8%, Pr_6O_{11} and Sm_2O_3 "pure"; purity of Gd_2O_3 not stated. All samples were protected against atmospheric moisture and carbon dioxide. The perchlorates of these metals were prepared by dissolving a known weight of the oxide in the equivalent amount of standardized decinormal aqueous perchloric acid, followed by careful evaporation to near dryness on a hot plate and then drying overnight in a hot-air oven at 120°. From the weights of oxide dissolved and of product obtained, the water content of the product $M(ClO_4)_3 \cdot nH_2O$ could be calculated, and these values were obtained for *n:* Y 3.7, La 1.1, Pr 1.0, Nd 3.0, Sm 2.2, Eu 3.5, Yb 6.0, Gd *ca.* 1. The rare earth perchlorates dissolve very readily in acetonitrile. The remaining metal perchlorates referred to in this paper were obtained from G. F. Smith Co.[2] All other salts and the organic compounds used were of ordinary reagent quality. Silver and magnesium perchlorate, lithium chloride and sodium iodide were dried in a vacuum oven at 60° and then dissolved as the anhydrous salts. The hydrated perchlorates of copper(II), manganese(II), cobalt(II), nickel(II), mercury(II), iron(II), iron(III), chromium(III) and aluminum were dried in a current of dry air and then dissolved as the hydrates, as described previously[1] for calcium and cadmium perchlorates.

Cell for Controlled Potential Electrolysis at the Mercury Pool Cathode.—The anode and cathode compartments of the cell were separated by means of two fritted glass discs of medium porosity. The space between the discs was filled with a solution of the supporting electrolyte in acetonitrile, which could be renewed at intervals during the electrolysis in order to prevent migration of undesirable ions from the anode to the cathode compartments. The anode and the cathode both consisted of mercury pools. The catholyte generally consisted of approximately 5 millimolar metal perchlorate in 0.25 molar indifferent electrolyte (tetraethylammonium perchlorate or bromide or tetrabutylammonium iodide) in acetonitrile. The anolyte and the "bridge" solution between the discs consisted of 0.25 molar indifferent electrolyte in acetonitrile. The catholyte was deaerated with Linde nitrogen, and a vigorous current of nitrogen was maintained through the solution during the electrolysis. In both the anode and the cathode compartments the mercury–solution interface was stirred during the electrolysis.

The cathode potential was controlled throughout the electrolysis to within a few millivolts by using a Fisher Controlled Potential Electro-Analyzer. The control circuit contained an aqueous saturated calomel electrode, which made electrolytic contact with the catholyte *via* an agar plug and a fritted glass disc; accidental introduction of water from the calomel electrode into the catholyte was prevented in the manner described previously.[1]

The rotated platinum micro electrode (hereafter referred to as "R.P.E.").—Platinum micro electrodes were constructed in the conventional manner by sealing a 2–3 cm. length of number 20 platinum wire into 6 mm. soft glass

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

[2] With the exception of beryllium perchlorate, which was prepared from beryllium carbonate and perchloric acid as described for the rare earth perchlorates above.

TABLE I

METAL IONS WHICH HAVE SIGNIFICANTLY DIFFERENT POLAROGRAPHIC PROPERTIES IN ACETONITRILE AND IN WATER

Decinormal sodium perchlorate as supporting electrolyte; all potentials refer to S.C.E.

Salt	Electrode reaction	Id	Slope[a]	$(E_{1/2})$AN	$(E_{1/2})$W	(E_0)W
$AgClO_4$	$Ag^+ \rightarrow Ag^0$	2.87	0.058	+0.32	*b*	+0.57
$Cu(ClO_4)_2 \cdot 6aq$	$Cu^{++} \rightarrow Cu^+$	2.37	*b*	*b*	*c*	−0.07
	$Cu^+ \rightarrow Cu^0$	2.37	.060	−0.36	*c*	+0.28
$Mn(ClO_4)_2 \cdot 6aq.$	$Mn^{++} \rightarrow Mn^0$	4.66	.028	−1.12	*ca.* −1.5	−1.29
$Co(ClO_4)_2 \cdot 6aq.$	$Co^{++} \rightarrow Co^0$	4.26	.037	−0.65	−1.20	−0.52
$Ni(ClO_4)_2 \cdot 6aq.$	$Ni^{++} \rightarrow Ni^0$	4.04	.031	−0.33	*ca.* −1.1	−0.49
$Fe(ClO_4)_3 \cdot 6aq.$	$Fe^{+++} \rightarrow Fe^{++}$	1.95	*b*	*b*	*b*	+0.53
	$Fe^{++} \rightarrow Fe^0$	3.99	.055	−1.00	−1.5	−0.68
$Cr(ClO_4)_3 \cdot 6aq.$	$Cr^{+++} \rightarrow Cr^{++}$	1.70	.100	0.00	−0.91	−0.65
	$Cr^{++} \rightarrow Cr^0$	3.48	.052	−1.12	−1.47	−0.80

[a] From analysis of waves obtained with 1 millimolar solutions. [b] Not a true wave. [c] No wave in non-complexing aqueous solutions.

tubing, leaving about 1 cm. length of the wire exposed to serve as the electrode. These electrodes were cleaned by immersion in hot concentrated nitric acid, followed by repeated rinsing with water. The oxide coat on the electrode was then removed by immersing the electrode for a few minutes in *ca.* 10^{-2} M ferrous sulfate solution containing a little sulfuric acid. The electrode was then washed repeatedly with distilled water and finally with acetonitrile. When not in use, all electrodes were kept immersed in acetonitrile.

Platinum micro electrodes were rotated at 600 r.p.m. with a synchronous motor. Current-voltage curves were obtained by manual measurement. The electrodes came to equilibrium very rapidly.

Results and Discussion

I. Metal Ions Which Have Significantly Different Polarographic Properties in Acetonitrile and in Water.—Many metal ions have appreciably different polarographic properties in acetonitrile and in water. These differences can in most cases be related to the fact that acetonitrile is a much weaker base than water; however, with silver and cuprous copper specific interaction occurs between the metal ion and acetonitrile. The metal ions discussed in this section may be divided into three groups: (a) those ions which react with acetonitrile in a more or less specific manner. Silver and cuprous ions have a general tendency to coordinate with compounds containing electron-donor nitrogen atoms, such as ammonia, amines and nitriles. The high solvation energies of silver and cuprous ions in acetonitrile are reflected, *inter alia*, in their relatively negative reduction potentials in this solvent; (b) those ions which are particularly strongly hydrated in aqueous solution, and which can be reduced at more positive potentials than the hydronium ion in water as solvent. Examples of such ions are manganese(II), cobalt(II) and nickel(II). These ions are reduced at more positive potentials in the relatively weak base acetonitrile, in which their solvation energies are comparatively low, than in the much stronger base water; (c) those ions which are particularly strongly hydrolyzed in aqueous solution, and whose reduction waves are often interfered with by hydrogen evolution. Examples of such ions are those of beryllium, aluminum and most of the rare earth metals. Magnesium is also included in this group, because in aqueous solution hydrogen evolution (from reduction of water by magnesium amalgam) interferes with the polarographic determination of this metal. These "acidic" cations are less solvolyzed in the relatively weak base acetonitrile than in water. Furthermore, as shown in a subsequent paper, the solvated proton is reduced at a much more positive potential in acetonitrile than in water.

Metal Ions Which Have Higher Solvation Energies in Acetonitrile than in Water. Silver.—In non-complexing aqueous solutions reduction of the silver ion at the D.M.E. sets in at potentials which are somewhat more positive than that at which anodic dissolution of mercury commences, with the result that the potentials on the wave are not related to the silver ion activity in the solution. In acetonitrile as solvent the silver ion is reduced at more negative potentials than corresponds to the anodic dissolution wave of mercury, the half-wave potential being about 0.3 volt more negative than the anodic dissolution potential of mercury[3] (see Table I). The fact that this wave is completely reversible is in harmony with the potentiometric data of Kahlenberg[4] and Koch,[5] who showed that in acetonitrile as solvent the Ag–Ag^+ couple obeys the Nernst equation.

Cuprous Copper.—In aqueous solution the uncomplexed cuprous ion is unstable and it disproportionates into cupric copper and copper metal. In acetonitrile as solvent, however, cuprous copper is stabilized: (a) Morgan[6] prepared a relatively stable solvate $CuNO_3 \cdot 4CH_3CN$ by adding metallic copper to a solution of silver nitrate in acetonitrile: $Ag^+ + Cu^0 \rightarrow Ag^0 + Cu^+$; (b) the cuprous halides have relatively high solubilities in acetonitrile; thus the solubility of cuprous iodide is *ca.* 35 g. per kilogram of acetonitrile at 18°,[7] as compared to its negligible solubility in water; (c) the authors found that solutions of cuprous perchlorate in acetonitrile are not appreciably attacked by atmospheric oxygen. In harmony with these facts reduction of the cuprous ion at the D.M.E. occurs at a relatively negative potential in ace-

(3) The relatively high solubility of silver iodide in acetonitrile (*ca.* 0.02 *M*; see K. Cruse and R. Huber, *Angew. Chem.*, **66**, 632 (1954)) is also indicative of strong coördination between acetonitrile and the silver ion, especially since the iodide ion is only very weakly solvated by acetonitrile (see P. Walden and E. J. Birr, *Z. physik. Chem.*, **144**, 269 (1929).

(4) L. Kahlenberg, *J. Phys. Chem.*, **4**, 709 (1900).

(5) F. K. V. Koch, *J. Chem. Soc.*, 524 (1928).

(6) H. H. Morgan, *ibid.*, **123**, No. 2, 2901 (1923).

(7) A. Naumann, *Ber.*, **47**, 247 (1914).

tonitrile as solvent[8] (see Table I). The wave corresponds to a reversible reduction involving one electron.

Metal Ions Which Are Reduced at More Positive Potentials than the Hydronium Ion in Aqueous Solution, and Which Have Lower Solvation Energies in Acetonitrile than in Water.—The polarographic properties of the ions discussed in this section are summarized in Table I. For purposes of comparison half-wave potential and standard potential data for aqueous solutions also are included.

Cupric Copper.—In non-complexing aqueous solutions the hydrated cupric ion gives a single wave at *ca.* 0 volt, corresponding to its reduction to copper amalgam. In acetonitrile as solvent cuprous copper is stabilized, with the result that in sodium perchlorate as supporting electrolyte cupric copper gives two reduction waves of equal height[9]; the first is not a "true" wave, since reduction of cupric copper sets in at a potential which is much more positive than that at which anodic dissolution of mercury commences (+0.6 volt). From experiments with the R.P.E. (*vide infra*) it appears that in acetonitrile the cuprous–cupric couple has an extremely positive standard potential of +1.0 volt (*vs.* S.C.E.).

In decinormal tetraethylammonium bromide as supporting electrolyte[10] cupric copper gives a single two-electron reduction wave which rises directly from the anodic dissolution potential of mercury in that medium (−0.5 volt). Hence the reduction potential of cuprous copper cannot be greatly affected by the presence of even a large excess of bromide ion; this is in striking contrast to the behavior of cations which are only weakly solvated by acetonitrile, *e.g.*, zinc[1] and manganese(II) ions.

Solutions of cupric perchlorate in acetonitrile are rapidly decolorized by shaking with metallic silver; cupric copper is thereby quantitatively reduced to the cuprous state, while an equivalent amount of silver goes into solution. The polarogram of such a solution first exhibits the silver and then the cuprous copper wave.

Manganese(II), Cobalt(II) and Nickel(II).—In non-complexing aqueous solutions reduction of the strongly hydrated manganese(II), cobalt(II) and nickel(II) ions at the D.M.E. requires a large overvoltage (Co > Ni > Mn), with the result that highly irreversible waves are obtained at much more negative potentials than would be predicted from the reversible standard potentials of the metal–metal ion couples (see Table I). The overvoltage required for the reduction of these hydrated ions usually is attributed to their slow rate of electroreaction.

The results obtained in acetonitrile as solvent are summarized in Table I. The waves for manganese and nickel are reversible, while that for cobalt deviates slightly from reversibility.[11] In all instances diffusion currents are proportional to concentration over the range tested (2.5×10^{-4} to 5×10^{-3} *M*).

The effect of water on the manganese and nickel waves was investigated. Table II illustrates the changes in diffusion current and half-wave potential on adding successive amounts of water to *ca.* 2.5 millimolar solutions of manganous and nickelous perchlorate in decinormal tetraethylammonium perchlorate as supporting electrolyte. The increase in the water content of the solution is accompanied by a gradual decrease in diffusion current, and, especially with nickel, by a rapid shift in half-wave potential to more negative values. This shift in half-wave potential may be attributed to the fact that the relatively strong base water should be able to compete successfully for the metal ion with the much weaker base acetonitrile. On increasing the water concentration, equilibria of the type $Ni(CH_3CN)^{++}{}_m + nH_2O \rightarrow Ni(H_2O)^{++}{}_n + mCH_3CN$ will be displaced more and more in the forward direction, accompanied by a shift in half-wave potential to more negative values and more and more deviation from reversibility. The gradual decrease in diffusion current can be attributed to the increasing viscosity of the solution; moreover, the nature of the diffusing species changes.[12]

TABLE II

EFFECT OF WATER ON HALF-WAVE POTENTIALS AND DIFFUSION CURRENTS OF MANGANOUS AND NICKELOUS IONS IN ACETONITRILE AS SOLVENT

Ion	Vol. % water added	i_d, μa.	$-E^{1/2}$	Remarks
Mn^{++}	0	17.6	1.12	Reversible wave, slope = 0.028
	0.4	17.1	1.17	Wave still revers., slope = 0.030
	2.0	16.4	*ca.* 1.25	Max. appears
	20	14.0	*ca.* 1.4	High max., wave drawn out
NI^{++}	0	14.0	0.33	Reversible wave, slope = 0.031
	0.4	13.8	0.36	Slope = 0.035
	1.0	13.6	0.70	Wave becomes drawn out
	4.0	13.4	*ca.* 1.2	Highly irreversible wave

The relative stability of manganous halide complexes in acetonitrile as solvent is shown by the fact that in decinormal tetraethylammonium bromide as supporting electrolyte, the manganese wave only starts at −2.3 volt. As in the case of zinc,[1] this behavior is in harmony with the postulate that complexes of metals with anions should be much more stable in acetonitrile than in water, unless

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(8) Cuprous copper has comparable half-wave potentials in acetonitrile (−0.36 volt) and in decinormal aqueous potassium thiocyanate (−0.39 volt).

(9) Two waves were also found by S. Wawzonek and M. E. Runner, *J. Electrochem. Soc.*, **99**, 457 (1952), but they erroneously attributed the second wave to reduction of free perchloric acid present in the cupric perchlorate sample used.

(10) Very intensely colored solutions are obtained by adding chloride or bromide ions to 0.01 *M* solutions of cupric perchlorate in acetonitrile; yellow with chloride, first yellow then blue with bromide. Addition of iodide ion liberates iodine, but no cuprous iodide precipitates.

(11) In aqueous solution the reduction of these ions requires smaller overvoltages in the presence of certain complex forming substances (*e.g.*, ammonia, pyridine, cyanide ion, thiocyanate ion) than in non complexing solutions. Apparently the electroreduction of these ions is likewise more rapid when they are coördinated with acetonitrile than when they are present as the aquo ions.

(12) In both instances the decrease in diffusion current is more rapid than would correspond to the increase in viscosity of the solution; this is additional evidence for the postulate that the nature of the diffusing species changes radically.

there is specific interaction between the metal ion and acetonitrile.

Ferric and Ferrous Iron.—In acetonitrile, as in water, the ferric ion gives two reduction waves at the D.M.E., corresponding to formation of ferrous ion and of metallic iron, respectively. In both solvents the first is not a "true" wave, since reduction of ferric ion sets in at a potential which is more positive than that at which anodic dissolution of mercury commences. Experiments with the R.P.E. (*vide infra*) showed that in acetonitrile as solvent and with sodium perchlorate as supporting electrolyte, ferric ion is reduced irreversibly to ferrous ion at *ca.* +1.1 volt.

In non-complexing aqueous solutions reduction of ferrous iron at the D.M.E. involves a large overvoltage of *ca.* 0.7 volt (compare Table I). The fact that it is reduced at a much more positive potential in acetonitrile than in water may be due to one or both of the following reasons: the solvation energy of the ferrous ion is very likely smaller in acetonitrile than in water, and the rate of its electroreduction may be more rapid in acetonitrile than in water.

Chromic and Chromous Chromium.—In acetonitrile, as in water, the chromic ion gives stepwise reduction at the D.M.E., corresponding to successive formation of chromous ion and metallic chromium. The relatively positive potential at which chromous ion is reduced in acetonitrile (see Table I) can be attributed to the same factors as for ferrous ion. The extremely positive potential at which chromic ion is reduced in acetonitrile must then be due mainly to the net effect of two opposing factors: the effect of the low solvation energy of the chromous ion, which is more than offset by the opposing effect of the low solvation energy of the chromic ion. This is indeed what would be expected, since in aqueous solution the chromic ion is much more strongly hydrated than the chromous ion, with the result that the decrease in solvation energy in going from water to acetonitrile as solvent should be much greater for the chromic ion than for the chromous ion. The same is true for the ferric–ferrous couple.

Chromous ion does not give an anodic wave at the D.M.E. in acetonitrile as solvent. Hence the chromous–chromic couple behaves irreversibly at the D.M.E. in acetonitrile (see also slope of chromic → chromous wave, Table I).

In acetonitrile as solvent metallic cadmium reduces chromic ion quantitatively to chromous ion.

On addition of tetraethylammonium bromide to a chromic perchlorate solution in acetonitrile, a green precipitate is first formed, which dissolves in excess of bromide solution to give an intense greenish-yellow solution. In 0.1 *N* tetraethylammonium bromide two reduction waves are observed at the D.M.E., the second twice as high as the first; the first wave rises directly from the anodic dissolution potential of mercury (−0.5 volt), while the second is a drawn-out wave which starts at −1.4 volt and reaches a diffusion plateau at −1.9 volt. The relative stability of chromous bromide complexes in acetonitrile can be explained in the same way as for zinc[1] and manganese. From the relative locations of the Cr(III) → Cr(II) and Cr(II) → Cr(O) waves in the absence and presence of bromide, it is apparent that the bromide complex of chromium(II) is much more stable than that of chromium(III).

Metal Ions Which Are Strongly Hydrolyzed in Aqueous Solution and Which Have Reduction Potentials Close to that of the Hydronium Ion.—In aqueous solution the direct polarographic determination of aluminum is difficult, while that of beryllium and magnesium is virtually impossible. The beryllium wave is poorly defined, and that of magnesium passes through a prominent maximum into an ill-defined diffusion region. Moreover magnesium gives an abnormally large apparent diffusion current, attributed to reduction of water by the magnesium amalgam formed. In acetonitrile as solvent beryllium, magnesium and aluminum give well-defined, though incompletely reversible, waves (see however below, solvolysis effects). Diffusion currents are proportional to concentration over a wide range; this is illustrated by Table III for a typical case, that of magnesium perchlorate in 0.2 *M* tetraethylammonium perchlorate as supporting electrolyte. Diffusion currents were measured at −2.4 volt at a drop time of 2.3 seconds and a rate of flow of mercury of 1.08 mg./sec.

TABLE III

DIFFUSION CURRENT OF MAGNESIUM AS A FUNCTION OF CONCENTRATION

Molarity M, $\times 10^4$	Diffusion current i_d, μa.	$(i_d/M) \times 10^{-3}$
1.000	0.458	4.58
5.000	2.31	4.62
10.00	4.60	4.60
30.00	13.8	4.60
60.00	27.8	4.63
100.0	47.1	4.71

The diffusion current constants and "half-wave potentials" of beryllium, magnesium and aluminum in 0.1 *N* tetraethylammonium perchlorate are listed in Table IV. Slopes of waves are not reported because all waves are drawn out.

TABLE IV

SOME POLAROGRAPHIC PROPERTIES OF BERYLLIUM, MAGNESIUM AND ALUMINUM

Salt	$(I_d)_{AN}$	$(-E_{1/2})_{AN}$[a]	$(-E_{1/2})_W$	$(E_{1/2})_{AN} - (E_{1/2})_W$
$Be(ClO_4)_2 \cdot 4aq.$	4.22	1.6	1.8	0.2
$Mg(ClO_4)_2$	3.82	1.84	*ca.* 2.2	*ca.* .4
$Al(ClO_4)_3 \cdot 9aq.$	6.60	1.42	1.75	.33

[a] For 1 millimolar solutions.

Yttrium, Lanthanum and the Rare Earth Metals.—In aqueous solution the trivalent ions of most of these metals are reduced directly to the metal amalgam at the D.M.E. Europium, ytterbium and samarium are the only exceptions; here reduction proceeds to the divalent ion. Subsequent reduction of divalent ytterbium and samarium to the metal amalgam also has been reported.[13] Of the eight trivalent ions discussed in this section, three, namely, europium, ytterbium and samarium,

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(13) See *e.g.*, I. M. Kolthoff and J. J. Lingane, "Polarography," 2nd Ed., Interscience Publishers, Inc., New York, N. Y., 1952, p. 436.

are reduced to the divalent state in acetonitrile as solvent (as in water). Yttrium, lanthanum, praseodymium, neodymium and gadolinium ions are reduced directly to the metal amalgam. Europium and ytterbium also give a second wave corresponding to reduction of the divalent ion to the metal amalgam, but with samarium no second wave was obtained.

TABLE V

POLAROGRAPHIC PROPERTIES OF EUROPIUM, YTTERBIUM AND SAMARIUM

Electrode reaction	I_d	Slope[a]	$(E_{1/2})_{AN}$	$(E_{1/2})_W$	$(E_{1/2})_{AN} - (E_{1/2})_W$
$Eu^{+++} \rightarrow Eu^{++}$	1.91	0.060	+0.15	−0.67	0.82
$Eu^{++} \rightarrow Eu^0$	3.80	.048	−1.67	[c]	..
$Yb^{+++} \rightarrow Yb^{++}$	1.88	.062	−0.57	−1.17	.60
$Yb^{++} \rightarrow Yb^0$	3.71	.060	−1.69	−2.0[d]	.3
$Sm^{+++} \rightarrow Sm^{++}$	2.25	.058	−1.62	−1.80	.18
$Sm^{++} \rightarrow Sm^0$	[b]	[b]	[b]	−1.96	..

[a] From analysis of waves obtained with 1 millimolar solutions. [b] No wave obtained. [c] No wave obtained in ammonium chloride as supporting electrolyte. [d] *p*H dependent.

The results obtained with solutions of europium, ytterbium and samarium perchlorates in decinormal tetraethylammonium perchlorate as supporting electrolyte are summarized in Table V. In all instances diffusion currents are proportional to concentration over the range tested (0.2 to 2.0 millimolar). The relatively positive potentials at which Eu(II) and Yb(II) and especially Eu(III) and Yb(III) ions are reduced in acetonitrile can be explained in the same manner as for chromium. The samaric ion is reduced at only a slightly more positive potential in acetonitrile than in water; in this respect its behavior deviates from that of the other trivalent ions discussed in this paper. A check of its behavior in water seems desirable.

The effect of water on the europium wave is as expected; *e.g.*, in the presence of 0.4% of water, $(E_{1/2})_1 = -0.20$ volt and $(E_{1/2})_2 = -1.69$ volt.

In acetonitrile, as in water, the polarographic properties of yttrium, lanthanum, praseodymium, neodymium and gadolinium are very similar; *e.g.*, with tetraethylammonium perchlorate as supporting electrolyte all of these ions give a single irreversible wave at −1.5 volt, the height of which corresponds to a three-electron reduction (I_d-values measured for 0.5 millimolar solutions in decinormal tetraethylammonium perchlorate; Y 6.1, La 5.6, Pr 5.7, Nd 6.0, Gd 6.3).[14]

Solvolysis Effects Encountered with Beryllium, Magnesium, Aluminum, Yttrium, Lanthanum and the Rare Earth Ions.—The polarograms obtained at higher concentrations (generally above 1 millimolar) of these cations in tetraethylammonium perchlorate as supporting electrolyte, always exhibit in the rising portion of the curve an irregular section over which the capillary does not function normally. Within this region, which generally extends over about 0.2 volt, the current does not increase regularly as the drop grows, and the current–voltage plot is erratic. In all instances it was observed that beyond a certain potential the interference stops abruptly: the current again increases smoothly during the lifetime of a drop, the current–voltage curve rises steeply, and soon a normal diffusion plateau is reached. Curve A (Fig. 1) illustrates this phenomenon for a typical case, that of 2 millimolar magnesium perchlorate in decinormal tetraethylammonium perchlorate as supporting electrolyte.

These observations can be explained by considering how solvolysis of the "acidic" ions discussed in this section may affect their polarographic behavior. It is postulated that the irregular sections of the current–voltage curves correspond to hydrogen evolution and consequent formation of an insoluble film of the solvolysis product on the surface of the mercury drop; *e.g.*, a possible reaction would be: $M(SH)_n{}^{m+} \rightleftarrows MS(SH)_{n-1}^{(m-1)+} + H^+$, where H^+ (the solvated proton) is reduced at the electrode and the species $MS(SH)_{n-1}^{(m-1)+}$ forms an insoluble film with the anions present. Such an insoluble film may be considered as a protective barrier, which not only functions as a high resistance and interferes with the diffusion of the reducible species to the electrode surface, but which may also prevent the liberated hydrogen from escaping into the solution, thereby forcing it up into the capillary. It has indeed been found on numerous occasions by microscopic observation that within the potential range corresponding to erratic behavior of the electrode, small gas bubbles force their way into the capillary, then to be pushed out again by the flow of mercury. This process would repeat itself at intervals of a few seconds as long as the cathode potential remains in the "critical" range, irrespective of whether this region is approached from the positive or from the negative side. As the cathode potential is gradually made more negative, the flow of gas bubbles into the capillary always stops abruptly at a certain reproducible potential.

It is noteworthy that hydrogen never shows any tendency to collect in the capillary during the electrolysis of hydrogenic acids,[15] such as perchloric acid, sulfuric acid, acetic acid, etc. This supports the view that an insoluble film is produced in those instances when gas bubbles enter the capillary.

Controlled Potential Electrolysis at the Mercury Pool Cathode.—Further evidence for the solvolytic effects postulated above was obtained from the large-scale electrolysis of beryllium, magnesium and lanthanum ions at the mercury pool cathode in the electrolysis cell described in the Experimental section. When the electrolysis is conducted at cathode potentials corresponding to the erratic sections of the polarograms of these ions, hydrogen is evolved until all the metal has been pre-

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(14) H. A. Laitinen and E. B. Mohr (private communication) attribute the waves obtained by Glockler, *et al.*, with all rare earths except Eu, Yb and Sm in aqueous medium to hydrolytic hydrogen evolution and precipitation of rare earth hydrous oxides at the electrode surface. The half-wave potentials reflect basicity differences rather than differences in amalgamation potentials. Other reasons given by them for their conclusion are: (1) the potential varies with *p*H, (2) amalgamations cannot actually be performed from aqueous solutions for Pr, Nd and Gd.

(15) That the electrolysis of such acids in acetonitrile indeed liberates hydrogen, was proved by conducting the electrolyses on a macro scale at the mercury pool cathode (*vide infra*).

cipitated[16] in the form of a white compound.[17] When, however, the electrolysis is conducted at cathode potentials corresponding to the diffusion plateaus of the polarograms, the metal amalgam is obtained.[18]

Elimination of Polarographic Solvolytic Effects.—In all instances addition of as little as one per cent. of water or a few tenths of a per cent. of acetic acid to the electrolysis solution eliminates the interference with the electrode process. The interfering film is apparently solubilized by addition of water or acetic acid. Addition of larger amounts of water quite generally causes a shift of the wave to more negative potentials, without affecting the magnitude of the diffusion currents significantly. A typical example is given in Fig. 1, which illustrates the effect of increasing concentrations of water on the reduction wave of 2 mM magnesium perchlorate in decinormal tetraethylammonium perchlorate as supporting electrolyte. When the water concentration exceeds 20%, the diffusion plateau of magnesium becomes erased.

Effect of Halide Ions on the Polarography of Yttrium and Praseodymium in Acetonitrile.—With tetraethylammonium bromide as supporting electrolyte yttrium and praseodymium give polarograms which are entirely free from irregularities, even at relatively high concentrations (2.5 mM); the waves occur at considerably more negative potentials than with tetraethylammonium perchlorate as supporting electrolyte (−1.95 volt as compared to *ca.* −1.5 volt), and addition of water causes a shift of the waves to more positive potentials, whereas in tetraethylammonium perchlorate as supporting electrolyte this shift is to more negative potentials. These observations are in harmony with the fact that in acetonitrile, which is a strongly differentiating solvent as far as the strength of electrolytes is concerned, yttrium and praseodymium bromides should be much weaker electrolytes than their perchlorates.[19] Addition of the relatively strong base water should increase the ionization of these bromides by formation of the aquo ions.

II. Anodic Waves of Halide and Hydroxyl Ions.—Anodic depolarization of the D.M.E. by halide, thiocyanate and hydroxyl ions occurs at much more negative potentials in acetonitrile than in water. The anodic dissolution potentials of mercury in millimolar solutions of these substances in water and in acetonitrile are compared in Table VI. In the absence of depolarizing substances, anodic dissolution of mercury occurs at *ca.* +0.4 volt in water and at +0.60 volt in acetonitrile.

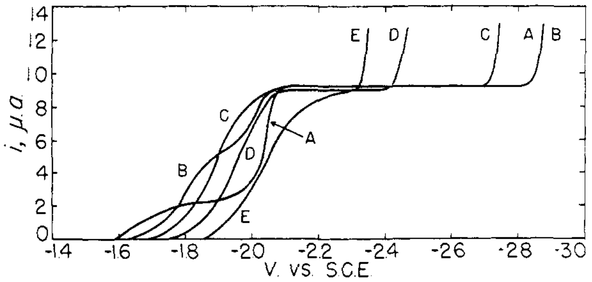

Fig. 1.—Polarogram of 2×10^{-3} M $Mg(ClO_4)_2$ in 0.1 M Et_4NClO_4: A, water-free; B, 0.25% water added; C, 1%; D, 6%; E, 20% water.

The relatively negative potentials at which hydroxyl, thiocyanate and halide ions depolarize the D.M.E. in acetonitrile, may be attributed to the combined effect of two factors: (a) the acidic properties of acetonitrile are extremely weak as compared to those of water; consequently anions have much lower solvation energies (or much higher absolute activities) in acetonitrile than in water; (b) the activity of the mercurous ion is relatively high in the very weak base acetonitrile; thus, in the absence of depolarizing substances, anodic dissolution of mercury occurs at a potential which is 0.2 volt more positive in acetonitrile than in water. On this basis it is to be expected that the dissociation constants and solubility products of the salts of mercurous mercury with depolarizing anions will be much smaller in acetonitrile than in water.

TABLE VI

ANODIC DISSOLUTION POTENTIALS OF MERCURY (E_a) IN MILLIMOLAR SOLUTIONS OF HALIDE AND HYDROXYL IONS

Anodic depolarizer	E_a in water	E_a in acetonitrile
OH^-	*ca.* 0.0	−0.90
I^-	− .1	− .45
Br^-	+ .1	− .35
Cl^-	+ .2	− .25
CNS^-	+ .1	− .10

The extremely negative potential at which hydroxyl ion depolarizes the D.M.E. in acetonitrile is remarkable. It must be attributed mainly to the extremely high absolute activity of this ion in acetonitrile. That acetonitrile shows little tendency to solvate the hydroxyl ion is indicated by the extremely low solubilities of hydroxides in it; thus sodium and potassium hydroxides are virtually insoluble in acetonitrile, and the solubility of tetramethylammonium hydroxide is only of the order of 1 or 2 mM.

The anodic waves produced by hydroxide, thiocyanate and halide ions are drawn out and, except in the case of thiocyanate ion, the diffusion current is not proportional to concentration, as illustrated by the data for a typical case, that of chloride ion: for $M \times 10^4 = 4$, 10 and 20, $(i_d/M) \times 10^{-3} =$ 6.65, 6.00 and 5.50, respectively, using a capillary with $m = 2.03$ mg./sec. and $t = 4.0$ sec.

Thiocyanate ion produces two incompletely resolved waves, but the total diffusion current (measured at +0.4 volt) is proportional to concentration over the range tested (0.5 to 5.0 mM), with an I_d-value of 2.63, which is of the order of magnitude expected for a one-electron reaction per thiocyanate ion.

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(16) The supernatant liquids were tested for beryllium with quinalizarin, for magnesium with titan yellow and for lanthanum with alizarin.

(17) Postulated to be a solvolysis product; no attempt was made to perform a quantitative analysis of this compound.

(18) The quantity of electricity used (determined by integration of the current–time curve) invariably amounts to only 80–90% of that which is calculated for quantitative deposition of the metal as the amalgam. This indicates that the metal amalgam cannot be the only product formed at the mercury pool, but the problem was not pursued any further.

(19) Bromide complexes also may be formed. Their stability will be decreased by adding water (see Part I, stability of zinc halide complexes in acetonitrile[1]).

III. **Voltammetry at Rotated Platinum Micro Electrode.**—Rotated micro-electrodes of noble metals like platinum or gold are particularly useful in acetonitrile as solvent because the latter is very resistant to direct electrolytic oxidation and reduction (not to electrolytically generated hydrogen). Thus, with decinormal sodium perchlorate as supporting electrolyte, the useful potential range of the platinum micro electrode in acetonitrile extends from +1.8 to −1.5 volt, as compared to the much narrower range of +1.1 to −1.1 volt attainable in water.

Residual currents never exceeded 2 microamp, at any potential at which diffusion currents were measured.

Some of the results obtained are summarized in Table VII.

TABLE VII

VOLTAMMETRY AT ROTATED PLATINUM MICRO-ELECTRODE

Salt	$M \times 10^4$	Support. electrolyte	Electrode reaction	"Half-wave potential"
$AgClO_4$	1.0	0.1 *M* $NaClO_4$	$Ag^+ \rightarrow Ag^0$	+0.1
$Cd(ClO_4)_2 \cdot 6aq.$	1.0	same	$Cd^{++} \rightarrow Cd^0$	−0.5
$Zn(ClO_4)_2 \cdot 6aq.$	1.0	same	$Zn^{++} \rightarrow Zn^0$	−0.9
$Fe(ClO_4)_3 \cdot 6aq.$	4.0	0.2 *M* $NaClO_4$	$Fe^{+++} \rightarrow Fe^{++}$	+1.1
$Fe(ClO_4)_2 \cdot 6aq.$	4.0	same	$Fe^{++} \rightarrow Fe^{+++}$	+1.6
$Hg(ClO_4)_2 \cdot 3aq.$	1.5	0.1 *M* $NaClO_4$	$2Hg^{++} \rightarrow Hg_2^{++}$	+0.7
			$Hg_2^{++} \rightarrow 2Hg^0$	+0.5
$Cu(ClO_4)_2 \cdot 6aq.$	2.0	same	$Cu^{++} \rightarrow Cu^+$	+1.0
			$Cu^+ \rightarrow Cu^0$	−0.5
$CuClO_4 \cdot aq.$	2	same	$Cu^+ \rightarrow Cu^0$	−0.5
			$Cu^+ \rightarrow Cu^{++}$	+1.0
LiCl	5	0.1 *M*	$6Cl^- \rightarrow 2Cl_3^-$	+1.1
		$(C_2H_5)_4NClO_4$	$2Cl_3^- \rightarrow 3Cl_2$	+1.7
$(C_2H_5)_4NBr$	5	same	$6Br^- \rightarrow 2Br_3^-$	+0.7
			$2Br_3^- \rightarrow 3Br_2$	+1.0
NaI	5	same	$6I^- \rightarrow 2I_3^-$	+0.3
			$2I_3^- \rightarrow 3I_2$	+0.6

Silver, cadmium and zinc ions give well-defined waves, with diffusion currents proportional to concentration over the range tested (2×10^{-5} to 2×10^{-4} *M*).

The reduction of ferric iron and the oxidation of ferrous iron occur irreversibly. Nevertheless it is evident that ferric iron is a much stronger oxidizing agent in acetonitrile than in water. Mercuric mercury gives two incompletely resolved reduction waves of approximately equal height, corresponding to reduction of Hg(II) to Hg_2(II) and of Hg_2(II) to Hg^0, respectively. It was verified visually that the second wave corresponds to deposition of mercury metal; moreover, after attaining the second limiting current and applying more positive potentials, a typical anodic dissolution current is observed at potentials more positive than +0.6 volt. Cupric copper gives two waves of equal height, corresponding to reduction of Cu(II) to Cu(I) and of Cu(I) to Cu^0, respectively. The half-wave potential of the anodic cuprous wave is equal to that of the first cathodic cupric copper wave. Consequently the cuprous–cupric couple behaves reversibly in acetonitrile; its extremely positive standard potential of approximately +1.0 volt can be attributed to the combined effect of two factors: the relatively low solvation energy of the cupric ion, and the high solvation energy of the cuprous ion in acetonitrile. Addition of water should cause a relatively large increase in the solvation energy of the cupric ion, and a relatively small decrease in the solvation energy of the cuprous ion. The combined effect of these two factors will be a shift in the standard potential of the cuprous–cupric couple to more negative values. The half-wave potential of the cupric–cuprous couple was found to be 1.0 volt in water-free acetonitrile, +0.8 volt with 4% water and +0.4 volt when 68% of water was present. The cupric–cuprous couple remains reversible even in the presence of 68% of water.

Chloride, bromide and iodide ions each give two anodic waves at the R.P.E. in acetonitrile. In all three cases the first wave (polarizing in the positive direction) is exactly twice as high as the second. It is postulated that the first wave corresponds to formation of the "trihalide" ion X_3^-[20] and the second to formation of the halogen; the following over-all reactions are postulated: $6X^- - 4e^- \rightarrow 2X_3^-$, followed by $2X_3^- - 2e^- \rightarrow 3X_2$. When excess of iodine is added to a solution of sodium iodide in acetonitrile, the iodide ion is converted into triiodide ion, and the resultant solution gives only the second wave, corresponding to oxidation of triiodide ion to iodine. The height of this wave is equal to the combined heights of the two anodic waves obtained in the absence of iodine. This is true for a freshly-prepared solution only since iodine solutions in acetonitrile rapidly form triiodide ion on standing.

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(20) Trihalide ions possess great stability in acetonitrile as solvent. A. I. Popov and N. E. Skelly, THIS JOURNAL, **76**, 5309 (1954), have shown that salts like tetramethylammonium tribromide are stronger electrolytes in acetonitrile than the corresponding quaternary ammonium halides.