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Solvent Effects on the Polarographic Reduction of Metal Ions. I. Benzonitrile–Acetonitrile

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Polarographic reduction of various cations has been investigated in benzonitrile. Comparison of the polarographic half-wave potentials obtained in benzonitrile and acetonitrile with infrared and chemical information on the interaction of the nitriles with cations suggests a bridge mechanism involving benzonitrile molecules in the reduction of cations in benzonitrile. Interesting effects of small amounts of water and residual oxygen on the reduction of barium and magnesium ions are discussed.

Acetonitrile, with a number of favorable solvent properties,[1–3] has been widely used in the past few years as a solvent for both inorganic and organic investigations.[2–14]

Of particular interest to us are the polarographic studies of the electrochemical behavior of cations and anions in this solvent.[3–7] The half-wave potentials for the reduction of cations in acetonitrile[3–6] are, in general, considerably less negative (less reducing) than the corresponding reductions in water. This has been attributed to lower solvation energies due to the less basic character of acetonitrile.

The ability of acetonitrile to solvate an ion lies in the presence of the C≡N group. Any change in the nature of the C≡N group, and as a result in the solvation energies, should then be accompanied by a corresponding change in the polarographic half-wave potentials. Because benzonitrile differs from acetonitrile in two interesting and significant ways: (1) it has delocalized electrons in the phenyl ring which are capable of interacting with the C≡N group, and (2) it has a large adjacent phenyl group as compared to the methyl group creating a steric problem, it was used in this study to determine what effect, if any, changes of this nature in the solvent have on the reduction potential of cations.

Experimental

Reagents.—Eastman practical grade benzonitrile was allowed to stand over calcium sulfate for several days, then decanted into a distilling flask and distilled from fresh calcium sulfate. The distillate was redistilled repeatedly from phosphorus pentoxide in an all glass apparatus (collecting only the center portion, b.p. 188 ± 0.5° (735 mm.)) until almost no black residue which was prevalent at the end of the earlier distillations remained in the distillation flask. The distillate was kept in the receiving flask under an atmosphere of dry nitrogen. The receiving flask was fitted with a glass delivery system with a Teflon stopcock. The solvent was forced out through the delivery system by the application of a positive pressure of nitrogen to an inlet tube.

Tetraethylammonium perchlorate was prepared from Eastman tetraethylammonium bromide as already described.[3] The tetraethylammonium perchlorate was recrystallized six times from water and dried in a vacuum oven at 70° for 48 hr. The bromide content of a 1 M solution of the perchlorate salt was determined chronopotentiometrically to be less than 10^{-4} M.

With the exception of barium and cadmium perchlorates, which were prepared from the respective carbonates by neutralization with an equivalent amount of standard perchloric acid then taken to dryness on a hot plate, the metal perchlorates were obtained from G. F. Smith and Co. All the metal perchlorates were dried in a vacuum oven at 60–70° for 48 hr., with the exception of ferrous perchlorate which undergoes considerable decomposition at this temperature and was, therefore, dried at 45° for 24 hr. No visible indication of decomposition was noted. Several of the less stable perchlorates were checked by polarographing in acetonitrile; no significant differences in $E_{1/2}$ values from those reported by Kolthoff and Coetzee[3,4] were observed. The dried perchlorates were desiccated over phosphorus pentoxide and all weighings were made in glass stoppered bottles to minimize contact with moisture in the air. The residual water content of the perchlorate salts was not determined; however, the colors of the dried materials in comparison to the corresponding hydrated salts, when the hydrated material is colored, indicated the drying operation greatly reduced the amount of water associated with the metal perchlorates. The dried cobalt(II) and nickel(II) perchlorates were, respectively, very pale pink and pale green in contrast to the deep red and green of the hexahydrates. Similarly the color of chromium(III) perchlorate was reduced from the deep blue-black of the hexahydrate to a light blue. Copper(II) perchlorate changed from the deep blue of the hexahydrate to a lighter blue, then finally to a light green.

The total water content of the benzonitrile solutions (containing supporting electrolyte and metal perchlorate) was found by Karl Fischer titration to be *ca.* $0.01M$, which was essentially that found for the solvent, benzonitrile.

Polarographic solutions of *ca.* 1 mmolar concentrations were used for two reasons: first, to keep the ratio of water to metal ion as small as possible and, second, to use solutions of approximately the same concentration as those employed by Kolthoff and Coetzee in their acetonitrile study.[15]

Apparatus.—A Leeds and Northrup Type E Electrochemograph was used to obtain the current–voltage curves. The electromotive force recorded by the instrument was checked with a potentiometer. Polarograms were corrected for iR drop across the cell. The resistance measurements were made with a conductance bridge. The temperature of the polarographic cell was maintained constant at 25.0 ± 0.2°.

The rotating platinum electrode was constructed in the conventional manner and cleaned with concentrated nitric

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(1) L. F. Audrieth and J. Kleinberg, "Non-Aqueous Solvents," John Wiley and Sons, Inc., New York, N. Y., 1953.

(2) G. J. Janz and S. S. Danyluk, THIS JOURNAL, **81**, 3846 (1959).

(3) I. M. Kolthoff and J. F. Coetzee, *ibid.*, **79**, 870 (1957).

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

(5) S. Wawzonek and M. E. Runner, *J. Electrochem. Soc.*, **99**, 457 (1952).

(6) A. I. Popov and D. H. Geske, THIS JOURNAL, **79**, 2074 (1957).

(7) A. I. Popov and D. H. Geske, *ibid.*, **80**, 1340 (1958).

(8) A. I. Popov and D. H. Geske, *ibid.*, **80**, 2976 (1958).

(9) A. I. Popov and R. E. Humphreys, *ibid.*, **81**, 2043 (1959).

(10) G. J. Janz and S. S. Danyluk, *ibid.*, **81**, 3850 (1959); **81**, 3854 (1959).

(11) S. Wawzonek, E. W. Blaha, R. Berkey and M. E. Runner, *J. Electrochem. Soc.*, **102**, 235 (1955); *ibid.*, **103**, 456 (1956).

(12) I. M. Kolthoff and J. F. Coetzee, THIS JOURNAL, **79**, 6110 (1957).

(13) D. E. Bublitz, G. Hoh and T. Kuwana, *Chemistry and Industry* (*London*), 635 (1959).

(14) H. Lund, *Acta Chem. Scand.*, **11**, 491 (1957); *ibid.*, **11**, 1323 (1957).

(15) With most of the perchlorates shifts in $E_{1/2}$ to more positive values by 0.01 to 0.07 v. have been observed both in benzonitrile and acetonitrile in going from 1 to 0.1 mmolar solutions. This cannot be due to the effect of water (increase in water to metal ion ratio) because this has been shown to shift $E_{1/2}$'s to more negative values.

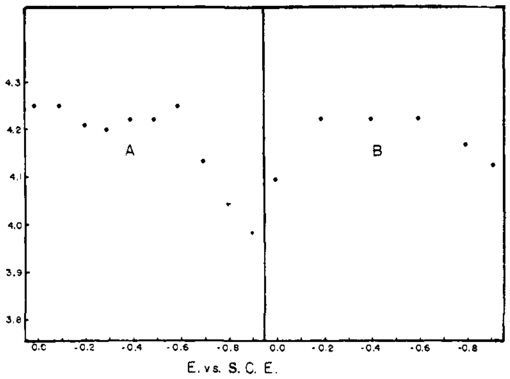

Fig. 1.—Influence of potential on drop time in benzonitrile: A, Et_4NClO_4 supporting electrolyte; B, 0.1 *M* $LiClO_4$ supporting electrolyte.

acid and chromic acid before use. A Sargent synchronous motor was used to rotate the platinum electrode at *ca.* 600 r.p.m.

The chronopotentiometric unit has been described.[16]

Cells.—The standard H type cell (number 7733-D) supplied with the Leeds and Northrup Electrochemograph was used with the dropping mercury electrode. Both arms of the cell were filled with the electrolysis solution. The saturated calomel reference electrode was placed into one side arm, with the tip of the calomel electrode well below the fritted disk of the cell, only when the solutions were being polarographed. In this manner the potassium chloride from the calomel electrode was prevented from diffusing through the frit into the polarographic compartment. The resistance of the cell increased when a plug of potassium chloride formed on the tip of the calomel electrode. The formation of the plug was, however, kept to a minimum by a flow of saturated potassium chloride solution from the calomel (1 drop every five minutes). The resistance was generally 4000 ohms. With this freely bleeding calomel electrode, resistance measurements during a run agreed within 200 ohms. Because of difficulty in measuring the high resistance of the cell, the *iR* correction was kept to a minimum by using concentrations which gave diffusion currents no larger than 10 μamp.

The cell used with the rotating platinum electrode was similar in construction to the dropping mercury cell, except for a larger sample compartment.

Oxygen free polarographic solutions were obtained by bubbling Matheson prepurified nitrogen through a capillary arm for five minutes. Because of the low vapor pressure of benzonitrile, the nitrogen was not presaturated with benzonitrile. The use of a gas dispersion tube with vigorous evolution of nitrogen for periods of 20 minutes was inefficient due to appreciable foaming; oxygen waves amounting to 1–2 μamp. always were present in the polarograms.

Drop Time *vs.* Potential.—Drop time *vs.* potential curves which follow very closely the electrocapillary curves of mercury were obtained (Fig. 1) for 0.1 *M* tetraethylammonium perchlorate and 0.1 *M* lithium perchlorate in benzonitrile to aid in the selection of suitable maximum suppressors. The drop time plotted represents the average for 30 drops. The curve obtained with tetraethylammonium perchlorate as supporting electrolyte exhibits a rather erratic section, involving a decrease in the drop time, extending from the initial increase at 0 volt and extending to −0.6 volt *vs.* s.c.e. Similar curves were obtained on four separate trials. The curve for lithium perchlorate as supporting electrolyte does not show this erratic behavior but does exhibit a plateau between −0.2 and −0.6 volt *vs.* s.c.e.

Results

Table I lists the half-wave potentials for the reduction of metal ions in benzonitrile and, for comparison, those obtained by Kolthoff and Coetzee[3,4] in acetonitrile. Popov and Geske[6] have also reported half-wave potentials for various cations in acetonitrile, but because their results are in good agreement with those compiled by Kolthoff and Coetzee, they have not been listed. The values given for benzonitrile were obtained with 0.1 *M* tetraethylammonium perchlorate as supporting electrolyte, as were those in acetonitrile listed above barium perchlorate. For those below barium perchlorate, sodium perchlorate was the supporting electrolyte.

TABLE I

POLAROGRAPHIC DATA[a]

Compound	Benzonitrile[b] $E_{1/2}$	Benzonitrile[b] Slope	Acetonitrile[c] $E_{1/2}$	Acetonitrile[c] Slope	$\Delta E_{1/2}$
$LiClO_4$	−1.82	0.058	−1.95	0.068	0.06
$NaClO_4$	−1.73	.065	−1.85	.059	.08
$Mg(ClO_4)_2$	−1.62	.082	−1.84	[d]	.22
$Ca(ClO_4)_2$	−1.73	.058	−1.82[g]	.045	.09
$Sr(ClO_4)_2$	−1.72	.074	−1.76	.072	.04
$Ba(ClO_4)_2$	−1.58	.032	−1.63	.044	.05
$Cr(ClO_4)_3$ Cr(III)/Cr(II)	−0.40	[d]	0.00[g]	.100	− .40
Cr(II)/Cr(O)	− .97	.034	−1.12[g]	.052	.15
$Mn(ClO_4)_2$	− .98	.032	−1.12[g]	.028	.14
$Fe(ClO_4)_3$ Fe(III)/Fe(II)	+ .7[e]		+1.1[g]		.40
Fe(II)/Fe(O)	− .79	.038	−1.00[g]	.055	.21
$Co(ClO_4)_2$	− .49	[f]	−0.65[g]	.037	.16
$Ni(ClO_4)_2$	− .29	.059	−0.33[g]	.031	.04
$Cu(ClO_4)_2$ Cu(II)/Cu(I)	+ .85[e]		+1.0[g]		.15
Cu(I)/Cu(O)	− .20	.058	−0.36[g]	.060	.16
$Zn(ClO_4)_2$	− .53	.030	− .70[g,h]	.035	.17
$Cd(ClO_4)_2$	− .17	.032	− .27[g]	.053	.10
$Al(ClO_4)_3$	−1.47	.048	−1.42[g]		− .05

[a] For mmolar solutions. [b] 0.1 *M* Et_4NClO_4 as supporting electrolyte. [c] 0.1 *M* $NaClO_4$ as supporting electrolyte, with the exception of Li, Na, Mg, Ca, Sr and Ba in 0.1 *M* Et_4NClO_4. [d] Drawn-out waves. [e] Chronopotentiometric determination. [f] Maximum. [g] $E_{1/2}$ of hydrated salts. [h] $Zn(NO_3)_2 \cdot 6H_2O$. $\Delta E_{1/2} = E_{1/2}$ (benzonitrile) − $E_{1/2}$ (acetonitrile).

The polarographic study of the alkali metal ions in benzonitrile is limited by the insolubility of the perchlorate salts of the alkali metals below sodium in the periodic table. Agitation of potassium perchlorate in benzonitrile for a period of 72 hr. failed to give a polarographically measurable concentration of potassium ion. Similarly ammonium perchlorate was found to be insoluble in benzonitrile.

The effect of small amounts of water on the reduction wave for alkaline earth metal ions was found to be very pronounced; with increasing water concentration, the waves are more irreversible and the half-wave potentials are shifted to more negative values. In the case of magnesium as the water concentration is increased from 0.3 mg. per ml. (0.02 *M*) to 6.2 mg. per ml. (0.3 *M*), the polarographic wave becomes more drawn out with a resulting shift in the half-wave potential from −1.62 to −1.68 volt *vs.* s.c.e.

The polarographic reduction of barium ion in benzonitrile with added increments of water re-

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(16) C. N. Reilley, G. W. Everett and R. H. Johns, *Anal. Chem.* **27**, 483 (1955).

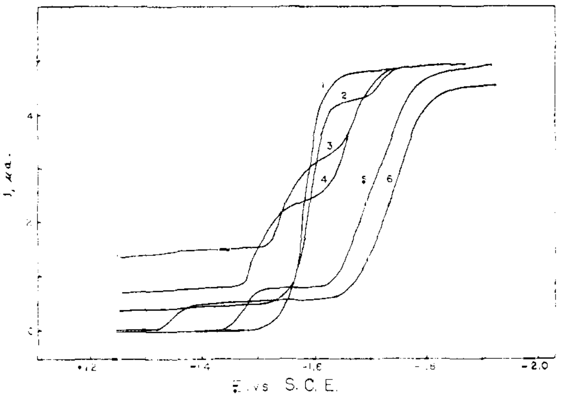

Fig. 2.—Effect of water on polarograms of 2×10^{-3} *M* $Ba(ClO_4)_2$ in 0.1 *M* Et_4NClO_4: 1, 0.01 *M* H_2O; 2, 0.02 *M* H_2O; 3, 0.1 *M* H_2O; 4, 0.13 *M* H_2O (approx.); 5, 0.2 *M* H_2O; 6, *M* H_2O. Oxygen is present in polarograms 2, 3 and 4.

vealed an interesting phenomenon. The results of this study are shown in Figure 2. The variation in the residual currents apparent in Fig. 2, curves 2–4, is due to the presence of oxygen and will be discussed in a later section.

It is apparent from Fig. 2 that the potential at which barium ion is reduced is dependent upon the relative degree of solvation of the ion by water and benzonitrile. As water displaces benzonitrile from the solvation sphere, the half-wave potential for the reduction of the metal ion becomes more negative tending to approach the value in aqueous systems. The shift of the second wave for barium ion to more negative half-wave potentials with increased water concentration is therefore expected. The shift of the first wave of barium ion to less negative values is, however, in contradiction to this view. Since the combined heights of the waves remain constant, the electrode process taking place in the first step in curves 3–6 must involve transfer of the same number of electrons per mole of barium as in the second step. Controlled potential electrolysis at −1.50 volt *vs.* s.c.e., corresponding to the plateau of the first wave, in the presence of 6.0 mg. per ml. of added water yielded a white precipitate on the surface of a mercury pool cathode. This indicates that the less negative wave is not due to the reduction of barium ion. Water in benzonitrile with tetraethylammonium perchlorate as supporting electrolyte does not yield a polarographic wave. However, the possibility exists that when coördinated with the barium ion, it does undergo polarographic reduction in benzonitrile, precipitating the barium ion as the hydroxide. This is the most feasible explanation for the observed experimental data.

$$2e + Ba(H_2O)_n(PhC{\equiv}N)_m{}^{+2} = Ba(OH)_2(H_2O)_{n-2}(PhC{\equiv}N)_m + H_2$$

In Fig. 2 the total height of all the waves is the same even though the residual currents for curves 2–4 are larger. The variation of the residual currents was due to varying amounts of oxygen in solution. Figure 3 shows similar data obtained for the reduction of magnesium ion in benzonitrile in the presence of varying amounts of oxygen. The first step in curve 1 has the same height as the magnesium wave of a completely deoxygenated solution (curve 3). The second step in curve 1 occurs at the same half-wave potential as oxygen. Oxygen yields a one-step reduction wave in benzonitrile. Deoxygenating the solution with nitrogen decreases at first the height of the second step. The first wave starts to decrease when the concentration of oxygen is less than that of the magnesium ion; from this point the magnesium reduction wave becomes apparent (curve 2). In every case when the oxygen concentration is below that of the magnesium ion the total height of the wave obtained is the same. The absence of the magnesium wave in curve 1 indicates that magnesium ion is being removed from solution. It appears that peroxide ion formed in the reduction of oxygen reacts with the magnesium ion to form insoluble magnesium peroxide, thus removing magnesium ion from the diffusion layer. The first step in curve 1 occurs at a less negative potential because the peroxide (reductant) produced is removed from the diffusion layer by magnesium ion. Controlled potential electrolysis with a mercury pool at a potential of −1.20 volt *vs.* s.c.e., corresponding to the diffusion plateau of the first wave of curve 2, yielded a white precipitate on the surface of the pool. This material was collected and identified as a peroxide, presumably magnesium peroxide.

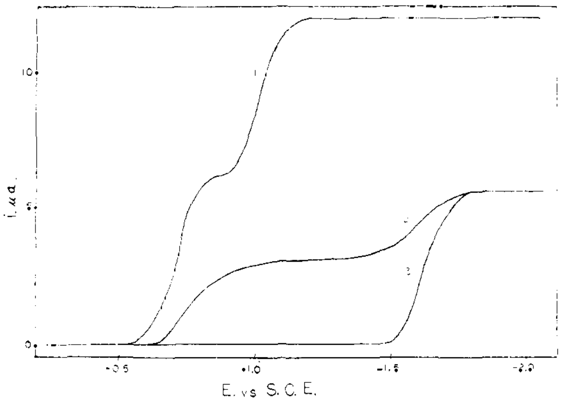

Fig. 3.—Effect of oxygen on polarograms of 2×10^{-3} *M* $Mg(ClO_4)_2$ in 0.1 *M* Et_4NClO_4; 1, no deoxygenation; 2, 2 minutes deoxygenation; 3, 8 minutes deoxygenation.

The reduction of cobalt(II) perchlorate yields a peak-type polarogram that is unaffected by 0.001 to 0.005% concentrations of methyl red, the sodium form of methyl red, ethyl cellulose or Surfactol-100.[17]

Popov and Geske[6] observed two waves for the reduction of nickel(II) perchlorate in acetonitrile.

The polarograms for the reduction of nickel(II) perchlorate in benzonitrile also indicate the presence of two nickel species. Two waves were observed, the second of which was accompanied by a peak-type maximum which is just suppressed by the addition of either 0.001% methyl red or the

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(17) With the exception of the cases of Ni^{++} and Cu^{++}, maximum suppressors did not change the position or the shape of the waves, except to eliminate the peaks. In a number of cases, decreasing the metal ion concentration (from 10^{-3} to 10^{-4} *M*) did not eliminate the maxima.

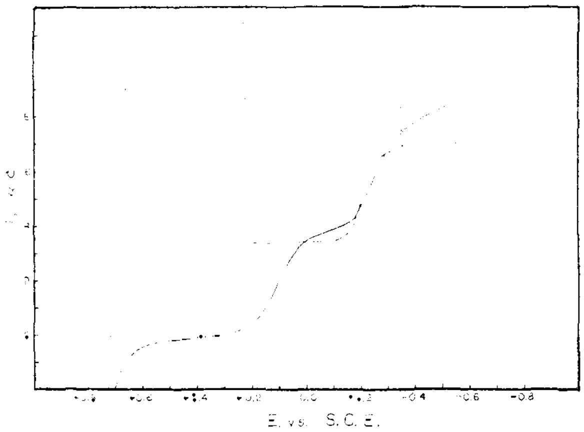

Fig. 4.—Effect of methyl red on polarograms of 2×10^{-3} M $Cu(ClO_4)_2$ in 0.1 M Et_4NClO_4: --------, no methyl red; – – –, 0.002% methyl red; ———, 0.01% methyl red.

sodium form of methyl red. With higher concentrations of methyl red, the second wave merges with the first to give a single wave with a half-wave potential corresponding to the first wave of the doublet. The effect of added water on the nickel waves was studied with solutions in which the maximum was suppressed with 0.001% methyl red. As the water concentration was increased, the second wave became a drawn-out extension of the first so that no wave separation was observable. A marked decrease in the diffusion current and increasing irreversibility of the wave accompanied increase in the water concentration.

It already has been demonstrated that small quantities of water have considerable effect on the properties of ions in benzonitrile. The two waves observed for nickel apparently result from a competition between water and benzonitrile for the nickel ion in much the same manner as these two solvents compete for the barium ion. The initial solution contains a sufficient quantity of water to yield an observable amount of the hydrated species in solution. This then accounts for the initial appearance of the second wave. Methyl red apparently changes or breaks up the solvation of the nickel ion by the small amount of water present because the addition of this compound eliminates the second wave. The stoichiometric relationship between the concentration of nickel ion and the methyl red concentration which eliminates the second wave indicates that the effect of methyl red takes place at or near the surface of the mercury drop. Since methyl red is present in such low concentration (0.005%), there is not enough to interact with all of the hydrated nickel species in solution. If it were a direct interaction with nickel in the bulk of the solution, the wave obtained would still show a considerable portion of the hydrated species.

A single well-defined wave was obtained for the reduction of 0.1 mmolar solution of nickel(II) perchlorate, but the $E_{1/2}$ value was shifted more positive by 0.07 v.[15]

The reduction of manganese, zinc and cadmium ions in benzonitrile gives peak-type polarograms in the absence of maximum suppressors. The peaks observed for manganese and zinc ions are small and easily suppressed by 0.001% of the sodium form of methyl red. With cadmium ion the peak is steep followed by a minimum. The polarographic maximum of cadmium ion and the minimum which followed were eliminated by decreasing the cadmium ion concentration to 1 mmolar and making the solution 0.005% with respect to the sodium form of methyl red.

The polarographic wave of aluminum(III) perchlorate has a well-defined diffusion plateau, but the foot of the wave is considerably drawn out. The addition of small amounts of water results in peak-type waves. These peaks are not suppressed by the sodium form of methyl red.

The reduction of chromium(III) proceeds stepwise with the successive formation of chromium(II) ion and metallic chromium. The height of the second wave is *ca.* twice that of the first. The first wave starts at 0.0 volt and rises gradually to a rounded maximum at *ca.* −0.4 volt *vs.* s.c.e. The second wave has a slightly rounded maximum which is eliminated by 0.001% of the sodium form of methyl red to give a well-defined wave. Polarograms obtained by dissolving the hexahydrate were essentially the same as for those of the anhydrous salt.

Iron(II) perchlorate yields a polarographic wave with a slight peak which is suppressed easily with 0.001% Surfactol-100.

The polarographic reduction of millimolar solutions of copper(II) reveals an interesting current phenomenon similar to that reported by Popov and Geske[6] for the reduction of this ion in acetonitrile. An abnormally large current rises from the potential at which dissolution of mercury occurs, levels off and continues to a potential of −0.4 volt *vs.* s.c.e. at which point it suddenly drops to a well-defined diffusion plateau. The effect of methyl red on the wave for copper is shown in Fig. 4. The potential at which the maximum drops may be shifted to more positive values by the addition of methyl red, ethyl cellulose or α-naphthol. The dotted curve shows the peak obtained in the absence of maximum suppressors. With 0.002% methyl red the drop to the diffusion plateau occurs at +0.3 volt *vs.* s.c.e. Under these conditions a well-defined polarographic wave is revealed accounting for exactly one-half of the total diffusion current obtained (broken curve). The slope obtained from this wave is 0.059, and the process is undoubtedly the reversible reduction of copper(I) to metallic copper. The Cu(II) → Cu(I) wave may be obtained at the dropping mercury electrode but only with a methyl red concentration comparable to the copper ion concentration (solid curve). With concentrations of methyl red below the copper ion concentration, the wave is only partially defined.

With 0.1 mmolar solutions of copper(II) perchlorate, this current phenomenon was not observed.

Popov and Geske[6] have interpreted the phenomenon of the abnormally large current obtained for the first step of the reduction of this ion as an interaction of the oxidant with the mercury drop to yield a mercury maximum. That this is probably not the case was demonstrated by the reduction of copper(II) perchlorate in benzonitrile at a rotating platinum electrode. With this technique a trace similar to that observed at the dropping mercury electrode was obtained, commencing at + 1.0 volt, proceeding through an abnormally large maximum current and finally dropping to a lower steady value at − 0.3 volt *vs.* s.c.e.

The reduction of copper(II) to copper(I) was also studied chronopotentiometrically. A well-defined but highly irreversible wave was obtained with an $E_{1/4}$ (analogous to polarographic $E_{1/2}$) value of +0.9 volt *vs.* s.c.e. This value is comparable to that obtained at the rotating platinum electrode. The copper(II) to copper(I) wave observed at the dropping mercury electrode with high concentrations of methyl red, therefore, must be due to the reduction of a copper(II) methyl red complex.

TABLE II

EFFECT OF SUPPORTING ELECTROLYTE ON HALF-WAVE POTENTIALS IN BENZONITRILE

	Et_4NClO_4		$LiClO_4$		
Compound	$E_{1/2}$	Slope	$E_{1/2}$	Slope	$\Delta E_{1/2}$[a]
$Ba(ClO_4)_2$	−1.58	0.032	−1.69	0.034	0.11
$Cr(ClO_4)_3$					
Cr(II)/Cr(O)	−0.97	.034	−1.04	0.044	.07
$Mn(ClO_4)_2$	− .98	.032	−1.11	.048	.13
$Fe(ClO_4)_2$	− .79	.038	−0.91	.041	.12
$Co(ClO_4)_2$	− .49	[b]	− .61	[b]	.12
$Ni(ClO_4)_2$	− .29	.059	− .37	[b]	.08
$Zn(ClO_4)_2$	− .53	.030	− .61	[b]	.08
$Cd(ClO_4)_2$	− .17	.032	− .24	.032	.07
$Al(ClO_4)_3$	−1.47	.048	−1.41	.038	− .06

[a] $\Delta E_{1/2} = E_{1/2}(Et_4NClO_4) - E_{1/2}(LiClO_4)$. [b] Maximum.

The polarographic behavior of iron(III) perchlorate is similar to that of copper(II) perchlorate. The half-wave potential of the ferric-ferrous couple is more positive than the potential for the dissolution of mercury; therefore an approximate value was obtained utilizing a rotating platinum electrode. The results of this study show that ferrous ion is irreversibly oxidized to ferric ion at a half-wave potential *ca.* +1.2 volt *vs.* s.c.e. Poor, difficult to evaluate and interpret current–voltage curves were obtained for the reduction of ferric to ferrous and ferrous to metallic iron at a rotating platinum electrode. From chronopotentiometric study, $E_{1/4}$ values of + 0.7 and −0.6 volt *vs.* s.c.e. were obtained for the reduction of ferric to ferrous and ferrous to metallic iron. The ferric to ferrous potential is markedly different from that for the oxidation of ferrous to ferric, but the ferrous to metallic iron potential is in fair agreement with that observed polarographically. Reverse scan (oxidation) after reduction of a ferric solution gave two step chronopotentiograms with $E_{0.22}$ values of +0.1 and +1.3 volt *vs.* s.c.e. corresponding to the oxidation of metallic iron to ferrous and ferrous to ferric.

Lithium Perchlorate as Supporting Electrolyte.—With the exception of aluminum ion, which is shifted in the positive direction, the metal ion perchlorates are reduced at more negative half-wave potentials in benzonitrile with 0.1 *M* lithium perchlorate than with 0.1 *M* tetraethylammonium perchlorate as supporting electrolyte. Table II lists the half-wave potentials for the reduction of the metal ions in each of the supporting electrolytes.

Effect of Supporting Electrolytes on the Half-wave Potential of Manganese(II).—The effect of supporting electrolytes on the polarographic reduction of manganese(II) was investigated in benzonitrile and acetonitrile. With 0.1 *M* lithium, sodium, and magnesium perchlorates as supporting electrolytes, the same half-wave potential is observed for the reduction of manganese in acetonitrile. The value (−1.15) is definitely more negative than that obtained with 0.1 *M* tetraethylammonium perchlorate as supporting electrolyte (−1.11).

A comparison of the half-wave potentials obtained for the reduction of manganese in benzonitrile with tetraethylammonium perchlorate and lithium perchlorate as supporting electrolytes has been presented in Table II. With 0.1 *M* magnesium perchlorate as supporting electrolyte, the reduction occurs at a half-wave potential of −1.10 volt *vs.* s.c.e. Sodium perchlorate is not sufficiently soluble in benzonitrile to be used as a supporting electrolyte.

The shifts observed between tetraethylammonium perchlorate and the other perchlorates as supporting electrolytes do not appear to be due to differences in liquid-junction potentials because shifts would also have been observed between values obtained with lithium, sodium and magnesium perchlorates as supporting electrolytes. That the shift is not a liquid-junction effect is also apparent from the data presented in Table II. The magnitude of the shifts does not remain constant, as would be expected if the shifts were due to a difference in the liquid-junction potential of the two supporting electrolytes, but changes with the ion undergoing reduction.

Discussion

The half-wave potentials in benzonitrile fall generally in the same order as those in acetonitrile, which is expected because of the chemical similarity of the two solvents. The reader is referred to the papers of Kolthoff and Coetzee and Popov and Geske for a discussion of the difference between the nitriles and water as solvents. Of greater interest, however, is the shift of the half-wave potentials to less negative values in benzonitrile.

As already has been discussed (effect of supporting electrolytes on the polarographic reduction of manganese ion), there is a shift in half-wave potentials for the reduction of metal ions in changing from tetraethylammonium perchlorate supporting electrolyte to sodium perchlorate supporting electrolyte. The half-wave potentials in acetonitrile are *ca.* 0.04 volt less negative with tetraethylammonium perchlorate as supporting electrolyte. Even with this correction applied where sodium perchlorate was the supporting electrolyte used, there still remains a decided difference in half-wave potentials in acetonitrile as compared with benzonitrile. Current investigation[18] in this Laboratory shows that when cations are added to these two nitriles new C≡N peaks appear in the 2240–2275 cm.$^{-1}$ infrared region. The $\Delta\nu$ values of the new C≡N peaks from that for the pure nitriles are larger for benzonitrile than acetonitrile which indicates that benzonitrile interacts more strongly with cations than does acetonitrile. Therefore, benzonitrile must be more basic than acetonitrile. The work of French and Roe[19] on the ionization of picric acid in acetonitrile and benzonitrile also indicates a greater availability of electrons (basicity) in benzonitrile. One can only conclude then that metal ions are more strongly solvated by benzonitrile than acetonitrile. The less negative values of the half-wave potentials for the reduction of metal ions in benzonitrile as compared to acetonitrile cannot, therefore, be explained on the basis of lower solvation energies arising from the less basic character of benzonitrile.

A plausible explanation for the ease of reduction of cations in benzonitrile consistent with the foregoing information is that the electrode process involves benzonitrile molecules constituting the solvation sphere serving as bridges for electron transfer.[20,21] Since acetonitrile and benzonitrile contain the C≡N group, the difference obviously is due to the contribution of the delocalized electrons of the phenyl ring in benzonitrile. The ease of reduction may also be in part the result of the fact that the dielectric constant of benzonitrile (25) is lower than that of acetonitrile (36).

Benzonitrile containing tetraethylammonium perchlorate does not exhibit a new C≡N peak in the infrared—an indication that the weak charge density around this large ion is insufficient to bring about an interaction with the benzonitrile molecule. The more negative half-wave potentials of metal ions with lithium, sodium, or magnesium perchlorate as supporting electrolyte are probably the result of these ions interacting with benzonitrile or acetonitrile and thereby decreasing the ability of the nitrile to function as an electron sink in the bridge mechanism.

It appears from the results of this investigation that the less negative values of the half-wave potentials of metal ions in acetonitrile and benzonitrile as compared to those in water are not the result solely of the lower solvation energies arising from the less basic character of the nitriles but also of a bridge mechanism involving the nitriles.

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Studies on Hydrolyzed Bismuth(III) Solutions. II. Light Scattering[1]

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The polymerization of the aquo-bismuth(III) ion has been investigated by light scattering measurements at 25°. In solutions where *ca.* 2 hydroxide ions are bound, on the average, per bismuth atom, the degree of polymerization was found to be 5.6. $NaClO_4$ was used as a supporting electrolyte to give $[Na^+] + [H^+] = 1.000\ M$. The value of the charge on the complex, *ca.* 4, indicates that some binding of gegenions from the solution occurs; the predominant complex, therefore, has the approximate formula $Bi_6O_6(ClO_4)_2^{+4}$. Measurements of the apparent molar refraction and apparent molar volumes of hydrolyzed and unhydrolyzed bismuth solutions show that both the molar refraction and molar volume of the bismuth-containing cation increase slightly as a result of the hydrolysis. The absence of depolarization suggests that the complex has a symmetrical rather than a chain structure.

Introduction

In a previous communication,[3] equations were derived relating the turbidity of solutions containing polynuclear complexes and supporting electrolyte to the charge and degree of polymerization of the complexes. These relations were tested with certain idealized systems similar to those used by Johnson, Kraus and Scatchard[4] in testing equations derived for the interpretation of sedimentation equilibrium experiments in an ultracentrifuge with a Schlieren optical system. These idealized systems were chosen to represent conditions found in systems with polymerized aquo-acids and bases.

In order to test further the relations describing the scattering of highly charged, low molecular weight species in the presence of supporting electrolyte, it was decided to study the light scattering of highly hydrolyzed bismuth(III) solutions. This system has been investigated by Holmberg, Kraus and Johnson[5] using sedimentation equilibrium measurements in the centrifuge with Schlieren optics. These experiments indicated that there were 5 or 6 bismuth atoms in the predominant complex present in solutions with *ca.* 2 hydroxide ions bound per bismuth atom. Some complexing

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