Conclusions

The values found for the replacement of one molecule of H_2O coördinated to Cu^{+2} by acetone (3.7) or by alcohol (1.8) are not unexpected. If it is assumed that the aquo ion is octahedral with but slight distortion, a statistical value of 6 for the equilibrium constant applies since there are six ways of replacing H_2O and but one of replacing acetone or alcohol. That the measured values do not differ much from the statistical expectation is consistent with the lack of significant spectral shifts, indicating that ligand field strengths of H_2O, acetone, and alcohol are about equal. Co^{+2} and Ni^{+2} have sharper absorption bands than does Cu^{+2} and their spectra show that the ligand field strengths for the three ligands, although nearly equal, decrease slightly: $H_2O >$ acetone $>$ alcohol. Consequently, the K_1 values show the trend expected purely on the basis of ligand field stabilization. All other factors, such as differences of inter-ligand interactions and differences of solvation outside the primary solvation shell, apparently are either small or tend to cancel.

The values found for the replacement of a second molecule of H_2O coördinated to Cu^{+2} by acetone (3.1×10^{-3}) and by alcohol (3.9×10^{-2}) are smaller than expected. If the second replacement occurs *cis* to the first, the statistical constant would be 2; if *trans*, 0.5. Space-filling molecular models show that a *cis* product cannot be dismissed on steric grounds. However, Jahn–Teller distortion for the copper ion could favor a *trans* product. In any case, the observed K_2 values are low even for the *trans* case. Two causes for the low values can be imagined. One would involve a specific interaction within the complex species, *e.g.*, *trans* effect, if the product is indeed *trans;* the other would be a general solvent effect operating from without, *e.g.*, a difference of solvation of product and reactants by the solvent in question. It is difficult to decide the relative importance of these two explanations, but what evidence there is would indicate that the second is of major importance. It would seem that a *trans* effect, or other specific interaction, should be most pronounced for the two more different ligands, *i.e.*, should depress K_2 more for alcohol than for acetone, whose ligand field strength is intermediate between H_2O and ethanol. This is contrary to fact. On the other hand, the solvent effect should cause the greater difference for the case of changing the solvent from mainly water to mainly acetone as opposed to a change from water to the more water-like alcohol. Whatever the cause, the abnormal depression of K_2 by both solvents is completely consistent with the failure to replace more than two of the first sphere solvent molecules by either acetone or ethanol.

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Polarography of the Rare Earth Elements and Other Inorganic Substances in Acetone as Solvent

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Cations, particularly the solvated proton and metal ions of high charge type, generally are reduced at less negative potentials in acetone than in water. The half-wave potentials (*vs.* the aqueous saturated calomel electrode) obtained at the dropping mercury electrode in 0.1 *M* tetraethylammonium perchlorate as supporting electrolyte were (in volts, with an asterisk denoting a reversible or near-reversible electro-reaction): oxygen, −0.92 and −1.4; sodium, −1.92; potassium, −1.97*; rubidium, −1.97*; magnesium, −1.75; cadmium, −0.18*; silver, more positive than the anodic discharge potential of mercury (+0.68 v.); copper(II) → copper(I), +0.53*; copper(I) → copper amalgam, +0.31*; samarium, europium, and ytterbium, a first wave (III → II) at −1.13*, −0.03, and −0.71*, respectively, and a second (2-electron) wave at −1.70, −1.79, and −1.71, respectively. All other rare earth elements gave only one (3-electron) wave near −1.4 v., with some irregularities, shown to be caused by solvolysis effects. It is likely that the second (2-electron) wave of samarium, europium, and ytterbium, as well as the single (3-electron) wave of the remaining rare earth elements, is caused by hydrogen evolution, rather than by amalgam formation. It is shown that the overpotential of hydrogen on mercury is approximately 0.8 v. smaller in acetone than in water. Iodide ion gives two anodic waves at the dropping mercury electrode, corresponding to successive formation of HgI_3^- and HgI_2, with half-wave potentials equal to −0.37* and +0.20* v.

Introduction

Acetone has been neglected as a solvent for electrochemical studies. Very few systematic quantitative investigations have been carried out in essentially anhydrous acetone, and these have been limited mainly to the conductometry of salts, particularly those of

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[2] From the M.S. thesis of Wei-San Siao, University of Pittsburgh, 1961.

substituted ammonium bases.[3–5] To our knowledge, only three polarographic studies (of somewhat limited scope) have been reported for acetone as solvent. Arthur and Lyons[6] obtained well defined reduction waves for acid chlorides and bromides, but erratic and incompletely developed waves for cadmium (in lithium chloride as supporting electrolyte).[7] Ozerov and Yakovleva[8] obtained polarograms for copper(II) and zinc chlorides, strontium and bismuth nitrates, cadmium iodide, and copper(I) bromide, with and without supporting electrolyte added (0.5 *M* lithium nitrate). Migal, *et al.*,[9] studied the polarography of hydrogen chloride in acetone and acetone–water mixtures with lithium chloride as supporting electrolyte, and found that the diffusion current constant increases with increasing concentration of hydrogen chloride.

For *practical* voltammetric analysis, acetone has several disadvantages. Its vapor pressure at ordinary temperatures is so high (229 mm. at 25°)[10] that it is essential to presaturate any gas which is used for deaeration with acetone vapor. Acetone is highly flammable and forms explosive mixtures with air (but it is not unduly toxic). It is very hygroscopic, and it is difficult to reduce its water content to below approximately 2×10^{-2} *M* without causing aldol-type condensation, which is catalyzed by both acid and base. Even those drying agents which are only mildly acidic (such as anhydrous magnesium sulfate) or mildly basic (such as alumina) cause significant condensation.[10a] Finally, solutions of the stronger acids in acetone are by no means ideally stable. On the credit side, acetone is a fair solvent for inorganic substances and a good one for many organic compounds. It has a convenient liquid range (−95.35 to +56.24°), a very low viscosity (0.316 cp.; *cf.* water, 0.894), and a dielectric constant (20.7) which is sufficiently high to make simple and convenient voltammetric instrumentation feasible. Furthermore, technical grade acetone is reasonably pure and relatively inexpensive, and it can be purified further quite easily (except if its water content must be reduced to a very low level).

For *theoretical* studies, acetone is a very interesting solvent. It is a typical and important example of a strongly differentiating "non-waterlike" solvent with an intermediate dielectric constant. It is comparatively inert, with acid and base properties that are weaker than those of water, although apparently not as weak as those of acetonitrile. In certain acid–base and other reactions it resembles acetonitrile more closely than it does water or the alcohols. Its enol content is very low (2.5×10^{-4}%),[11] and probably need not be considered in most reactions.

Experimental

Purification of Solvent.—Technical grade acetone was dried over anhydrous calcium sulfate, Drierite, (25–50 g./l.) for 2 weeks, with occasional shaking. It then was decanted and distilled from fresh Drierite (10 g./l.) under a high reflux ratio through a 65 × 2.5 cm. vacuum jacket column packed with glass helices. The first and last 10% fractions were rejected. The purified solvent (b.p. 56.2°) was stored in brown bottles, from which it was dispensed by means of glass siphons. During distillation and dispensing, contact with the atmosphere was made through a small drying tube packed with anhydrous magnesium perchlorate (*caution:* acetone vapor in contact with magnesium perchlorate constitutes an explosion hazard). The water content of the solvent was determined by the acetyl chloride method of Bryant, Mitchell, and Smith,[12] and also by measuring the volume of hydrogen evolved by calcium hydride (with due allowance for the slow reaction of calcium hydride with acetone itself.)[13] The conventional (direct) Karl Fischer method is not applicable, since the (alpha) hydrogen atoms of acetone are readily substituted by halogens. Various batches of acetone purified as described above generally contained between 15 and 25 m*M* water. Such concentrations of water are by no means ideally low, but it was considered preferable for most purposes to leave this water in the solvent, rather than risk contamination with condensation products introduced by more powerful drying agents. For one experiment only, in which the presence of water would have been particularly objectionable (polarography of perchloric acid), the solvent was first distilled from Drierite, and then from a small amount of phosphorus pentoxide, when the solvent in the distillation flask turned red; only the middle 50% fraction (correct b.p.) was collected.

Other Chemicals.—Tetraethylammonium perchlorate, which was used throughout as supporting electrolyte, was prepared as described elsewhere.[14] The rare earth metal perchlorates were prepared from weighed amounts of the corresponding oxides (99.8–99.9% pure, obtained from American Potash and Chemical Corporation, Lindsay Chemical Division) by a method described before.[15] Cadmium perchlorate was prepared in a similar manner from a weighed amount of cadmium oxide, obtained by heating reagent grade cadmium carbonate to 600°. Sodium perchlorate monohydrate (Fisher Purified) was recrystallized from water and dried in a vacuum oven at 100°. Reagent grade potassium iodide (Allied), rubidium iodide (Fisher), and anhydrous magnesium perchlorate (Fisher) were dried at 110°. Copper(II) perchlorate hexahydrate (G. F. Smith) was dried in a current of dry air at room temperature for 2 hr.; the concentration of the solution was calculated on the assumption that the solute was the hexahydrate. Silver perchlorate (G. F. Smith) was dried in a vacuum oven at 50°. Perchloric acid (Allied) was used in the form of an anhydrous solution in acetic acid as solvent, prepared as described elsewhere.[16] Sulfuric acid (Allied) was used in the form of a 96% by weight solution in water.

Polarographic Cell.—The dropping mercury electrode (hereafter designated d.m.e.) had these characteristics at a mercury

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[3] P. Walden, H. Ulich, and G. Busch, *Z. physik. Chem.*, **123**, 429 (1926).

[4] M. B. Reynolds and C. A. Kraus, *J. Am. Chem. Soc.*, **70**, 1709 (1948).

[5] M. J. McDowell and C. A. Kraus, *ibid.*, **73**, 3293 (1951).

[6] P. Arthur and H. Lyons, *Anal. Chem.*, **24**, 1422 (1952).

[7] In solvents such as acetone or acetonitrile, which have only slight hydrogen bonding capacity, solvation of anions is generally very weak, with the result that anion complexes of metals (such as the chloro complexes of cadmium) are very stable. It is reported in this communication that with the non-complexing salt tetraethylammonium perchlorate as supporting electrolyte, cadmium gives a well defined, nearly reversible wave in acetone as solvent.

[8] A. M. Ozerov and A. V. Yakovleva, *Zh. Priklad. Khim.*, **29**, 124 (1956); *Chem. Abstr.*, **50**, 10565 (1956).

[9] P. K. Migal, Ya. I. Tur'yan, and N. I. Bondarenko, *Zh. Fiz. Khim.*, **30**, 2301 (1956); *Chem. Abstr.*, **51**, 8549 (1957).

[10] All physical constants quoted (for 25°, if temperature dependent) were obtained from: (a) A. Weissberger and E. S. Proskauer, "Organic Solvents," 2nd Ed., revised by J. A. Riddick and E. E. Toops, Jr., Interscience, New York, N. Y., 1955; (b) "International Critical Tables" (1928).

[11] G. Schwarzenbach and C. Wittwer, *Helv. Chim. Acta*, **30**, 669 (1947).

[12] W. M. D. Bryant, J. Mitchell, Jr., and D. M. Smith, *J. Am. Chem. Soc.*, **62**, 3504 (1940).

[13] J. F. Coetzee and W.-S. Siao, unpublished results.

[14] I. M. Kolthoff and J. F. Coetzee, *J. Am. Chem. Soc.*, **79**, 870 (1957).

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

[16] J. F. Coetzee and I. M. Kolthoff, *ibid.*, **79**, 6110 (1957).

height (uncorrected for back pressure) of 70 cm.: m = 1.54 mg./sec., t = 4.5 sec. with open circuit in a 0.1 M solution of tetraethylammonium perchlorate in acetone. The aqueous saturated calomel electrode (s.c.e.) served as reference electrode. A special salt bridge, described before,[14] was used to prevent accidental introduction of water into the electrolysis solution. The complete cell (d.m.e. plus salt bridge plus s.c.e.) had a resistance of approximately 1000 ohms (at maximum drop size) with 0.1 M tetraethylammonium perchlorate as supporting electrolyte. All potentials were corrected for the iR-drop across the cell.

Recording of Polarograms.—All polarograms were obtained with a recalibrated Leeds and Northrup Electrochemograph Type E recording polarograph. For the analysis of polarograms, rising sections of waves were obtained manually. Electrolysis solutions were deaerated with nitrogen (Airco Prepurified) which had been presaturated with acetone vapor in a train of wash bottles containing acetone, using efficient gas dispersion tubes (Fisher medium porosity) in the wash bottles and also in the electrolysis solution.

All data reported apply to a temperature of 25°, with the d.m.e. in 0.1 M tetraethylammonium perchlorate as supporting electrolyte and the s.c.e. as reference electrode.

Results and Discussion

Selected Alkali and Other Metal Ions.—Well defined waves were obtained for the reduction of sodium, potassium, rubidium, cadmium, and copper(II) salts in acetone as solvent (Table I). Silver and magnesium perchlorates gave waves with well defined diffusion plateaus, but the silver wave exhibited a maximum, while that of magnesium was not symmetrical, its upper section (corresponding to *ca.* 25% of the total height) being somewhat drawn out. The behavior of magnesium is similar to that of the rare earth elements (see below). From the analytical point of view, the polarography of magnesium presents no problem in acetone, while it is very unsatisfactory in water.

It is seen from the results presented in Table I that the waves of potassium and rubidium are reversible, while that of cadmium approaches reversibility. Copper(II) gives two reversible waves of approximately equal height, corresponding to the successive reductions II → I and I → 0 (amalgam). Stepwise reduction of copper(II) also is observed in acetonitrile[15] and isobutyronitrile,[17] but not in non-complexing aqueous solutions. Silver ion is reduced at relatively positive potentials in acetone, as it is in water, but not in acetonitrile or isobutyronitrile.

Voltammetric data obtained in acetone, acetonitrile,

TABLE I

POLAROGRAPHY OF SELECTED CATIONS IN ACETONE AS SOLVENT

Salt[a]	Concn., $M \times 10^3$	I_d[b]	Slope[c]	$(E_{1/2})_{\text{acetone}}$[d]	$(E_{1/2})_{\text{water}}$[d]
$NaClO_4$	*ca.* 6	. . .	0.12	−1.92	−2.11
KI	1.03	2.70	.060	−1.97	−2.13
RbI	0.51	2.76	.059	−1.97	−2.03
	1.02	2.76	.059	−1.97	. . .
$Mg(ClO_4)_2$	*ca.* 1	. . .	*ca.* 0.06[e]	−1.75	*ca.* −2.2
$Cd(ClO_4)_2 \cdot aq.$	0.80	4.52	0.035	−0.18	−0.59
$Cu(ClO_4)_2 \cdot aq.$					
II → I	0.64	2.14	.056	+0.53	[h]
I → 0		2.26	.055	+0.31	[h]
$AgClO_4$	1.01	2.59	[f]	[f,g]	[f]

[a] Supporting electrolyte: 0.1 M $(C_2H_5)_4NClO_4$. [b] Diffusion current constant $I_d = i_d/Cm^{2/3}t^{1/6}$. [c] Slope of $E_{\text{d.m.e.}}$ *vs.* log $[i/(i_d - i)]$ plot, equal to $0.059/n$ v. for reversible reduction, where n = number of electrons involved. [d] All half-wave potentials *vs.* aqueous saturated calomel electrode. See also note *e* under Table II. [e] For major (initial) section of wave. However, wave is not symmetrical; see text. [f] Not true wave: Ag^+ already is reduced at potentials more positive than that at which anodic dissolution of Hg begins. [g] Maximum in region +0.68 to +0.35 v. [h] Direct reduction of Cu(II) to Cu^0 (amalgam).

TABLE II

POLAROGRAPHY OF THE RARE EARTH ELEMENTS IN ACETONE, AND COMPARISON OF HALF-WAVE POTENTIALS IN ACETONE, ACETONITRILE, AND WATER

	In acetone as solvent				Half-wave potentials[c,e]		
Element	$M \times 10^3$[a]	Reduction	I_d[b]	E_d[c,d]	Acetone[a,f]	Acetonitrile[a,f,g]	Water[h,i]
Pr	0.976	$3e^-$	5.9	−1.30	−1.47	−1.5	−1.8
Nd	.989	$3e^-$	5.4	−1.30	−1.49	−1.5	−1.82
Sm	.994	III → II	1.94	−1.04	−1.13	−1.62	−1.80
		II + $2e^-$	3.90	−1.53	−1.70	[j]	−1.96
Eu	1.101	III → II	1.87	+0.15	−0.03	+0.15	−0.67
		II + $2e^-$	3.79	−1.69	−1.79	−1.67	[j]
Gd	0.496	$3e^-$	6.1	−1.20	−1.49	−1.5	−1.8
Tb	1.038	$3e^-$	5.8	−1.25	−1.38		−1.85
Dy	.144	$3e^-$	5.6	−1.27	−1.44		−1.85
Ho	0.983	$3e^-$	5.5	−1.28	−1.44		−1.85
Er	1.027	$3e^-$	5.8	−1.28	−1.43		−1.85
Tm	0.994	$3e^-$	5.8	−1.25	−1.44		−1.85
Yb	.997	III → II	2.06	−0.58	−0.71	−0.57	−1.17
		II + $2e^-$	4.09	−1.42	− .71	−1.69	[j]

[a] Perchlorates in all cases, with 0.1 M $(C_2H_5)_4NClO_4$ as supporting electrolyte. [b] Diffusion current constant $I_d = i_d/Cm^{2/3}t^{1/6}$. [c] All potentials *vs.* aqueous saturated calomel electrode. [d] E_d = decomposition potential (beginning of wave). Slope of III → II wave of Sm, Eu, and Yb = 0.067, 0.12, and 0.064 v., respectively. Slope of II + $2e^-$ wave of Eu = 0.058 v. See also note *f*. [e] Half-wave potentials of reversible waves obtained in usual manner from $E_{\text{d.m.e.}}$ *vs.* log $[i/(i_d - i)]$ plots. For irreversible waves, apparent half-wave potentials taken at $i = i_d/2$. [f] Irregularities present in waves near −1.8 v. in acetone and −1.6 v. in acetonitrile. Attributed to solvolysis effects; see text. [g] Reference 15. [h] Supporting electrolyte: LiCl for Pr and Gd, $(CH_3)_4NI + H_2SO_4$ for Nd and Sm, NH_4Cl for Eu and Yb, none added for remaining elements. [i] Collected from references given in I. M. Kolthoff and J. J. Lingane, "Polarography," 2nd Ed., Interscience, New York, N. Y., 1952. [j] No wave reported.

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(17) J. F. Coetzee and J. L. Hedrick, to be published.

isobutyronitrile, and water will be compared in a subsequent communication.

Acetone is a suitable solvent for polarographic studies of very electropositive (active) metals, since (a) its cathodic polarization limit is at a relatively negative potential (—2.46 v.), and (b) the reduction potentials of these metals are less negative in acetone than in a solvent such as water. In addition to the active metals listed above, special attention was devoted to the polarography of the rare earth elements, which is incompletely understood even for water as solvent.

Rare Earth Elements.—The results obtained with solutions of the perchlorates of 11 rare earth elements in acetone as solvent are presented in Table II. Only three of these elements (samarium, europium, and ytterbium) are reduced to the divalent state (as in water and acetonitrile). Europium also gives a well defined second wave corresponding to a 2-electron reduction, but 1 mM solutions of ytterbium(III) and samarium(III) each appears to give three waves of approximately equal height, with a total diffusion current corresponding to a 3-electron reduction. The remaining elements, at a concentration of approximately 1 mM (0.5 mM in the case of gadolinium), appear to give two waves each, with the first approximately twice as high as the second, and the total diffusion current again corresponding to a 3-electron reduction. If no further evidence were available, it might be concluded that in all cases except that of europium stepwise reduction to the univalent state occurs in acetone.[18] That this is not the case is proved by the results of additional experiments, which showed that the narrow plateau near −1.65 v. (Fig. 1, curves A and B) (a) is not present at a lower (4×10^{-4} M) ytterbium concentration, (b) moves to less negative potentials and becomes ill defined at higher (2×10^{-3} M) ytterbium concentrations, (c) is not a regular diffusion controlled plateau (Table III), and (d) is eliminated by adding small amounts of water (curves C and D in Fig. 1). We conclude that this additional, anomalous wave is caused by reduction of solvated protons produced by solvolysis reactions such as

$$M(SH)_n{}^{m+} + SH \rightleftharpoons MS(SH)_{n-1}{}^{(m-1)+} + SH_2{}^+ \xrightarrow{+e^-} SH + \frac{1}{2} H_2 \uparrow$$

where SH is a proton donor (acetone itself, or water, if present in sufficient concentration). This explanation is supported by the observation that as long as the potential remains in the region of the anomalous plateau, the dropping mercury electrode shows erratic behavior, in that the current does not increase regularly during the life of a drop (particularly at higher ytterbium concentrations). This erratic response undoubtedly is caused by formation of an insoluble film of the solvolysis product on the electrode surface. An essentially similar phenomenon has been observed with several active metals in acetonitrile as solvent, and the same explanation was given.[15,20]

It is concluded that reduction of samarium(II), europium(II), and ytterbium(II), and of the remaining rare earth elements in their +3 oxidation states, at the dropping mercury electrode in acetone as solvent, probably leads to hydrogen evolution, and not to amalgam formation.

The following unexplained phenomenon may merit further study. Several current–voltage curves obtained with solutions of ytterbium(III) perchlorate in acetone, using 0.1 M tetraethylammonium perchlorate as supporting electrolyte, exhibited a further increase in current at potentials more negative than −2.1 v. However, these regions were poorly reproducible,

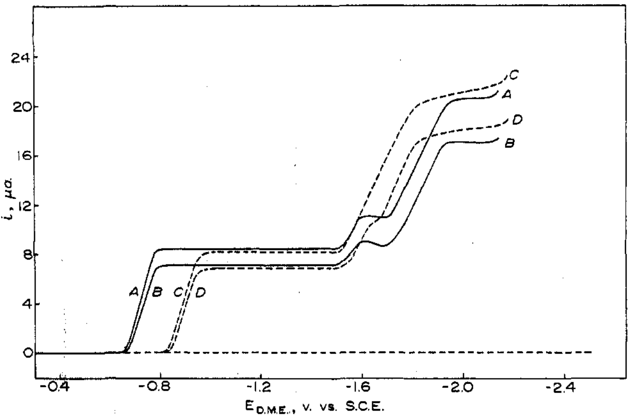

Fig. 1.—Polarography of ytterbium as a function of mercury height and water concentration; in all cases, 2×10^{-3} M $Yb(ClO_4)_3$ with 0.1 M $(C_2H_5)_4NClO_4$ as supporting electrolyte: A and C, h = 80 cm.; B and D, h = 60 cm.; A and B, no water added; C and D, 8×10^{-2} M water added.

TABLE III

EFFECT OF MERCURY HEIGHT ON YTTERBIUM WAVES

Mercury height, cm.[a]	Total current, μa.[b]		
	−1.50 v.	−1.65 v.	−2.00 v.
78 (A)	8.3	11.4	20.7
58 (B)	6.8	8.6	17.1
A/B[c]	1.22	1.33	1.21

[a] Corrected for a back pressure of 2 cm. The interfacial tension, σ, between mercury and many organic solvents is of the order of 350 dynes cm.$^{-1}$. Assuming this value for acetone, and substituting into the expression[19]

$$\text{back pressure} = 7.7 \times 10^{-3} \sigma m^{-1/3} t^{-1/3}$$

it is found that for m = 1.54 mg./sec. and t between 2 and 4 sec., the back pressure is equal to approximately 2 cm. [b] Total current actually measured at the potentials given (values not adjusted for different drop times). In all cases, 2×10^{-3} M $Yb(ClO_4)_3$ in 0.1 M $(C_2H_5)_4NClO_4$. [c] Theoretical value for a current that is entirely diffusion controlled = $(78/58)^{1/2}$ = 1.16.

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(18) A stable +1 oxidation state of a rare earth element has not been reported. For example, see L. B. Asprey and B. B. Cunningham, "Unusual Oxidation States of Some Actinide and Lanthanide Elements," in F. A. Cotton, Ed., "Progress in Inorganic Chemistry," Vol. II, Interscience, New York, N. Y., 1960.

(19) I. M. Kolthoff and J. J. Lingane, "Polarography," 2nd Ed., Interscience, New York, N. Y., 1952, p. 78.

(20) I. M. Kolthoff and S. Ikeda, *J. Phys. Chem.*, 65, 1020 (1961).

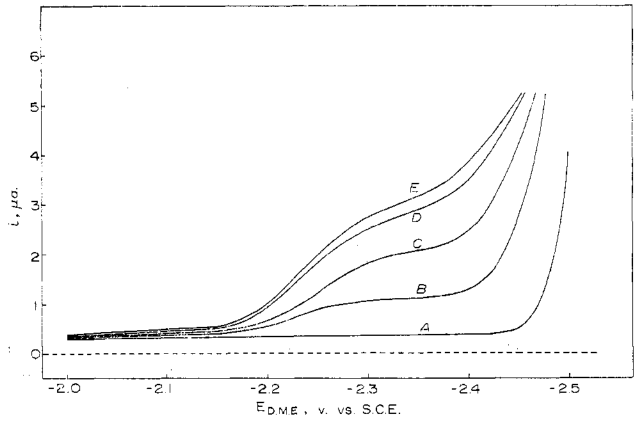

Fig. 2.—Effect of water on residual current curve of acetone: supporting electrolyte, 0.1 *M* $(C_2H_5)_4NClO_4$; A, no water added; B, C, D, and E: 1.7×10^{-2}, 3.4×10^{-2}, 5.6×10^{-2}, and 1.1×10^{-1} *M* water added.

and were not studied further. It is possible that this further increase in current was caused by reduction of free water (see below). In cases where the further increase occurred, the total current at -2.4 v. (corrected for drop time) was considerably more than three times as large as the current on the first wave.

The half-wave potential reported for the first samarium wave in acetonitrile (Table II) seems anomalous, and should be redetermined.

Perchloric and Sulfuric Acids.—Conductance measurements carried out in this Laboratory[21] showed that perchloric acid is extensively (but not completely) dissociated in acetone as solvent ($K_a = 2.5 \times 10^{-3}$). It gives a very well defined wave at the dropping mercury electrode in acetone. For a 1 m*M* solution, with 0.1 *M* tetraethylammonium perchlorate as supporting electrolyte, its half-wave potential is equal to -0.68 v.,[22] and its diffusion current constant is equal to 3.5. On adding water, its half-wave potential shifts very rapidly to more negative values: -0.92, -0.97, -1.00, and -1.10 v. for 2×10^{-2}, 8×10^{-2}, 1.3×10^{-1}, and 5.8×10^{-1} *M* water added, respectively. This shift can be attributed to gradual displacement of the following series of equilibria on adding water, which is a stronger base, and also a better hydrogen bonding agent for anions, than acetone

$$HClO_4 + (CH_3)_2CO \rightleftharpoons (CH_3)_2COH^+ClO_4^- \rightleftharpoons (CH_3)_2COH^+ + ClO_4^- \overset{+H_2O}{\rightleftharpoons} H_2OH^+ + ClO_4^-{}_{\text{hydrated}} + (CH_3)_2CO$$

The diffusion current constant changes very little when small amounts of water are added. Hence the mobilities of the two species of solvated proton (or ion pairs) involved must be very similar.

In the presence of 0.1 *M* tetraethylammonium perchlorate, a large fraction of 1×10^{-3} *M* perchloric acid will be present as undissociated ion pairs. The dissociation constant of tetraethylammonium perchlorate ion pairs, calculated from our Shedlovsky plot for the conductivity data obtained by Walden, Ulich, and Busch,[3] is equal to 5.6×10^{-3}. Hence, for 0.10 *M* tetraethylammonium perchlorate, $[ClO_4^-] = 2.2 \times 10^{-2}$, and if 1.0×10^{-3} *M* perchloric acid ($K_a = 2.5 \times 10^{-3}$) also is present, the solvated proton concentration will be equal to 1.0×10^{-4} *M*. Indicator measurements have shown that acetone is a weaker base than water by approximately four powers of ten (referred to its proton acceptor power).[21] Since the reduction of 1.0 m*M* perchloric acid in the presence of 0.10 *M* tetraethylammonium perchlorate occurs at a potential which is 0.90 v. less negative in acetone than in water (ignoring liquid junction potentials), it follows that the overpotential of hydrogen on mercury is smaller in acetone than in water by approximately $0.90 + (4 \times 0.03) - (4 \times 0.06) = 0.78$ v.

The half-wave potential of 1 m*M* sulfuric acid, with 0.1 *M* tetraethylammonium perchlorate as supporting electrolyte, in acetone containing 2×10^{-2} *M* water, is equal to -1.16 v., and its diffusion current constant is equal to 2.7. Hence, acetone acts as a differentiating solvent in the polarographic reduction of perchloric and sulfuric acids, although not quite as strikingly as acetonitrile does.[16]

Oxygen.—An air-saturated solution of acetone containing 0.1 *M* tetraethylammonium perchlorate gives a well defined reduction wave at the dropping mercury electrode, with a very negative half-wave potential of -0.92 v. and a diffusion current of 28 μa. (for m = 1.54 mg./sec. and t = 4.6 sec.). A small second wave also is produced, rising from -1.3 to -1.5 v., and with a total diffusion current at -1.6 v. of 33 μa. (t = 3.6 sec.). The general features of the polarography of oxygen in acetone apparently are qualitatively similar to those observed in acetonitrile.[16] The reduction mechanism of oxygen in solvents which have very weak proton donor properties is incompletely understood, and should be studied further.

Water.—Addition of water to a 0.1 *M* solution of tetraethylammonium perchlorate in acetone results in the appearance of a small, drawn out wave starting at -2.15 v. (Fig. 2). However, the diffusion current (measured at -2.35 v.) is not directly proportional to the water concentration. This wave may be caused by direct reduction of water, but it also is possible that it results from the presence of some impurity which requires protons for its reduction. A typical example of such behavior is the reduction of acrylonitrile in acetonitrile.[24]

Anodic Waves of Iodide Ion.—Iodide ion (added as both potassium and rubidium iodides) gives two anodic waves at the dropping mercury electrode in acetone as solvent, with 0.1 *M* tetraethylammonium perchlorate as supporting electrolyte. The total anodic diffusion current (I_d = 2.96) is nearly 1.5 times as great as that on the first wave (polarizing in a positive direction).

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[21] J. F. Coetzee and D. K. McGuire, to be published.

[22] Slope of $E_{\text{d.m.e.}}$ *vs.* $\log [i/(i_d - i)]$ plot = 0.071 v. The $E_{\text{d.m.e.}}$ *vs.* $\log [i^{3/4}/(i_d - i)]$ plot[23] is not linear, with gradually decreasing slope (to smaller numbers) as potential becomes more negative.

[23] Reference 19, p. 245.

[24] J. F. Coetzee, G. P. Cunningham, D. K. McGuire, and G. R. Padmanabhan, *Anal. Chem.*, **34**, 1139 (1962).

Iodide, and the other halides as well, behaves in a similar manner in isobutyronitrile as solvent.[17] For both solvents we attribute the formation of the two anodic waves of iodide ion to the successive electro-reactions

$$\mathrm{Hg} + 3\mathrm{I}^- - 2\mathrm{e}^- \rightleftharpoons \mathrm{HgI_3}^-$$

and

$$\mathrm{Hg} + 2\mathrm{HgI_3}^- - 2\mathrm{e}^- \rightleftharpoons 3\mathrm{HgI_2}$$

It can be shown that a plot of the potential of the dropping mercury electrode as a function of the quantity log $[i/(i_\mathrm{d} - i)^3]$ (for the first wave), and log $[i^3/(i_\mathrm{d} - i)^2]$ (for the second wave), should be linear with a slope of 30 mv. in each case for a reversible process. Excellent linear plots were indeed obtained, with slopes of 34 and 32 mv. and half-wave potentials of −0.37 and +0.20 v., respectively.

The anodic waves of halide ions and the stability of mercury(II) halide complexes in various solvents will be discussed elsewhere.[17]

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The System Ammonium Fluoride–Hydrogen Fluoride–Water at 0 and −20°

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The system NH_4F–HF–H_2O has been investigated at 0 and at −20°. The solid phases at 0° are NH_4F, $NH_4F \cdot HF$ and $NH_4F \cdot 3HF$, while at −20°, $NH_4F \cdot HF$, $NH_4F \cdot 3HF$, and H_2O were found.

Introduction

The system ammonium fluoride-hydrogen fluoride-water (NH_4F–HF–H_2O) provides an interesting study for the interaction of three compounds which are quite similar in some respects and in others show quite different properties. The binary phase diagrams of all combinations of the three compounds have been reported.[2–4] Recently, studies of the solid solution of ammonium fluoride in ice have been reported.[5]

We have studied the ternary system at 0 and −20°, using Schreinemakers' wet residue method.[6]

Experimental

Whenever possible, solutions with solid phases were made up from distilled water, reagent grade aqueous HF, and ammonium bifluoride ($NH_4F \cdot HF$). For very low HF concentrations it was necessary to use NH_4F. It was not used for higher HF concentrations since it tends to carry along some water. The solution of $NH_4F \cdot HF$ in solutions of high HF concentration is much less exothermic than that of NH_4F. For very high HF concentrations anhydrous HF was used along with the aqueous HF. The anhydrous HF was the middle fraction obtained from a commercial cylinder. This was distilled from the cylinder into a polyethylene collection bottle and redistilled through an all-polyethylene system. The first and last fractions of each distillation were discarded. The liquid HF could be saturated with $NH_4F \cdot HF$ to reduce its vapor pressure and stored until needed.

Samples of appropriate composition were made up in 1-oz. or 2-oz. narrow-mouthed polyethylene bottles and placed in ethylene glycol–water baths whose temperatures were controlled to +0.02° in the case of the 0° bath and ±0.10° for the −20° bath. Samples were agitated periodically in the bath but were not analyzed for at least 4 days. After that, the liquid phase of one sample out of a given set was analyzed daily until analysis indicated a constant composition. After this, the rest of the samples in the set were analyzed. Usually, at least 5 days was required at 0° and 7 days at −20° for a set of samples to come to equilibrium.

Liquid phase samples were withdrawn from the bottles with a 10-ml. polyethylene syringe fitted with a hypodermic needle, and immediately placed into a tared polyethylene weighing bottle and weighed. Wet residue samples were obtained by decanting most of the liquid phase and removing some of the residue with a thin-bladed spatula. They also were weighed in a tared polyethylene bottle. After the sample weights were obtained, the samples were washed carefully with distilled water into a glass volumetric flask containing excess NaOH solution. Aliquots could be taken for analysis.

All samples were analyzed for nitrogen using the Winkler[7] modification of the standard Kjeldahl technique. Total fluoride was determined by titration in aqueous solution with standard $Th(NO_3)_4$ solution. It was not possible to determine HF directly by a simple acidity titration since the sample solutions provide considerable buffering action.

Discussion and Results

The results of the analyses of the solutions and their wet residues are given in Tables I and II and representative points have been plotted in Fig. 1 and 2. Table III gives the results for one set of samples indicating the existence of $NH_4F \cdot 2HF$ as a solid phase. We were not able to reproduce these results. We assume that these points are not properly part of the equilibrium phase diagram, but rather represent a state of pseudo-equilibrium.

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