H_2O_2 in anhydrous hydrogen peroxide shows "chain conductances" but this is greatly reduced in the presence of water.[5]

Acknowledgment.—One of us, (M.K.), would like to express his appreciation to the Becco Division of the Food Machinery and Chemical Corporation for the invitation to participate in this investigation and two of us (M.K. and G.M.N.), would like to thank the Simonize Company for its contribution to the Illinois Institute of Technology Chemistry Department Fund for fundamental research.

CHICAGO, ILL.

(5) Private communication, W. K. F. Wynne-Jones.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CAPE TOWN]

Electrochemical Behavior in Anhydrous Formic Acid. II. Polarographic Investigation of Some Inorganic Cations

BY T. A. PINFOLD AND F. SEBBA

RECEIVED FEBRUARY 29, 1956

The half-wave potentials of bismuth, antimony, lead, tin, cadmium, thallium, indium, nickel and zinc with a variety of supporting electrolytes in anhydrous formic acid have been measured. These elements were found mostly to give very well defined waves and, with the exception of nickel to undergo reversible reduction. Except in the case of tin and indium, which form weak formato complexes, formic acid showed itself to be a solvent with small solvating power. The series of half-wave potentials was found to follow closely that in aqueous solution with the exception of nickel, zinc and cadmium. The potentials of these elements were more positive than in aqueous solution, a phenomenon which was attributed to hydration of the ions in aqueous solution as opposed to the absence of solvation in formic acid. The diffusion current constants of the elements studied were found to be appreciably lower in formic acid than in water. Anomalous behavior was observed for the half-wave potential of thallium which was found to shift appreciably to more positive values on increase of the supporting electrolyte concentration.

Introduction

Although anhydrous formic acid exhibits all the properties required by a solvent for ideal polarographic characteristics, no study of the dropping mercury electrode in this medium has hitherto been described. Formic acid, besides having a high dielectric constant (56.1 at 25°[1]) and considerable ionizing properties, also exhibits a strong solvent action upon many organic compounds. Furthermore, it has been shown by Pleskov[2] to be a solvent with small complexing power, a feature which enhances its value for the examination of ions which are normally hydrated in aqueous solution. The above author also showed that the standard electrode potentials in formic acid of the elements he studied differed little from the values found in aqueous solution. Exceptional behavior was shown by zinc and cadmium, the potentials of which were displaced to more positive values. This shift was attributed to hydration of the ions in aqueous solution as opposed to the absence of solvation in formic acid.

The present investigation embodies the determination of the half-wave potentials of nine inorganic cations in a variety of supporting electrolytes in anhydrous formic acid and the diffusion current constants for each.

Experimental

Materials.—The purification of the formic acid used is described in a previous paper.[3] The best value of the conductivity found for formic acid was 6.734×10^{-5} mho/sq. cm. All samples of acid used froze at 8.40° and when examined polarographically showed residual currents which were small. To determine the amount of water absorbed by the solvent during a complete polarographic measurement the water content of the anhydrous formic acid after use in a run, was estimated by measurement of the depression of the freezing point and by Karl Fischer titrations. Both methods showed close agreement, a maximum value of 0.07% of water being found.

The following reagents were dried by heating in an oven at 130° for 5 hours and cooled over anhydrous calcium chloride: potassium chloride, tartar emetic, nickel chloride hexahydrate, sodium tartrate, sodium formate, stannous chloride, sodium bromide and cadmium chloride. Sodium citrate was dried at 180° for 3 hours, oxalic acid at 90° for 2 hours and lead acetate at 100° for 3 hours. Ammonium formate was recrystallized from absolute alcohol and then desiccated over concentrated sulfuric acid *in vacuo*. Zinc chloride was dried at 130° for 5 hours and cooled in a stoppered bottle over phosphorus pentoxide. Indic chloride was prepared by treatment of metallic indium with aqua regia and purified by sublimation and dried at 120° for 5 hours. The remainder of the salts used were dried in a desiccator over anhydrous calcium chloride for 5 days.

Apparatus.—All potentials were measured with reference to the quinhydrone-in-formic acid electrode (Q.F.A.E.); the same polarographic cell was used as in the measurements on this electrode previously described.[3] The capillary tube used had an internal radius of 0.0409 mm. and was 12.45 cm. long. All measurements were carried out at 25.00 ± 0.01°. Nitrogen, dried over phosphorus pentoxide, was bubbled through a tube of anhydrous formic acid before being passed through the polarographic cell to remove dissolved oxygen. As it previously had been shown that the measured and calculated values of the drop rate of mercury in formic acid agreed to within 1%, all subsequent values were calculated as described by Kolthoff and Lingane.[4]

Results

The results are tabulated in Table I where the potentials quoted are referred to the saturated calomel-in-formic acid electrode (S.C.F.A.E.). These values were obtained by subtracting -0.538 volt from the potential as measured against the quinhydrone-in-formic acid electrode. Thus the half-wave potential of lead using a 0.5 M sodium formate supporting electrolyte was -0.76^2 volt *vs.* Q.F.A.E. and therefore -0.22^4 volt *vs.* S.C.F.-A.E. A measure of the reversibility of the electrode reaction was obtained by plotting E *vs.*

---

(1) J. F. Johnson and R. H. Cole, THIS JOURNAL, **73**, 4536 (1951).

(2) V. Pleskov, *Acta Physicochim. URSS*, **21**, 41 (1946).

(3) T. A. Pinfold and F. Sebba, THIS JOURNAL, **78**, 2095 (1956).

(4) I. M. Kolthoff and J. J. Lingane, "Polarography," Interscience Publishers, Inc., New York, N. Y., 1952, p. 80.

TABLE I

Supporting electrolyte	Bi^{+++}	Sb^{+++}	Pb^{++}	Sn^{++}	Cd^{++}	Tl^{+}	In^{+++}	Ni^{++}	Zn^{++}
0.5 *M* sodium formate	+0.13(6)	0.00(0)	−0.22(4)	−0.28(1)	−0.33(7)			−0.61[c]	−0.70(6)
0.5 *M* sodium formate + 2% water	+ .12(9)	− .00(3)	− .22(7)	− .28(4)	− .34(2)				− .71(1)
2.0 *M* sodium formate	+ .11(4)	− .02(3)	− .24(2)	− .30(7)	− .35(6)				− .73(3)
0.2 *M* sodium fluoride + 0.5 *M* sodium formate	+ .13(2)			− .33(3)	− .34(4)	−0.38(2)	−0.46(4)		
0.4 *M* sodium fluoride + 0.5 *M* sodium formate	+ .11(7)			− .35(5)	− .34(9)		− .48(5)		
0.5 *M* potassium chloride							− .46(7)		
1.0 *M* potassium chloride							− .49(4)	− .34(4)	
2.0 *M* potassium chloride								− .35(2)	
0.5 *M* potassium chloride + 0.5 *M* sodium formate	− .01(6)[a]	− .07(3)[a]							
1.0 *M* potassium chloride + 0.5 *M* sodium formate	− .05(0)[a]	− .09(3)[a]							
0.2 *M* sodium bromide + 0.5 *M* sodium formate				− .39[b]	− .58(5)		− .46(4)		
.4 *M* sodium bromide + 0.5 *M* sodium formate					− .62(1)		− .48(5)		
.5 *M* potassium sulfate				− .28(2)	− .35(6)	− .40(8)		− .61[c]	− .70(6)
.5 *M* potassium sulfate + 0.5 *M* sodium formate	+ .11(3)	+ .00(4)							
.25 *M* oxalic acid + 0.5 *M* sodium formate	+ .06(7)	− .06(9)[a]	− .27(2)[a]	− .34(6)			− .41(6)		
.5 *M* oxalic acid + 0.5 *M* sodium formate	+ .05(9)	− .08(1)[a]		− .35(9)			− .42(5)		
.25 *M* sodium acetate + 0.5 *M* sodium formate			− .23(2)			− .37(4)			

[a] Accuracy of measurement ±0.005 volt. [b] Accuracy of measurement ±0.02 volt. [c] Accuracy of measurement ±0.1 volt.

log $i/(i_d - i)$ where i_d is the diffusion current and i the current at an applied potential of E. The slope of this plot referred to as tan α should be 0.020, 0.030 and 0.059 for reversible one-, two- and three-electron reductions. The accuracy of the measurements in each case was about ± 0.003 volt, unless otherwise specified. The electro-reducible ion concentration was approximately 10^{-3} g. ions/l. in all the measurements made.

TABLE II

Ion	Diffusion current constant	tan α
Bi^{+++}	2.8	0.018–0.024
Sb^{+++}	3.9	.022 or .023
Pb^{++}	1.9	.029– .033
Sn^{++}	1.8	.033 or .034
Cd^{++}	2.2	.030– .033
Tl^{+}	1.9	
Zn^{++}	2.3	.032– .034
In^{+++}	3.9	
	(monoformato complex)	

No unexpected characteristics were noticed except in the case of the ions of nickel, indium and thallium.

As in aqueous solution, the reduction of nickel was found to proceed irreversibly. The slope of the wave was abnormally small, extending over 0.2 volt. The half-wave potential was greatly influenced by the addition of 1% (v./v.) of water, which changed this characteristic potential by about 0.02 volt, 2% (v./v.) of water causing a shift of 0.05 volt to more negative potentials. This increased negative shift is explained by the great ease of formation of the hexa-aquo nickel ion.

Addition of water also reduced the height of the wave. Water, which has a lower viscosity than formic acid, should, if anything, increase the wave height. This decrease is explained by the appreciable increase in the size of the nickel ion on hydration, a reduction in its diffusion coefficient and a corresponding decrease in the diffusion current.

As in aqueous solution,[5] the addition of chloride ions to the nickel salt solution shifted the reduction potential appreciably to more positive values. The reduction was found to proceed more reversibly, the wave having a more normal slope. These effects appear to be due to the formation of complexes between the chloride and nickel ions which apparently are reduced more reversibly than the uncomplexed nickelous ion.

Indic ions were found to undergo complex formation in a formate supporting electrolyte, giving rise to the ionic species $[In(OOCH)]^{++}$ and $[In(OOCH)_2]^{+}$. This was shown by the occurrence of two distinct slopes in the plot of the half-wave potential against the log of the formate ion concentration. These slopes corresponded to coordination numbers for the metal of one and two. The first of these complex ions was found to undergo a slightly irreversible reduction causing a negative shift in the half-wave potential, which consequently varied depending on the relative amounts of indic and formate ions. A similar phenomenon occurred in sulfate medium where the two com-

---

[5] M. Pablick, *Coll. Czech. Chem. Commun.*, **3**, 223 (1931).

plexes were believed to be $[In(SO_4)]^+$ and $[In(SO_4)_2]^-$. The most positive values of the half-wave potential of indium in the above media was about −0.32 volt *vs.* S.C.F.A.E.

It has been found in aqueous solution that large concentrations of sulfate ion greatly suppressed the diffusion current of indium.[6] Although the diffusion current was decreased by increasing the concentration of sulfate ion in formic acid, the suppression was not much in excess of that expected, due to increase in viscosity of the medium.

The waves obtained from other supporting electrolytes were also well defined. In these media, indium formed strong complexes all of which were reversibly reduced, and hence the half-wave potential, in each, was a constant value.

The reduction of thallium, using a 0.5 *M* sodium formate supporting electrolyte, was found to be irreversible. On increase of the sodium formate concentration, the reduction became more reversible and the half-wave potential shifted in a positive direction. The variation of the half-wave potential with concentration of supporting electrolyte is shown in I, Fig. 1.

To show conclusively that this shift was not due to increase of liquid junction potential, the concentration of sodium formate in the anode and cathode compartments was made the same for each measurement. As the salt effect of the quinhydrone-in-formic acid electrode has been shown to be inappreciable,[3] this operation was permissible. As expected the positive shifts were even greater, showing the liquid junction potential to act in the opposite direction.

It can be seen from II, Fig. 1, at point A that the reduction of thallium first became reversible when the concentration of sodium formate was about 2.7 *M* and the half-wave potential −0.29 volt *vs.* S.C.F.A.E. Thereafter the plot ceased to be curved and a linear relationship was obtained. The value of tan α, having dropped to 0.059 at this concentration, remained constant on further increase of sodium formate.

Although not examined in such detail, the reduction in all the other media was irreversible and increase of the supporting electrolyte decreased both the half-wave potential and the value of tan α as in sodium formate. No waves were obtained using a chloride or bromide supporting electrolyte due to the high insolubility of these thallous salts in formic acid.

It was also noticed that the addition of 2% (v./v.) of water caused a positive shift of 0.003 volt in the half-wave potential instead of a change to more negative values, as with all the other elements.

Diffusion Current Constants.—The measurement of the quantity $i_d/m^{2/3} t^{1/6} c$ was carried out for each element in a supporting electrolyte of 0.5 *M* sodium formate, the values being tabulated in Table II. A value for nickel is not included because of the poor shape of the waves in a formate medium. Due to the higher viscosity of formic acid, 1.329 centipoise,[7] the diffusion current constants are appreciably lower than in aqueous solution.

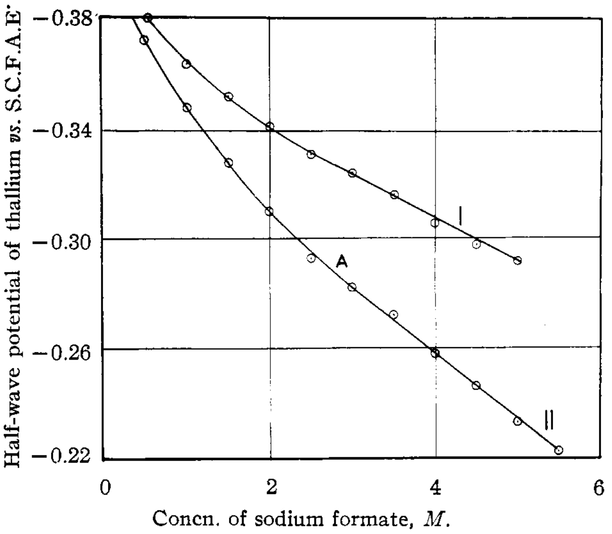

Fig. 1.

It was noticed for several of the above elements that the addition of sodium formate greatly enhanced their solubility in anhydrous formic acid. A similar observation has been made[8] on the increased solubility of cupric formate in formic acid by the addition of ammonium formate.

Discussion

In order to make a comparison between the half-wave potentials in aqueous solution and those in anhydrous formic acid solution, the results have been tabulated in Table III. The potentials in water[9,10] are quoted with reference to the saturated calomel electrode, the supporting electrolyte being 1 *M* nitric acid. The half-wave potential of indium in both solvents was obtained with a 1 *M* potassium chloride supporting electrolyte. The potentials in formic acid are quoted with reference to the saturated calomel-in-formic acid electrode.

TABLE III

Cation	Half-wave potential Formic acid *vs.* S.C.F.A.E.	Water *vs.* S.C.E.	Difference, v.
Bismuth	+0.14	−0.03	0.17
Antimony	.00	− .17	.17
Lead	− .22	− .41	.19
Tin	− .28	− .44	.16
Thallium	− .29	− .47	.18
Indium	− .49	− .60	.11
Cadmium	− .34	− .59	.25
Zinc	− .71	−1.0	.3
Nickel	− .61	−1.1	.5

It will be seen that, with the exception of cadmium, zinc and nickel, there exists an almost constant difference between the values, showing the series of half-wave potentials in the two solvents to be much the same. The anomalous behavior of these three elements is due to lack of solvation in

---

(6) Ref. 4, p. 520.

(7) J. Lange, *Z. physik. Chem.*, **A187**, 27 (1940).

(8) A. W. Davidson and V. Holm, THIS JOURNAL, **53**, 1350 (1931).

(9) Ref. 4, part III.

(10) J. E. Page and F. A. Robinson, *J. Soc. Chem. Ind.*, **61**, 93 (1942).

formic acid, as described earlier by Pleskov.[2] The effect of hydration of these ions may be compared to complex formation, causing a shift of the half-wave potential to more negative values.

It is significant that the value of -0.29 volt *vs.* S.C.F.A.E. for the half-wave potential of thallium is well in accord with the corresponding value in aqueous solution.

Conclusion

The disadvantages of anhydrous formic acid as a solvent for polarographic investigations are due largely to its acidic nature. The use of supporting electrolytes such as cyanides, hydroxides or ammonia is excluded; due to its reducing properties, formic acid solutions of iodides and nitrates are also unsuitable. Further, the range of measurable potentials is restricted to values between $+0.2$ and -0.8 volt *vs.* S.C.F.A.E.

Anhydrous formic acid does, however, show some very useful advantages. Besides being a solvent with small solvating power the addition of as much as 2% (v./v.) of water has been shown to exert little effect. Dissolved oxygen, the presence of which is so undesirable, is more readily removed than from aqueous solution by bubbling nitrogen through the solvent; ten minutes degassing is usually sufficient. Polarographic maxima (over-currents) were seldom encountered in this investigation, their irregular appearance being discussed elsewhere.[11]

Acknowledgment.—The authors wish to express their sincere appreciation to the Council for Scientific and Industrial Research, Pretoria, for a bursary to T.A.P.

(11) F. Sebba and T. A. Pinfold, *J. Colloid Sci.*, **11**, in press (1956).

CAPETOWN, SOUTH AFRICA

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, BROOKHAVEN NATIONAL LABORATORY]

The Radiation Induced Decomposition of Ferrous Ammonium Sulfate[1]

BY EVERETT R. JOHNSON[2]

RECEIVED OCTOBER 12, 1955

The radiation induced decomposition of ferrous ammonium sulfate has been studied by the dissolution of the irradiated salt in deaerated water with subsequent wet and gaseous analyses. The products of decomposition were found to be ferric ion, sulfite ion and hydrogen.

This report concerns some results obtained from a study of the radiation induced decomposition of crystalline ferrous ammonium sulfate and ferrous sulfate (anhydrous and crystalline). More exactly, this work may be described as a study of the chemical effects produced upon the dissolution of irradiated ferrous salts in deaerated water. This research is part of a general program on radiation chemistry being initiated in this Laboratory.

Experimental

C.P. $FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$ (small crystals), $FeSO_4 \cdot 7H_2O$ (small crystals) and $FeSO_4$ (anhydrous powder) as purchased were irradiated with 2 Mev. cathode rays. The sample (about 11 g.) to be irradiated was put into the sample holder and connected to a vacuum line and pumped to a pressure of 10^{-5} mm. Helium at atmospheric pressure was then admitted to the system and the sample holder now filled with gas was removed from the vacuum line and capped. The sample was then irradiated for varying times at room temperature. The irradiated sample was removed from the holder and placed in the vacuum system. When the vacuum was 10^{-6} mm. that portion of the line containing the irradiated sample was isolated and deaerated water distilled onto the sample at liquid N_2 temperature. The sample plus water was warmed to about 40° and maintained at this temperature until the sample dissolved. The solution was now frozen and any liberated gases toeplered over into the analysis portion of the vacuum system. The gases were then analyzed in the usual manner.[3]

The sample holder was simply a shallow aluminum cylinder ($^1/_2$ in. thick, 2 in. i.d., $^3/_{16}$ in. deep) covered with a mica window (0.038 g./cm.^{2}). A $^1/_4$ in. o.d. piece of brass tubing threaded on one end and soldered to a commercial Kovar-glass tapered joint on the other end, served as a connection to the vacuum system. The mica window was held in place by sandwiching it between the aluminum cylinder and a $^1/_2$ in. thick Micarta toroid, 2 in. i.d.

All irradiations were done with 2 Mev. cathode rays from a Van de Graaff accelerator purchased from the High Voltage Engineering Corp.

Ferric ion was determined by dissolving a separate sample in 0.8 *N* H_2SO_4 and measuring the extinction at 305 mμ. Sulfite ion was determined by a method described elsewhere.[4] No interference in the determination of sulfite ion was found by the presence of ferric ion in the concentration range studied.

All chemicals were C.P. and were used as purchased.

Results

Figure 1 shows a plot of the Fe^{3+}, $SO_3^=$ and H_2 produced as a function of dose for a dose rate of approximately 0.63×10^{18} e.v./g./sec. As can be seen the yield of decomposition products is linear up to a dose of 30×10^{19} e.v./g.,[5] after which there was a definite falling off (not shown in Fig. 1) of the yield with absorption of radiation. At a total dose of 3.8×10^{21} e.v./g., the yield of ferric ion was 0.67 molecule 100 e.v. absorbed. A similar decrease in yield with dose has been found by others. Hydrogen was the only gas produced. Careful analyses showed in all cases that no oxygen or nitrogen was formed during the radiation. Stoichiometry requires that for each H_2 formed two ferric ions must be found, and the same applied to sulfite formation.

The arithmetic mean value for the rate of $SO_3^=$ formation is 0.43 molecule 100 e.v., and that for H_2 is 0.35 molecule/100 e.v. The mean value of

---

(1) Research performed under the auspices of the U. S. Atomic Energy Commission.

(2) Chemistry Department, Stevens Institute of Technology, Hoboken, New Jersey.

(3) E. R. Johnson and A. O. Allen, THIS JOURNAL, **74**, 4147 (1952).

(4) C. J. Hochanadel, J. A. Ghormley and T. J. Sworski, *ibid.*, **77**, 3215 (1955).

(5) These results indicate that ferrous ammonium sulfate can be used as a dosimeter for very high intensity radiation.