stirred without the dislodging of the hanging drop, and pre-electrolysis limiting currents were relatively large (diffusion layer thickness of the order of 10^{-3} cm.). Because of vigorous stirring, the pre-electrolysis current dropped within 1–2 seconds to an average constant value upon switching on. The area of the hanging drop was reproducible with an error smaller than 1% (a conservative estimate) in a given medium.[26]

The stirring achieved with the rotated propeller stirrer was not uniform, and rapid fluctuations of the pre-electrolysis current about a constant average value were observed. Non-uniform stirring also caused deformation of the hanging drop, and consequently the stirrer was stopped at the end of pre-electrolysis. A time interval of 4 seconds was allowed to elapse before anodic stripping. The small loss in sensitivity gain was more than compensated by improvement in accuracy.

A cell in which the hanging drop was suspended on a rotating glass tube with gold-plated platinum tip also was

(26) The reproducibility would be improved by polarizing the dropping mercury electrode at a constant potential (not so cathodic as to cause any appreciable metal deposition) instead of letting the electrode acquire the mixed potential corresponding to the condition that the algebraic sum of faradaic and capacity currents is equal to zero.

used but was not studied in detail. This type of electrode might well be more advantageous than the combination of hanging drop and stirrer.

Instrumentation for the control of the potential of the hanging drop and the stripping current (current-step method) was conventional. Pre-electrolysis was carried out at -1 volt (*versus* S.C.E.) in all the experiments. Time intervals during pre-electrolysis and between stripping and pre-electrolysis were controlled manually with an electric timer. The utilization of time relays would be advantageous and would require only simple instrumentation. Recordings were made with a Tektronix cathode-ray oscilloscope, model 531, with preamplifier 53D.

Solution composition: 0.5 mM Cd^{++} in 1 M potassium chloride; oxygen removal by nitrogen. The temperature was approximately 25°; it did not vary by more than 1–2 degrees in a series of determinations.

BATON ROUGE, LOUISIANA

The Silver–Silver Chloride Electrode in Formic and Acetic Acids as Solvents

BY L. M. MUKHERJEE[1]

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This paper explains the observed behavior of the Ag/AgCl electrode in formic and acetic acids, as solvents, in terms of the dielectric constant and autoprotolysis constant of each medium.

Introduction

Suitable reference electrodes are not easily obtainable for use in formic and acetic acid solutions. Cells employed in previous studies[2,3] of acids and bases in acetic acid, for instance, seem to consist essentially of an aqueous calomel reference electrode in conjunction with chloranil or glass electrode, both with and without salt bridge. To eliminate the difficulties encountered with the use of the calomel electrode, Fritz[4] and Glenn[5] recommended the Ag/AgCl electrode as a reference standard in acetic acid. Accordingly, the purpose of the present investigation is to determine the standard potential of the Ag/AgCl electrode (relative to hydrogen electrode as zero) in both formic and acetic acids with a view to test its performance as a reference electrode and also to explain the observed E^0 values in terms of the properties of the solvents themselves.

Experimental

Cells of the following type were studied in both the solvents

$$\text{Pt, H}_2; \text{ HCl}_{\text{non-aq}}; \text{ AgCl/Ag}$$

$$E_{\text{obs}} = E^0 - \frac{2RT}{F} \ln a^0 \pm \text{HCl}$$
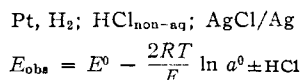
(1) Chemistry Department, The Florida State University, Tallahassee, Florida.

(2) N. F. Hall and J. B. Conant, THIS JOURNAL, **49**, 3047 (1927).

(3) (a) P. C. Markunas and J. A. Riddick, *Anal. Chem.*, **23**, 337 (1951); (b) R. T. Moore, *et al.*, *ibid.*, **23**, 1639 (1951); (c) C. N. Pifer and E. G. Wollish, *ibid.*, **24**, 300 (1952); (d) W. Seaman and E. Allen, *ibid.*, **23**, 592 (1951).

(4) J. S. Fritz, *ibid.*, **22**, 1028 (1950).

(5) R. A. Glenn, *ibid.*, **25**, 1916 (1953).

The observed e.m.f.'s were extrapolated to obtain the standard potential E^0 of the silver–silver chloride electrode by the procedure outlined by Harned,[6] taking into account the Gronwall–LaMer–Sandved extended terms. Due to incomplete ionization of HCl in formic acid and acetic acid, the extrapolation formula has been modified in each case by replacing the concentration C by α. C ($= \sqrt{KC}$) where α and K represent, respectively, the degree of dissociation, and the dissociation constant of HCl as obtained from the previous conductance data in the particular medium. The values of the dissociation constant of HCl in formic and acetic acids used in the present case refer, respectively, to the work of Schlesinger and Martin[7] and of Kolthoff and Willman.[8]

Of the solvents employed in the present study, acetic acid was purified as: 99–100% glacial acetic acid (E. Merck) was refluxed with a little solid $K_2Cr_2O_7$ for about 5 hours on a sand-bath and then distilled in an all-glass Pyrex apparatus provided with $CaCl_2$ guard tube directly into a clean, dry Jena bottle. The distillate so obtained was then frozen out, the liquid portion was discarded and the crystals (m.p. 16.6°) were collected and stored in Jena bottles which were kept in a closed chamber containing some dehydrated silica gel. The sample so obtained was finally characterized by ultraviolet spectrophotometry.

One hundred per cent. A.R. quality formic acid (E. Merck) was used as such without any initial treatment; the acid and the prepared solutions as well were preserved in a closed chamber kept in a refrigerator.

Solutions of HCl were obtained by absorbing in the respective solvents, in almost complete absence of air, HCl gas prepared from concd. H_2SO_4 and NaCl (E. Merck, G.R., oven-dried at 105–110°) and dried by passing through concd. H_2SO_4. Due to very low solubility of HCl in acetic acid, solutions of concentrations higher than 0.00533 N could not be studied in this solvent. Aliquots of the HCl solutions so prepared were taken in water and then estimated either by weighing as AgCl or by back titration of $AgNO_3$ added in

(6) H. S. Harned, THIS JOURNAL, **60**, 336 (1938).

(7) H. I. Schlesinger and A. W. Martin, *ibid.*, **36**, 1589 (1914).

(8) I. M. Kolthoff and A. Willman, *ibid.*, **56**, 1007 (1934).

excess against standard KCNS in aqueous solution. The concentrations were calculated in molarity.

The hydrogen electrode assembly and the silver–silver chloride electrode employed were the same as those described before.[9]

After preparation the silver–silver chloride electrodes were kept short-circuited for some time and finally preserved in dilute aqueous solution of KCl in the dark. The electrodes were usually washed thoroughly with water and then with the desired solvent prior to use in non-aqueous solutions. Before and after the experiments, the electrodes (viz., the hydrogen and the silver–silver chloride electrodes) were checked in aqueous solutions of known activities of hydrogen or halide ions as the case may be.

The e.m.f.'s were recorded at intervals of about 30 minutes for 3 to 4 hours at $35 \pm 0.25°$ with the help of a Leeds and Northrup Type K2 potentiometer and a Hartmann Braun galvanometer till the values were constant within ± 0.0001 volt. An additional thermionic amplifier was used to aid the measurements in acetic acid solutions because of their high resistance.

Results and Discussions

The results obtained in the present study together with the relevant details are given in Table I. The E^0 of silver–silver chloride (relative to hy-

TABLE I

E^0 Ag/AgCl $= -0.11995$ v. (molar); -0.13022 v. (molal) (formic acid) $= -0.61800$ v. (molar); -0.62084 v. (molal) (acetic acid).   AgCl $+ {}^1/_2H_2 \rightleftharpoons$ Ag $+$ H$^+$ $+$ Cl$^-$; temp. $= 35°$

Formic acid $pK_{HCl} = 1.398$, $D = 58.5$ (16°), $a^0 = 6$ Å.		Acetic acid $pK_{HCl} = 9.292$, $D = 6.15$ (20°), $a^0 = 5$ Å.	
Concn. of HCl, M	E.m.f. obsd. (v.) cor. to 1 atm. H₂ press.	Concn. of HCl, M	E.m.f. obsd. (v.) cor. to 1 atm. H₂ press.
0.00033	0.17695	0.00090	0.14000
.00120	.15100	.00098	.13770
.00146	.14690	.00125	.13165
.00187	.14065	.00139	.12900
.00273	.13140	.00144	.12515
.00362	.11570	.00226	.10100
.00468	.10730	.00311	.08130
.00563	.09910	.00533	.04970
.00655	.09410		
.00844	.08155		
.01690	.05500		

(9) L. M. Mukherjee, J. Phys. Chem., 58, 1042 (1954).

drogen electrode as zero) is found to be -0.11995 and -0.61800 volt, respectively, in formic and acetic acids.

It follows from a consideration of the actual values of the standard reduction potentials for the silver–silver chloride electrode in the two solvents, viz., formic and acetic acids, that the reaction AgX $+ {}^1/_2H_2 \rightarrow$ Ag $+$ H$^+$ $+$ X$^-$ is more likely to occur in the former solvent than in the latter. The reason for this difference in behavior probably lies in the combined effect of the dielectric constant and the autoprotolysis constant both of which are relatively high in the case of formic acid ($D = 58.50$ and $pK_s = 6.20$ for formic acid; $D = 6.15$ and $pK_s = 14.45$ for acetic acid). It appears that the effect due to its large autoprotolysis constant acts in such a way that the influence of the fairly high dielectric constant is substantially reduced. This is also evident from the large difference in the E^0 value of the silver–silver chloride electrode obtained in formic acid and that secured in a 20 wt. % of dioxane–water mixture—a medium of nearly the same dielectric constant as that of formic acid but of much lower proton activity which seems almost equal to that of water.

Conclusions

1. The E^0 of the Ag/AgCl electrode relative to hydrogen electrode is found to be -0.11995 v. in formic acid and -0.61800 v. in acetic acid in the molar scale.

2. The large difference in E^0 obtained in the two solvents probably can be ascribed to the combined role of the dielectric constant as well as the autoprotolysis constant of the solvents concerned and not simply to the influence of any one of these two factors.

CALCUTTA 9, INDIA

The Hydrogen Fluoride Solvent System. IV. Metallic Complexes in Liquid HF[1]

BY A. F. CLIFFORD[2] AND J. SARGENT

Evidence is presented for the existence in liquid HF of complexes of Co(II), Co(III), Ni(II), Cu(II), Zn(II), Hg(II) and Pb(II). In particular the system Ni(II)–CH₃CN is discussed and evidence presented for the existence of the ions NiCH₃CN^{+2} and Ni(CH₃CN)₄$^{+2}$. The instability constant for the former was found to be 1.4×10^{-3}.

Introduction

The existence of metallic complexes in a solvent so extremely acidic as liquid hydrogen fluoride, in which the complexing agents themselves must exist

(1) Presented before the Division of Physical and Inorganic Chemistry, 119th National A.C.S. Meeting, Cleveland, Ohio, April 10, 1951.

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largely in cationic form, is of practical and theoretical interest.[3]

As one of the commonest types of complex ion in water is the ammono complex, such as Cu(NH₃)₄$^{+2}$, so in the search for complexes in liquid HF, one

(3) The acid–base relationships in liquid HF have been treated by A. F. Clifford, et al., in Parts I, II and III of this Series, J. Inorg. Nucl. Chem., in press.