Measurements of R_0(H) and R_0(F) in Alcohol–Hydrogen Fluoride Mixtures

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The variation of the acidity function (R_0(H)) in alcohol–hydrogen fluoride mixtures was determined by measuring the hydrogen electrode potential vs. the ferrocene–ferrocenium system. The variation of the fluoride activity function (R_0(F)) was determined by measuring the lanthanum trifluoride monocrystal electrode potential vs. the ferrocene–ferrocenium system. Values of R_0(H) and R_0(F) functions are given for methanol–, ethanol–, propanol–, and butanol–hydrogen fluoride mixtures.

Introduction

Hydrogen fluoride and alcohol–hydrogen fluoride mixtures are very strongly acidic media, comparable with water–hydrogen fluoride or water–sulfuric acid mixtures.

Acidity levels of water–hydrogen fluoride mixtures have been determined by several workers (*1–3*) using the Hammett acidity function H_0. However, the acidities of highly acidic mixtures obtained on the basis of the Hammett acidity function are known to be only approximate (*4*).

Tremillon (*5*) and Vedel (*6*), on the basis of this observation, have postulated that the use of the acidity function R_0(H) should lead to more valid results. Trémillon et al. (*7*, *8*) have shown the value of the R_0(H) acidity function for acidity level measurements in water–hydrogen fluoride acid media of HF content up to 100% (in weight).

Theory

The basic theories have been developed in general reviews (*9*) and applied to HF–H_2O mixtures in previous studies (*7*, *8*, *10*). R_0(H) and R_0(F) functions are defined from measurements of the potentials, respectively, of the hydrogen electrode and of the lanthanum trifluoride monocrystal electrode vs. the potential of a system which may be assumed independent of the solvent. The expressions of these functions are

$$R_0(\mathrm{H}) = -15.2 + \frac{F}{2.3RT}(E^\circ_{\mathrm{HF}} - E_{\mathrm{S}}) \quad (1)$$

$$R_0(\mathrm{F}) = 13.6 + \frac{\mathrm{F}}{2.3RT}(E'_{\mathrm{S}} - E^{\circ\prime}_{\mathrm{HF}}) \quad (2)$$

where E_S is the potential of the H^+ indicator electrode, E'_S the potential of the F^- indicator electrode in the medium, E°_{HF} the standard potential of the hydrogen electrode (H^+), and $E^{\circ\prime}_{HF}$ the standard potential of the lanthanum trifluoride electrode in pure hydrogen fluoride. All these potential are referred to the $E_{1/2}$ potential of the reference system ferrocene/ferrocenium ion.

Results and Discussion

This paper deals with acidity level and fluoride activity level determinations in alcohol–hydrogen fluoride mixtures on the basis of R_0(H) and R_0(F) measurements.

Due to the HF acidity and ROH (where R is an alkyl group) basicity, alcohol–hydrogen fluoride mixtures are strongly ionized according to the following equilibrium:

$$2HF + ROH \rightleftarrows ROH_2^+ + HF_2^- \quad (3)$$

(where ROH_2^+ and HF_2^- are solvated species).

Due to this equilibrium, a given mixture of alcohol and hydrogen fluoride is buffered with ROH_2^+ and HF_2^- ions. NMR studies (*3*, *11*) of protonated alcohols have shown that only 10% of ethanol molecules are protonated in a 50% HF mixture. The degree of protonation rises slowly with the mole fraction of HF, and only in the range 85–100% HF is there a rapid rise to about 80% ionization. This behavior is in agreement with the behavior of a relatively strong base in a strongly acidic solvent. Since H_2O and alcohols are bases of comparable strength, one would expect the change in R_0(H) to be similar to that in water–HF mixtures.

The results of R_0(H) measurements are given in Table I and Figure 1. The R_0(H) function for methanol shows a behavior comparable to that of water–HF mixtures. The pK_a of the protonated alcohols decreases from methanol to butanol.

This property is reflected in the acidity function by the fact that R_0(H) values decrease from methanol to butanol in a given medium. As the medium is buffered by ROH_2^+ and HF_2^- ions, the pK_a depends on the equilibrium in solutions and the buffer action of the alcohol.

The fluoride activity decreases as the hydrogen fluoride concentration increases. The following equilibrium

$$HF + F^- \rightleftarrows HF_2^- \quad (4)$$

is responsible of this reduced activity of fluoride ions. Thus, in methanol–hydrogen fluoride mixtures, the R_0(F) function is similar to that in H_2O–HF systems. The evolution of the fluoride activity is the inverse of the acidity and decrease of fluoride activity from methanol to butanol is obtained. Table I and Figure 2 show the behavior of the R_0(F) function in these systems. The buffer action of alcohol in highly concentrated hydrogen fluoride solutions

$$ROH_2^+ + F^- \rightleftarrows ROH + HF \quad (5)$$

brings the fluoride activity of these mixtures to a value close to that of the H_2O–HF system.

Experimental Section

Experimentally, R_0(H) was obtained by measuring the hydrogen electrode potential vs. the ferrocene/ferrocenium couple, the standard potential of which is supposed to be independent of the solvent:

$$R_0(\mathrm{H}) = R_0(\mathrm{H})_{\mathrm{HF}} + (E^\circ_{\mathrm{HF}} - E^\circ_{\mathrm{S}})/54.18 \quad (6)$$

where E°_{HF} is the standard potential of the hydrogen electrode in pure hydrogen fluoride and E°_S is the potential in a given medium.

The measurements were carried out as follows: polarograms of ferrocene/ferrocenium solutions at a dropping mercury electrode were recorded under dry nitrogen atmosphere and the half-wave potentials were taken as the standard potentials. The solution was then saturated with pure hydrogen under a pressure of 1 atm. E°_S was determined by measuring the potential

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Table I. R_0(H) and R_0(F) in Alcohol-HF Mixtures

	methanol-HF		ethanol-HF		propanol-HF		butanol-HF	
[HF], %	R_0(H)	R_0(F)	R_0(H)	R_0(F)	R_0(H)	R_0(F)	R_0(H)	R_0(F)
10	+2.5	−0.8				−0.9	+1.5	−0.1
15	+0.9	+0.7	+2.5	−0.5	+1.0	+1.3	−2.0	+2.0
20	−0.8	+2.0	−0.5	+2.1	−2.2	+3.0	−4.2	+3.9
25	−2.1	+3.2	−2.5	+3.9	−4.2	+4.7	−6.0	+5.5
30	−3.4	+4.2	−4.2	+5.2	−5.7	+6.2	−7.4	+6.9
35	−4.6	+5.1	−5.7	+6.3	−7.2	+7.1	−8.4	+7.8
40	−5.8	+5.7	−7.0	+7.0	−8.3	+7.7	−9.3	+8.1
50	−8.0	+6.9	−9.4	+8.1	−10.0	+8.5	−10.9	+8.4
60	−9.9	+8.1	−11.3	+9.1	−11.4	+9.4	−12.2	+8.9
70	−11.6	+9.3	−12.6	+10.4	−12.6	+10.3	−13.2	+9.7
80	−12.0	+10.8	−13.6	+11.5	−13.7	+11.3	−14.2	+10.8
90	−14.2	+12.2	−14.5	+12.5	−14.5	+12.4	−14.9	+12.2
100	−15.2	+13.6	−15.2	+13.6	−15.2	+13.6	−15.2	+13.6

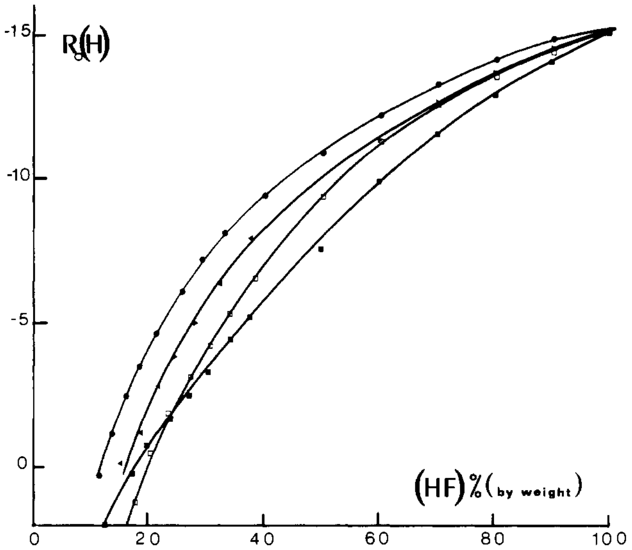

Figure 1. Plots of R_0(H) against the concentration for methanol-HF (■), ethanol-HF (□), propanol-HF (▼), and butanol-HF (●).

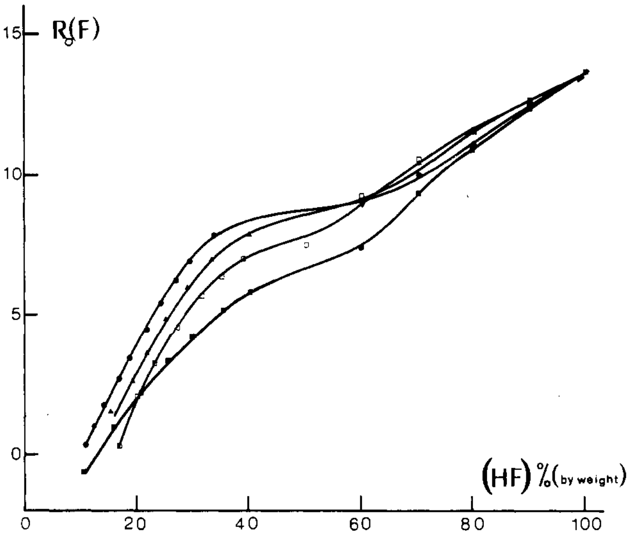

Figure 2. Plots of R_0(F) against the concentration for methanol-HF (■), ethanol-HF (□), propanol-HF (▼), and butanol-HF (●).

of platinized platinum electrode immersed in this medium. The reversibility of the ferrocene/ferrocenium and H^+/H_2 systems at dropping mercury electrodes and platinized platinum electrodes, respectively, was verified by a logarithmic analysis of the corresponding polarograms. The temperature for all measurements was maintained at 25 °C for solutions up to 50% HF and at 0 °C for higher concentration in HF.

R_0(F) was obtained by measuring the lanthanum fluoride monocrystal electrode potential vs. the ferrocene/ferrocenium couple.

$$R_0(F) = R_0(F)_{HF} + (E°_S - E°_{HF})/54.18 \qquad (7)$$

where $E°_{HF}$ is the potential of the lanthanum trifluoride monocrystal electrode in pure hydrogen fluoride and $E°_S$ is the potential in a given medium.

The measurements were carried out as follows: $E°_S$ was determined by measuring the potential of a lanthanum electrode immersed in this medium. The half-wave potential of the ferrocene/ferrocenium system was taken as the standard potential.

Solutions were prepared by using ACS-grade alcohols. For concentrations lower than 50% in HF, a stock solution was prepared by bubbling hydrogen fluoride gas (Matheson 99.9%) in alcohol until saturation. The concentration was determined by titration of the solutions which were obtained from dilution of the stock solution. For higher concentrations up to 100% in HF, the solutions were prepared in vacuo by addition of pure alcohol to a fixed volume of pure hydrogen fluoride. The concentration was established from the weight of each part of the solution.

Registry No. Methanol, 67-56-1; ethanol, 64-17-5; propanol, 71-23-8; butanol, 71-36-3; hydrogen fluoride, 7664-39-3; fluoride, 16984-48-8.

Literature Cited

(1) Bell, R. P.; Bascombe, K. N.; McCoubrey, J. C. *J. Chem. Soc.* **1956**, 1286–91.
(2) Hyman, H. H.; Kilpatrick, M.; Katz, J. J. *J. Am. Chem. Soc.* **1957**, *79*, 3668–71.
(3) Dallinga, G.; Gaaf, J.; Mackor, E. L. *Recl. Trav. Chim., Pays-Bas* **19708** *89*, 1068–78.
(4) Hinman, R. L.; Lang, J. *J. Am. Chem. Soc.* **1964**, *86*, 3796–806.
(5) Tremillon, B. "La Chimie en Solvant Nonaqueux", 1st ed.; Presses Universitaires de France: Paris, 1971.
(6) Vedel, J. Thèse, Université Paris VI, 1967.
(7) Vaillant, A.; Devynck, J.; Trémillon, B. *Anal. Lett.* **1973**, *6*, 1095–9.
(8) Ménard, H.; Masson, J. P.; Devynck, J.; Trémillon, B. *J. Electroanal. Chem.* **1975**, *63*, 163–70.
(9) Strehlow, H. "The Chemistry of Nonaqueous Solvents"; Lagowski, J. J., Ed.; Academic Press: New York, 1966; Vol. 1.
(10) Vaillant, A.; Devynck, J.; Trémillon, B. *J. Electroanal. Chem.* **1974**, *57*, 219–24.
(11) Olah, G. A.; Namanworth, E. *J. Am. Chem. Soc.* **1966**, *88*, 5327–8.

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