[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF BROWN UNIVERSITY]

Unilateral Triple Ion Formation in Aqueous Hydrofluoric Acid

BY CHARLES BUSHNELL WOOSTER

The phrase "unilateral triple ion formation" has been coined[1] to describe the situation in which a single ionic equilibrium of the type, $B^- + AB \rightleftarrows AB_2^-$, is superposed on the customary binary ionization of the electrolyte, AB, and to distinguish this situation from that in which the corresponding equilibrium $A^+ + AB \rightleftarrows A_2B^+$, is also involved.[2] In a previous paper[1] it has been shown that with suitable approximations the conductance function for unilateral triple ion formation may be obtained in the linear form[3]

$$\left(\frac{f\Lambda}{m}\right)^2 \frac{C}{(1 - \Lambda/\Lambda_0)} = \Lambda_0{}^2K + \frac{(2\Lambda_0\lambda_0 - \Lambda_0{}^2)K}{k}\left(1 - \frac{\Lambda}{\Lambda_0}\right) C \quad (1)$$

and this equation was applied successfully to the conductivity of dilute solutions of the metal ketyl, sodium benzophenone, in liquid ammonia. Because of the unusual character of this electrolyte and also due to the fact that additional equilibria must be considered in the analysis of this conductance curve in the more concentrated regions, it is very desirable to test equation 1 independently by applying it to another electrolyte. However, instances of unilateral triple ion formation are relatively rare since they may generally be expected to occur only when some specific interaction (formation of a chemical bond) between a simple ion and an ion pair is possible.[4] The only well established instance seems to be in aqueous hydrofluoric acid solutions where the equilibrium, $F^- + HF \rightleftarrows HF_2^-$, was first suggested by Pick,[5] who carried out an analysis of the conductance data by assuming arbitrary values for the limiting conductivity of the triple ion. His conclusions were substantially verified by Davies and Huddleston[6] through a study of the anionic transference numbers.[7]

It is the purpose of this paper to present the results of applying equation 1 to the analysis of the conductance curves for aqueous hydrofluoric acid solutions and to compare them with the results which may be obtained by a substantially independent method from the transference data of Davies and Huddleston. The use of equation 1 involves the assumption that only the solute species H^+, F^-, HF and HF_2^- and the equilibria $HF \rightleftarrows H^+ + F^-$ and $HF_2^- \rightleftarrows HF + F^-$ need be considered and that the species F_2^{--} and H_2F_2 are present only in negligible proportions, if at all. Since it is probable that the hydrofluoride ion owes its existence to hydrogen bridge formation,[8] it is evident that there is no corresponding justification for assuming the existence of F_2^{--}. The existence in the gaseous state[9] of H_6F_6 suggests the possible presence of H_2F_2 (or higher polymers) in solution, but the results of the present analysis decisively exclude this possibility in aqueous solutions of hydrofluoric acid at concentrations 1 *N* and less. This result may be interpreted as indicating that H_2F_2 is a very strong acid or that the addition of a second proton to the hydrofluoride ion greatly weakens the hydrogen bridge, or both. In Section III the results obtained from the data on hydrofluoric acid are applied to the interpretation of the conductivity of potassium hydrofluoride.

I. Analysis of the Conductance Curve

The conductance data of Deussen[10] were chosen as the most reliable of those available and two series, one at 25° and one of probably lesser accuracy at 0° were employed in the calculations. In order to apply equation 1 it is also necessary to have independent values of the limiting equivalent conductance, the dielectric constant and the

---

[1] Wooster, THIS JOURNAL, **59**, 377 (1937).

[2] Fuoss and Kraus, *ibid.*, **55**, 2387 (1933).

[3] C is the total concentration in equivalents (as AB) per liter, Λ is the equivalent conductance, $K = [A^+][B^-]/[AB]$, the constant for binary dissociation, $k = [B^-][AB]/[AB^-_2]$, the dissociation constant for the triple ion equilibrium, Λ_0 the limiting value of Λ, λ_0 the sum of the limiting values of the mobility of the triple ion and of the single ion with opposite charge, f the activity coefficient defined by $-\log f = \beta\Lambda_0{}^{-1/2}\sqrt{C\Lambda}$ and m a mobility coefficient defined as $1 - \alpha\Lambda_0{}^{-3/2}\sqrt{C\Lambda}$. The constants α and β have the same significance as in the paper of Fuoss and Kraus [THIS JOURNAL, **55**, 476 (1933)]. In water at 25° $\alpha = 0.228\Lambda_0 + 59.7$ and $\beta = 0.504$; at 0°, $\alpha = 0.220\Lambda_0 + 29.0$ and $\beta = 0.486$.

[4] It is also conceivable, of course, that coulomb forces alone occasionally may give rise to a situation which closely simulates unilateral triple ion formation in media of appropriate dielectric constant, if one of the simple ions is much larger than the other and particularly if the larger ion is unsymmetrical.

[5] Pick, *Nernst's Festschrift*, 360 (1912).

[6] Davies and Huddleston, *J. Chem. Soc.*, **125**, 260 (1924).

[7] The only other attempt at analysis of these conductance data is that of Kendall [THIS JOURNAL, **39**, 7 (1917)] on the basis of a more or less empirical equation for "transition electrolytes."

[8] Huggins, *J. Org. Chem.*, **1**, 409 (1936).

[9] Simons and Hildebrand, THIS JOURNAL, **46**, 2183 (1924).

[10] Deussen, *Z. anorg. Chem.*, **44**, 312 (1905).

viscosity. The values which were used, $\Lambda_0 = 404$, $D = 78.57$, $\eta = 0.00895$ at 25° and $\Lambda_0 = 255$, $D = 88$, $\eta = 0.01794$ at 0°, were obtained from a variety of sources but do not differ in any important respect from the values given in the "International Critical Tables."

Plots of $f^2C\Lambda^2/m^2(1-\Lambda/\Lambda_0)$ against $C(1-\Lambda/\Lambda_0)$ appear in Fig. 1 where curve I represents values based on the measurements at 25° and curve II at 0°. It is evident that, in accordance with the requirements of equation 1, the points fall very nearly on a straight line. By applying the method of least squares to the ten points covering the dilution range 1–512 liters at 25° the values 351.5 for the slope and 112.4 for the intercept were obtained and in a similar way a slope of 201.1 and intercept of 71.2 were obtained from nine points at 0° over the dilution range 1–256 liters. The lines in Fig. 1 are drawn in accordance with these values from which the equilibrium constants are found to be $K = 6.89 \times 10^{-4}$ at 25° and 10.95×10^{-4} at 0°, $k = 0.320(2\,\lambda_0/\Lambda_0 - 1)$ at 25° and $0.354\ (2\lambda_0/\Lambda_0 - 1)$ at 0°. The ionization constant obtained at 25° differs very little from that (6.9×10^{-4}) obtained by other investigators[11] but the value at 0° is somewhat higher than that in the literature[11] (9×10^{-4}).

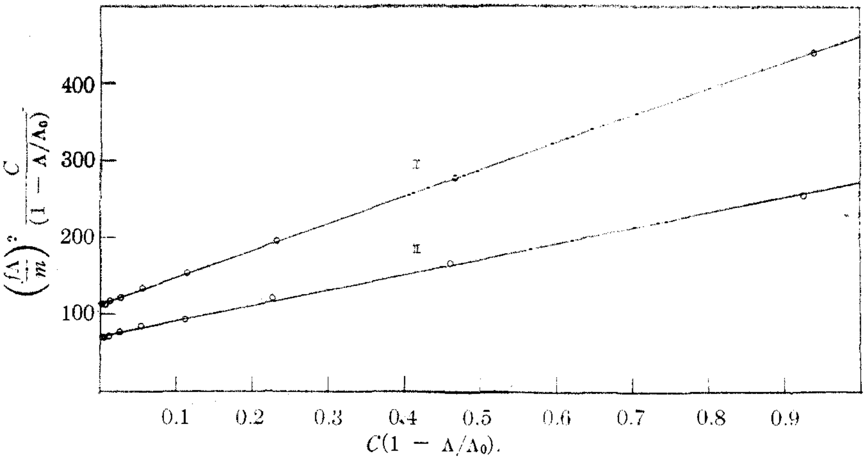

Fig. 1.—Unilateral triple ion formation in aqueous hydrofluoric acid.

The excellent agreement with equation 1 at such high total concentrations requires some explanation which is afforded by the facts that due to the low value of the ionization constants and the high values of the triple ion dissociation constants[12] the dielectric constant of the medium reduces the interionic (coulomb) forces so much that the approximate forms of the Debye–Hückel–Onsager equations employed serve adequately to calculate the effective values of the activity and mobility coefficients.

The applicability of equation 1 to unilateral triple ion equilibria is also determined by the degree to which the ratio λ_0/Λ_0 approximates unity, since this approximation was used to dispose of a second order term in the derivation of the equation. In general, this ratio may not be obtained directly from the conductance data and the sole available test of the validity of this approximation may often be the extent to which the linear form of equation 1 is satisfied by the data. In the present instance, however, additional information is available from two sources. First, the difference between λ_0 and Λ_0 is determined entirely by the difference in the limiting mobilities of the simple anion (F^-) and the triple anion (HF_2^-) which is doubtless so small in comparison with the high mobility of the hydrogen ion (351 at 25° and 229 at 0°) that the ratio λ_0/Λ_0 cannot differ widely from unity. Second, the value for the limiting mobility of the triple anion which may be obtained from the transference data (see Section II) yields the value $\lambda_0 = 437$ at 25° so that at this temperature $\lambda_0/\Lambda_0 = 1.08$. The maximum alteration in the slope of the plot due to neglect of the second order term in deriving equation 1 is given in percentage by $100(1 - \lambda_0/\Lambda_0)^2/[(2\lambda_0/\Lambda_0 - 1) + (1 - \lambda_0/\Lambda_0)^2]$ which on substituting 1.08 for λ_0/Λ_0 becomes 0.55% and is well within the limits of the experimental errors involved in Deussen's measurements.

It may also be noted at this point that evaluation of the ratio λ_0/Λ_0 permits the calculation of $k = 0.371$ at 25° and (assuming λ_0/Λ_0 independent of temperature as it would be if Walden's rule applies) 0.411 at 0°.

Using the slopes and intercepts given above the conductance curve (Λ against $\log V$) has been calculated as previously described[1] and the re-

---

[11] "International Critical Tables," McGraw-Hill Book Co., Inc., New York, N. Y., 1929, Vol. VI, p. 260.

[12] The order of magnitude of k is given by 0.320 at 25° and 0.354 at 0° since the coefficient $(2\lambda_0/\Lambda_0 - 1)$ does not differ widely from unity.

sults appear in Fig. 2 where the smooth curves represent the calculated values and the circles represent the experimental points. The arrows indicate the limits beyond which the smooth curve represents an extrapolation, the experimental points in these regions not having been used in determining the slopes and intercepts given. The experimental points lie very close to the calculated curve except in the most dilute region. Due to experimental difficulties in maintaining a constant temperature at 0° under the conditions of Deussen's measurements, the data at this temperature, particularly in the more dilute region, are less reliable than that at 25°.

II. Analysis of Transference Data

By combining values for the anionic transference numbers with those for the equivalent conductances at various concentrations, Davies and Huddleston[6] have calculated the values for the triple ion dissociation constant and the mobility, U, of the triple ion which appear in the second and third rows of Table I.

TABLE I

CONSTANTS FROM TRANSFERENCE DATA AT 25°

V	1	2	4	8	16	32
k	0.212	0.215	0.210	0.199	0.165	0.137
U	73.0	68.3	64.9	61.0	53.4	47.3
k corr.	0.338	0.338	0.324	0.356	0.340	0.288
U_0	85.6	83.6	83.5	89.0	89.3	84.3

It may be observed that Davies and Huddleston's values of k show an average deviation of 13.7% from the mean 0.190 which, itself, is much lower than the figure 0.371 obtained in the previous section. The two values are not strictly comparable, however, since these authors introduced no corrections for the effect of interionic forces on the activities and mobilities of the ions. The effect of this omission is particularly evident in their values for the mobility of the triple ion, which show a 12.1% average deviation from the mean and a pronounced trend toward decreasing values of U with decreasing concentration, whereas the true mobilities of ions should increase with decreasing concentration.

In the fourth and fifth rows of the table are given values of k and of the *limiting* mobility of the triple ion, U_0, which have been obtained from the same data by introducing activity and mobility coefficients.

This method of calculation uses Davies and Huddleston's equations[13] with the following substitutions: K/f^2 for K_1[14]; 351 m_a for a, and 53 m_b for b. The figures 351 and 53 represent the limiting mobilities of the hydrogen and the fluoride ions and the m's are mobility coefficients calculated by the use of the following form of Onsager's equation for the mobility of an ion of the type j.

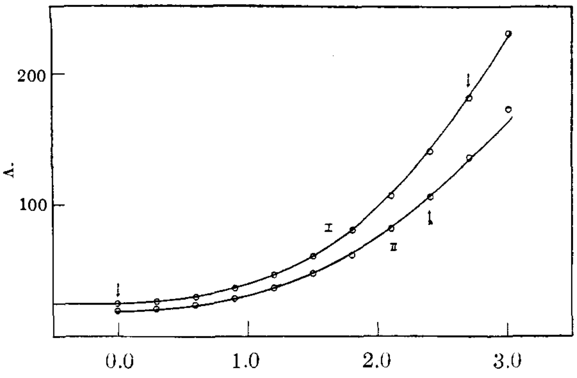

Fig. 2.—Conductance curves for aqueous hydrofluoric acid.

$$\Lambda_j = \Lambda_j{}^0 \left\{ 1 - \left[\frac{8.15 \times 10^5}{(DT)^{3/2}\,\Lambda_0{}^{1/2}} + \frac{41}{\Lambda_j{}^0 (DT)^{1/2} \eta \Lambda_0{}^{1/2}} \right] \sqrt{C\Lambda} \right\} \quad (2)$$

In the present instance this reduced to the following values for the mobility coefficients, $m_a = 1 - 0.0156\sqrt{C\Lambda}$ and $m_b = 1 - 0.0395\sqrt{C\Lambda}$. The values for the limiting mobility of the triple ion were obtained from the values, U, of the mobility at various concentrations also by the use of equation 2 in the reduced form

$$U_0 = \frac{U + 1.49\sqrt{C\Lambda}}{1 - 0.0113\sqrt{C\Lambda}} \quad (3)$$

It is evident on inspection of Table I that the "corrected" calculations give more consistent values of k (0.331 ± 4.9%) and of U_0 (85.9 ± 2.6%) which, unlike U, should be independent of concentration. It is further noteworthy that the value of k from transference data now agrees reasonably well with that obtained substantially independently[15] from conductance data. Al-

---

[13] Equation 9 of Davies and Huddleston[6] (p. 267) is in error due to a misprint and should read

$$[F'] = \frac{p - r}{2b} - \frac{\sqrt{(p - r)^2 - 8bK_1(aC - p)}}{2b}$$

[14] For the sake of consistency the value 6.89×10^{-4} was used for K instead of the figure 7.4×10^{-4} employed by Davies and Huddleston. It may also be noted that their $K_2 = 1/k$.

[15] It is true that U_0 from transference data was used to obtain $k = 0.371$ from conductance data, but this apparent dependence could be avoided easily by comparing $k = 0.320\ (2\lambda_0/\Lambda_0 - 1)$ from conductance data alone with $k = 0.286\ (2\lambda_0/\Lambda_0 - 1)$ from transference data by the "corrected" method of Davies and Huddleston; the direct comparison of the k values is more convenient, however.

though the difference of 11.4% between these values is greater than the average deviation of the transference k values from the mean, it must be noted that the error in U_0 is also involved in making the comparison. Furthermore, it is doubtful that the precision of the transference data is sufficient to render the mean value 0.331 reliable to within less than 12% as an *absolute* value of k.[16]

III. The Conductivity of Potassium Hydrofluoride

Data for the conductivity of potassium hydrofluoride over the dilution range 50–1000 liters based on the measurements of Walden[17] are given in the "International Critical Tables"[11] (p. 251).

Since the conductivity of this electrolyte exceeds that of potassium fluoride at corresponding concentrations, Walden concluded that the salt decomposed into potassium fluoride and hydrofluoric acid. Although his conclusion appears to be substantially correct at low concentrations, it was based partly on the erroneous assumption that the mobility of the hydrofluoride ion could not exceed that of the fluoride ion.

In view of the results obtained with hydrofluoric acid in Sections I and II and the fact that potassium fluoride is a strong electrolyte, it is likely that only the following solute species: K^+, H^+, F^-, HF_2^-, HF and equilibria: $HF \rightleftarrows H^+ + F^-$, $HF_2^- \rightleftharpoons HF + F^-$ need be considered in interpreting the conductivity of potassium hydrofluoride, but this restriction is insufficient to permit direct analysis of the data. It is possible, however, to use the equilibrium constants and mobilities which have been obtained for independent calculations of the equivalent conductance at various concentrations.

The equivalent conductance is related to the total concentration and the concentrations of the several ionic species (indicated by the terms in parentheses) by equation 4

$$C\Lambda = 74m_{K^+}(K^+) + 83m_{HF_2^-}(HF_2^-) + 53m_b(F^-) + 351m_a(H^+) \quad (4)$$

where the numerals are the values of the limiting mobilities and the m's represent the Onsager mobility coefficients. The mobility and activity coefficients may be approximated with sufficient accuracy for the present calculations by setting the total ion concentration equal to $2C$ so that

$$-\log f = 0.504\sqrt{C} \text{ and } Mj = 1 - (0.228 + 29.9/\Lambda j^0)\sqrt{C}$$

The concentration (K^+) is given directly by $(K^+) = C$, and the concentrations of the other four species are related by the following four independent equations.

$$(H^+)(F^-)/HF = K/f^2 \quad (5)$$

$$(HF)(F^-)/(HF_2) = k \quad (6)$$

$$C = (HF_2^-) + (HF) + (H^+) \quad (7)$$

$$2C = 2(HF_2^-) + (HF) + (F^-) \quad (8)$$

On solving these simultaneously it is possible to obtain the concentration of the fluoride ion from the cubic equation

$$(F^-)^3 + k(F^-)^2 + k[K/f^2 - C](F^-) - 2CkK/f^2 = 0 \quad (9)$$

by the usual methods, and the other two ionic concentrations by successive substitution in equations 10 and 11

$$(HF_2^-) = (F^-)[2C - (F^-)]/[k + 2(F^-)] \quad (10)$$

$$(H^+) = (F^-) + (HF_2^-) - C \quad (11)$$

Using the values $K = 6.89 \times 10^{-4}$, $k = 0.368$, the following results were obtained at $C = 0.0200$: $(F^-) = 0.02007$, $(HF_2^-) = 0.00098$, $(H^+) = 0.00105$, $(HF) = 0.01797$ and $\Lambda = 136.0$; the observed value of Λ is 138.

At lower concentrations decomposition of the hydrofluoride ion is so great that the solution of the cubic equation becomes too sensitive to the value of k to be useful. A better approximate calculation of Λ is then obtained by setting $(HF_2^-) = 0$, so that the other ion concentrations are given by equations 12 and 13.

$$2(H^+) = -[C + K/f^2] + \sqrt{[C + K/f^2]^2 + 4KC/f^2} \quad (12)$$

$$(F^-) = C + (H^+) \quad (13)$$

The complete results are given in Table II.

It is unfortunate that data are not available at higher concentrations where the triple ion equilibrium plays a more important part, although it is true that at much higher ion concentrations the interionic coulomb forces will

---

(16) In fact, it is probable that a part of the self-consistency of the results from transference data is due to the fact that Davies and Huddleston used values interpolated from a smoothed curve and not the direct experimental measurements. The same values were used in the above calculations in order to obtain results comparable with those of Davies and Huddleston. Since the conductance data are much more precise than the transference data, and since a satisfactory equation for the conductance curve is now available, it would seem a more advisable procedure to use the experimentally determined transference data in combination with interpolated (and, where necessary in the concentrated region, extrapolated) conductance data. This method applied to the ten transference measurements in the concentration range 2.33 to 0.327 moles per liter yielded $k = 0.327 \pm 5.8\%$, $U_0 = 83.0 \pm 6.1\%$, from which it is evident that the results are less self consistent, although the agreement of the mean with the results from the conductance equation is substantially unchanged: k from conductance equation using $U_0 = 83.0$ to calculate λ_0 is 0.368. The difference from 0.327 is 11.8% of the mean.

(17) Walden, *Z. physik. Chem.*, **2**, 49 (1888).

TABLE II

THE CONDUCTIVITY OF AQUEOUS POTASSIUM HYDROFLUORIDE AT 25°

C	0.020	0.006	0.005	0.002	0.001
Λ exptl.	138	150	167	217	270
Λ calcd.	136.0	163.3	169.6	217.7	265.5
% Dev.	1.45	8.87	1.56	0.32	1.67

complicate the analysis. The relatively large deviation at $C = 0.006$ is, of course, due to the error introduced by neglecting the concentration of the hydrofluoride ion; at lower concentrations this error becomes of less importance.

Summary

It has been shown that the conductance function for unilateral triple ion formation applies satisfactorily to the conductance data for aqueous hydrofluoric acid at 25 and at 0°. The constants determined in this way are consistent with the substantially independent values which may be obtained from transference measurements and they may be employed successfully to calculate the conductivity of potassium hydrofluoride solutions.

PROVIDENCE, R. I. RECEIVED APRIL 20, 1938

[JOINT CONTRIBUTION FROM THE CHEMISTRY LABORATORIES OF CANISIUS COLLEGE AND OF THE UNIVERSITY OF MARYLAND]

The Critical Increment of Ionic Reactions. III. The Influence of Dielectric Constant and Ionic Strength

BY JAMES LANDER[1] AND W. J. SVIRBELY

Recently,[2] equations were derived which predicted the influence of dielectric constant and ionic strength upon the critical increments of ionic reactions. The critical increments obtained by means of the theoretical equations were then compared with the experimental critical increments obtained for the reaction between ammonium and cyanate ions in methanol–water mixtures of constant dielectric constants. In the present investigation, the same reaction was studied over a temperature range of 30 to 60° in mixtures of water with ethylene glycol at the fixed dielectric constants of 63.5, 60, 55, 50, 45 and 40 in order to observe if there would be any specific medium effects due to the use of a different solvent. The experimental critical increments were then compared with the values obtained by means of the theoretical equations.[2]

Experimental

The ethylene glycol used was Eastman Best Grade (Highest Purity). The glycol was distilled and the fraction boiling sharply at 197° (uncorr.) was used. All other materials were prepared or purified as described in previous papers[3] which also describe the procedure used in this investigation. All temperatures were checked against a thermometer calibrated by the Bureau of Standards. Thermostat temperatures were maintained constant within ±0.01°. Dielectric constants for glycol–water mixtures were taken from the work of Åkerlöf.[4]

Average values of the limiting velocity constants were determined by means of the equation[3b,2]

$$k_0t = \left\{ \frac{1 + 4A\sqrt{C}}{C} \right\} - \left\{ \frac{1 + 4A\sqrt{C^0}}{C^0} \right\} \quad (1)$$

and are listed in Table I. Deviations (δ) of the experimental value of $C/(1 + 4\,A\sqrt{C})$ from the value calculated from the average k_0 are plotted[3b] against the experimental values of this function in Figs. 1 and 2. The filled circles represent values of $C^0/(1 + 4A\sqrt{C^0})$. In Table II, we give velocity constants (k_1) at $\sqrt{\mu} = 0.194$ obtained from k_0 by the relation[3b]

$$k_1 = k_0/(1 + 2A\sqrt{\mu}) \quad (2)$$

In Fig. 3, log k_0 is plotted against $1/T$ for the various media. These lines, as well as those obtained by plotting log k_1 against $1/T$, can be expressed by the general equation

$$\log k = \log K - (E/4.58T) \quad (3)$$

Values of log K_0 and E_0 and of log K_1 and E_1 obtained by means of equation (3) are listed in Tables I and II, respectively. The tables also contain values of k_0 and k_1 calculated by equation (3) using the tabulated values of log K and E.

---

[1] From the thesis presented to the Graduate Committee of Canisius College by James Lander in partial fulfilment of the requirements for the degree of Master of Science, June, 1938.

[2] (a) Svirbely and Warner, THIS JOURNAL, **57**, 1883 (1935); (b) Svirbely and Schramm, *ibid.*, **60**, 330 (1938).

[3] (a) Warner and Stitt, *ibid.*, **55**, 4807 (1933); (b) Warner and Warrick, *ibid.*, **57**, 1491 (1935).

[4] Åkerlöf, *ibid.*, **54**, 4125 (1932).