The correct value of the limiting conductance and the extent of ionization of these salts, were calculated using the method of Fuoss and Kraus.[15] Since the dissociation constants were greater than 10^{-3} the results were recalculated using the method proposed by Fuoss and Shedlovsky.[16] Figs. 1 and 2, respectively, indicate the results obtained by the two methods and the respective dissociation constants are given in Table III.

TABLE III

CALCULATED LIMITING CONDUCTANCES AND DISSOCIATION CONSTANTS

Salt	Λ_0 (calcd.)	F. and K. method $K \times 10^2$	F. and S. method, $K \times 10^2$
$(CH_3)_4NCl$	193.1	1.30	1.29
$(CH_3)_4NBr$	192.7	4.58	2.41
$(CH_3)_4NI$	195.3	4.94	3.62
$(CH_3)_4NIBrCl$	197.2	..	..
$(CH_3)_4NIBr_2$	193.0	..	..
$CsIBr_2$	187.1	..	..

Thus the two treatments agree, in that the tetramethylammonium polyhalides behave as strong electrolytes in acetonitrile, while the tetramethylammonium halides are considerably associated. Cesium dibromoiodide likewise appears to be a strong electrolyte.

It is interesting to note that there is a large difference in the solubilities of the simple halides and of the polyhalides in acetonitrile. The polyhalogen complexes are easily dissolved in this solvent and may form solutions containing as much as 40 g. of the polyhalide per 100 ml. of solvent at 25°. On the other hand, the simple halides dissolve with great difficulty, the solubility of the tetramethylammonium chloride, bromide and iodide being 0.265, 0.170 and 0.183 g., respectively, per 100 ml. of solvent at the same temperature.[7b,17]

It seems from the above data that the polyhalide ions are considerably more solvated by acetonitrile than the simple halide ions. This is probably to be expected since it is well known that compounds capable of acting as Lewis bases strongly polarize interhalides, especially if the latter contain iodine. This increased solvation, then can likewise account for the fact that the polyhalides form stronger electrolytes in acetonitrile than the simple halides.

Acknowledgment.—This work was partially supported by a grant from the Research Corporation.

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[15] (a) R. M. Fuoss and C. A. Kraus, THIS JOURNAL, **55**, 476 (1933); (b) R. M. Fuoss, *ibid.*, **57**, 488 (1935).

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING OF THE UNIVERSITY OF CALIFORNIA BERKELEY]

Complexing of Magnesium Ion by Fluoride Ion

BY ROBERT E. CONNICK AND MAAK-SANG TSAO

RECEIVED MAY 14, 1954

The complexing of magnesium ion by fluoride ion was measured by the "ferri"[1,2] method. The equilibrium quotient for complex formation at 25° and an ionic strength of 0.50 is 20. The heat and entropy changes are 4 ± 2 kcal. and 19 ± 7 e.u., respectively. Upper limits were set for fluoride complexing of calcium and barium ions. The available data on fluoride complexes of positive ions are consistent qualitatively with an ionic type of binding.

The fluoride complexing of a number of $+3$[1-7] and $+4$[2,8,9] ions has been studied recently, but of the $+2$ ions only beryllium[4,10] has been investigated quantitatively. To clarify the effects of charge and radius on the stability of such complexes it was desirable to have data on the other alkaline earth ions.

Experimental

The method was essentially that employed by Brosset and Orring[1] and Dodgen and Rollefson[2] in their studies of fluoride complexing of Al^{+3} and Th^{+4}, respectively. Complexing of the $+2$ cation is determined indirectly by studying its effect on the fluoride complexing of Fe^{+3}, as measured potentiometrically through the Fe^{++}-Fe^{+++} couple.

Two cells were used—a reference cell and a sample cell. Each cell consisted of a pair of half cells connected by an agar-agar bridge of 1.5 *M* sodium perchlorate. Each half cell contained 5.87×10^{-4} *M* ferric perchlorate, 2.315×10^{-4} *M* ferrous perchlorate and equal concentrations of perchloric acid. The sample half cells contained equal concentrations of alkaline earth perchlorate. To all half cells was added sufficient sodium perchlorate to give an ionic strength of 0.50.

Successive portions of sodium fluoride solution were added to one half cell of the reference and sample cells and the e.m.f. recorded. With no fluoride present the e.m.f.'s were less than 0.2 mv., usually less than 0.1 mv., and became constant within five minutes after addition of fluoride. Platinum electrodes were used. The solutions were stirred, and the cell and stirrer were coated with paraffin to prevent attack of the glass by hydrofluoric acid.

A magnesium perchlorate solution was prepared by dissolving analytical reagent grade magnesium oxide in perchloric acid. Barium and calcium perchlorate solutions were similarly prepared from $Ba(OH)_2$ and $CaCO_3$. Sodium perchlorate solutions were made by neutralization of perchloric acid with sodium carbonate. Pure iron wire was dissolved in excess perchloric acid and partially oxidized with hydrogen peroxide to give a mixed ferrous and ferric perchlorate solution. Distilled water was re-distilled from alkaline permanganate for use in all solutions.

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The experimental data are given in Tables I and II for magnesium ion at 25 and 15°. E and E' refer to the reference and sample cells, respectively. The symbol $\Sigma(X_0)$ designates the stoichiometric concentration of X present before addition of sodium fluoride. All concentrations are in moles per liter of solution, M, at room temperature.

TABLE I

MAGNESIUM FLUORIDE COMPLEX AT 25.00 ± 0.05° AND IONIC STRENGTH 0.50

0.503 M sodium fluoride stock solution; initial volume 110 ml.

	Expt. 1 $\Sigma(H_0{}^+) = 0.01719\ M$ $\Sigma(Mg_0{}^{++}) = 0.0349\ M$		Exp. 2 $\Sigma(H_0{}^+) = 0.02025\ M$ $\Sigma(Mg_0{}^{++}) = 0.1331\ M$		Exp. 3 $\Sigma(H_0{}^+) = 0.00994\ M$ $\Sigma(Mg_0{}^{++}) = 0.0416\ M$	
NaF added, ml.[a]	E, mv.	E', mv.	E, mv.	E', mv.	E, mv.	E', mv.
0.1994	41.53	40.82	39.13	37.21	47.90	46.66
0.399	74.16	72.72	69.62	65.54	87.77	84.85
0.598	96.81	94.75	90.67	85.14	115.39	111.26
0.798	114.43	111.98	106.86	100.21	137.23	131.74
0.997	129.40	126.49	120.66	112.65	156.00	148.94
1.196	142.89	139.32	132.92	123.57	173.05	164.31
1.396	155.14	150.94			188.90	178.21
1.595	166.56	161.72				

[a] All volumes for experiment 3 were 0.4% less.

TABLE II

MAGNESIUM FLUORIDE COMPLEX AT 14.97 ± 0.05° AND IONIC STRENGTH 0.50

0.503 M sodium fluoride stock solution; initial volume 110 ml.

	Exp. 1 $\Sigma(H_0{}^+) = 0.01078\ M$ $\Sigma(Mg_0{}^{++}) = 0.0416\ M$		Exp. 2[a] $\Sigma(H_0{}^+) = 0.01921\ M$ $\Sigma(Mg_0{}^{++}) = 0.1247\ M$		Exp. 3 $\Sigma(H_0{}^+) = 0.0446\ M$ $\Sigma(Mg_0{}^{++}) = 0.1247\ M$			Exp. 4 $\Sigma(H_0{}^+) = 0.01078\ M$ $\Sigma(Mg_0{}^{++}) = 0.1247\ M$		
NaF added, ml.	E, mv.	E', mv.	E, mv.	E', mv.	NaF added, ml.	E, mv.	E', mv.	NaF added, ml.	E, mv.	E', mv.
0.1987	46.43	45.22	39.75	38.08	0.1987	28.68	28.07	0.0496	9.5	9.12
0.397	84.78	82.11	70.89	67.35	0.397	50.51	49.50	0.2483	58.13	53.62
0.596	110.90	107.21	92.28	87.35	0.596	66.10	64.74	0.447	92.58	84.36
0.795	131.43	126.66	109.02	102.80	0.795	78.32	76.63	0.646	117.05	105.87
0.994	148.68	142.90	123.26	115.76	0.994	88.66	86.58	0.844	136.83	122.69
1.192	163.93	157.28	135.50	126.62	1.494	109.47	106.63	1.043	153.97	136.70
1.391	177.75	169.83			1.994	126.20	122.63			
1.590	190.30	181.45			2.494	140.53	136.06			
					2.994	153.57	147.90			

[a] Sodium fluoride volumes same as for exp. 1; ionic strength 0.47.

Interpretation.—The reference cell was used in conjunction with the sample cell to eliminate as far as possible any effect on activity coefficients when sodium perchlorate was replaced by magnesium perchlorate. It is believed these effects were small; *e.g.*, the two half cells containing no fluoride (from the reference and sample cells) when measured against each other gave an e.m.f. of less than 0.5 mv., except in one case. In interpreting the data it was assumed that the various activity coefficient ratios which were involved remained constant at constant ionic strength.

The e.m.f. of the reference cell was plotted against the total concentration of added sodium fluoride. From this curve was read the total fluoride concentration corresponding to a given E' of the sample cell. This value subtracted from the total fluoride of the sample cell gave the concentration of fluoride complexed by the alkaline earth ion. The net result of complexing of fluoride by the alkaline earth ion is to make it appear that there is less than the added fluoride in the sample cell.[11]

In interpreting the magnesium data, the following reaction was assumed

$$\mathrm{Mg}^{++} + \mathrm{HF} = \mathrm{MgF}^+ + \mathrm{H}^+ \qquad (1)$$

$$Q = \frac{(\mathrm{MgF}^+)(\mathrm{H}^+)}{(\mathrm{Mg}^{++})(\mathrm{HF})} \qquad (2)$$

where parentheses indicate concentrations in moles per liter and Q is the equilibrium quotient.

The ratio $(\mathrm{HF})/(\mathrm{H}^+)$ should be the same for the sample and reference cells at equal e.m.f.'s; it was calculated for the reference cells from the equilibrium quotients given in Table III.

TABLE III

EQUILIBRIUM QUOTIENTS FOR CALCULATION OF $(\mathrm{HF})/(\mathrm{H}^+)$

Ionic Strength, 0.50 (sodium perchlorate)

Reaction	Q at 25°	Ref.	Q at 15°	Ref
$\mathrm{Fe}^{+3} + \mathrm{HF} = \mathrm{FeF}^{+2} + \mathrm{H}^+$	189	2	192	7
$\mathrm{FeF}^{+2} + \mathrm{HF} = \mathrm{FeF_2}^+ + \mathrm{H}^+$	10.4	2	11.5	7
$\mathrm{FeF_2}^+ + \mathrm{HF} = \mathrm{FeF_3} + \mathrm{H}^+$	0.58	2	1.0	7
$\mathrm{Fe}^{+3} + \mathrm{H_2O} = \mathrm{FeOH}^{+2} + \mathrm{H}^+$	1.9×10^{-3}	2	1.18×10^{-3}	7
$\mathrm{HF} = \mathrm{H}^+ + \mathrm{F}^-$	1.23×10^{-3}	7	1.42×10^{-3}	7

It was found convenient to plot a calculated curve of $(\mathrm{HF})/(\mathrm{H}^+)$ as a function of the e.m.f. and to read $(\mathrm{HF})/(\mathrm{H}^+)$ from this graph.

If MgF^+ and Mg^{++} are assumed to be the only magnesium species, equation 2 can be rearranged to give

$$\frac{1}{1 - \dfrac{(\mathrm{MgF}^+)}{\Sigma(\mathrm{Mg}^{++})}} = 1 + Q\frac{(\mathrm{HF})}{(\mathrm{H}^+)} \qquad (3)$$

A plot of the left side *versus* $(\mathrm{HF})/(\mathrm{H}^+)$ should give a straight line of slope Q and intercept unity. The data for the two temperatures are presented in Figs. 1 and 2. The consistency of the points justifies the assumption that only reaction 1 is important. The slopes yield Q values of 2.4×10^{-2} and 2.3×10^{-2} at 25 and 15°, respectively. The corresponding values for reaction (4) are 20 and 16, all at ionic

$$\mathrm{Mg}^{++} + \mathrm{F}^- = \mathrm{MgF}^+ \qquad (4)$$

strength 0.50 (sodium perchlorate). It is estimated that these latter values will be increased about fourfold in going to zero ionic strength. From the data at the two temperatures, ΔH and ΔS of eq. 4 are calculated to be 4 ± 2 kcal. and 19 ± 7 e.u., respectively, at an ionic strength of 0.50.

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(11) Correction for the small volume difference between the sample and reference solutions is negligible.

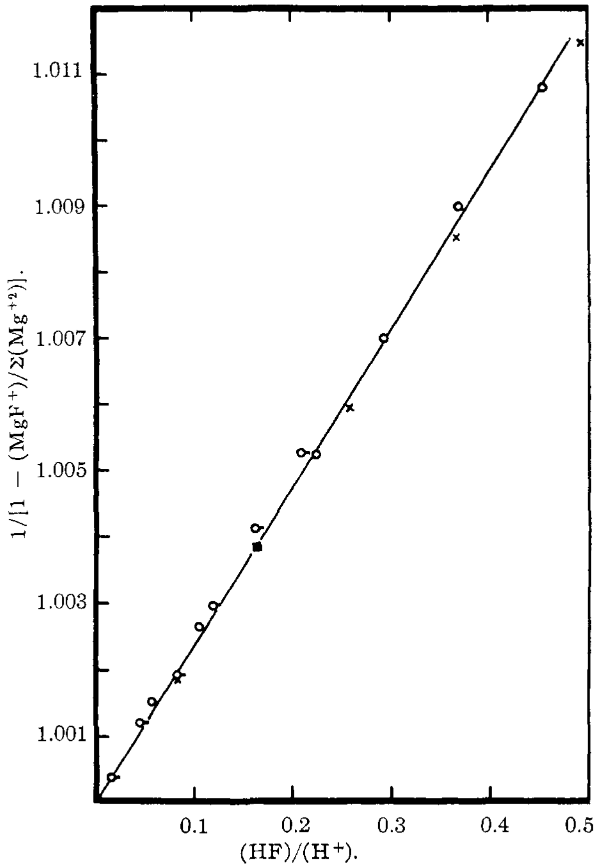

Fig. 1.—Magnesium fluoride complex at 25°: O, exp. 1, o-, exp. 2; X, expt. 3.

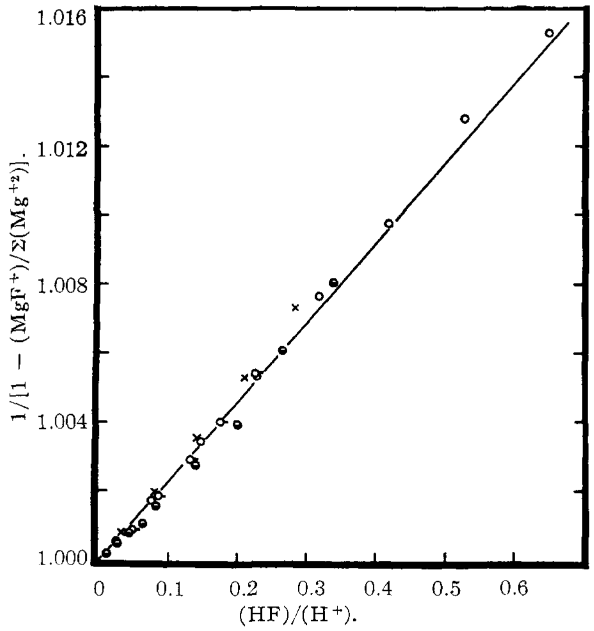

Fig. 2.—Magnesium fluoride complex at 15°: O, exp. 1; o-, exp. 2; ⊖, exp. 3; X, exp. 4.

The sample cells containing calcium and barium gave in all cases e.m.f. readings within 0.2 mv. of the reference cell. These small differences fell within the limit of experimental accuracy and showed no systematic trend. If it is assumed that complexing equivalent to an e.m.f. difference of 0.5 mv. would have been detected, upper limits to Q (eq. 2) for calcium and barium can be calculated to be 4×10^{-3} and 1×10^{-3} at 25° and an ionic strength of 0.50. The limit for calcium could not be lowered further because of the low solubility of the fluoride.

Charge and Radius Effects in Fluoride Complexing.—The logarithm of the equilibrium constant for the formation of the first fluoride complex at 25° has been plotted *versus* the cationic radius for all cations where data are available, in Fig. 3.

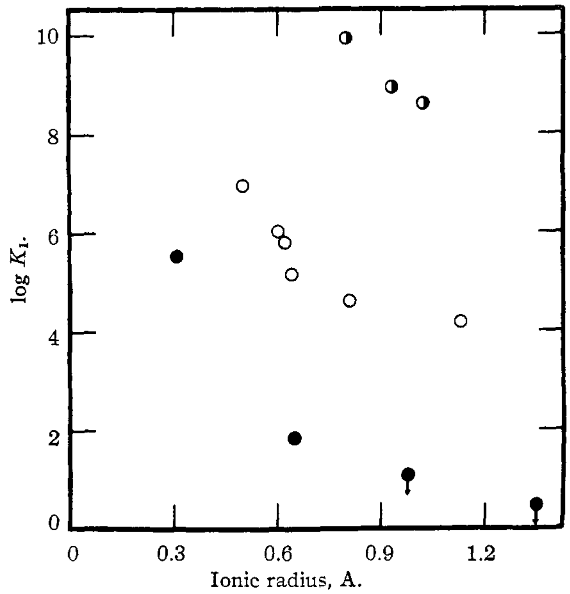

Fig. 3.—Equilibrium constants for formation of first fluoride complex as a function of the cationic radius. Reading from left to right: ●, Be^{++},[4] Mg^{++}, Ca^{++}, Ba^{++}; O, Al^{+3},[1] Fe^{+3},[2] Ga^{+3},[3] Cr^{+3},[3] In^{+3},[6] Ce^{+3},[6]; ◑, Zr^{+4},[9] Pu^{+4},[8] Th^{+4}.[2] The data of reference 8 were recalculated to allow for chloride complexing and the second fluoride complex.

The equilibrium quotients were corrected to zero ionic strength by means of empirical relationships reported for similar reactions.[12-15] The ionization constant of hydrofluoric acid was taken to be 6.7×10^{-4} at 25°.[7,16] The two points in the lower right corner for calcium and barium are only upper limits. To a first approximation the complexing appears to be a function of the charge and radius alone, that is, the data for ions of a given charge lie fairly well on smooth curves. At constant radius the equilibrium constant becomes larger with increasing ionic charge while for constant charge there is a trend toward smaller values as the radius increases. Both of these effects are to be expected qualitatively for an ionic type of complex.

On the basis of a simple coulombic model the free energy of complexing by fluoride ion is

$$\Delta F = -\frac{Z_+ e^2}{Dd} - T\,\Delta S' \qquad (5)$$

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where Z_+ is the cationic charge number, e the electronic charge, D the dielectric constant, d the sum of the fluoride and cation radii and $\Delta S'$ the entropy change in bringing together two species at one molar concentration, omitting their effect on the solvent. The latter value is estimated to be approximately -4 e.u.[17] When $-(\Delta F + T\Delta S')/Z_+$ is plotted *versus* d for the ions of Fig. 3, the $+2$ ions still lie somewhat below the $+3$, and the $+3$ below the $+4$. A decrease in the effective dielectric constant with increasing charge would account for such a trend.

For a given charge the variation of ΔF with radius is experimentally an higher inverse power of d than given by equation 5, if D is constant. Again such an effect can be explained by a variable dielectric constant which increases as d increases. Such a variation would be expected to arise from dielectric saturation in the intense electric fields near the cations.

Qualitatively the available data on fluoride complexing appear to be in agreement with the picture of an ionic type of complex. A quantitative treatment cannot be given at the present time.

One of us (M.S.T.) wishes to acknowledge the generous support of an American Association of University Women fellowship.

BERKELEY, CALIFORNIA

[17] This entropy change can be estimated roughly as minus R times the logarithm of the ratio of the number of positions available to the negative ions (or positive ions) before and after they are complexed. If the coördination number of the positive ion is assumed to be 6, there are $6N$ positions available to the negative ions when complexed, where N is Avogadro's number. Before complexing there are $55.6N$ positions. The resulting entropy change is -4 e.u. We are indebted to Professor H. S. Frank for this calculation.

[CONTRIBUTION FROM THE COATES CHEMICAL LABORATORY, LOUISIANA STATE UNIVERSITY]

Influence of Foreign Electrolytes and Temperature in Electrochemical Kinetics. An Application of Polarography and Voltammetry at Constant Current

BY PAUL DELAHAY AND CALVIN C. MATTAX

RECEIVED MARCH 15, 1954

Conditions under which the effect of foreign electrolytes in electrochemical kinetics can be studied quantitatively are discussed. The influence of various salts of potassium and sodium (KF, KCl, KBr, KI, KNO_3, $K_4Fe(CN)_6$, $NaClO_4$, Na_2SO_4) on the rate of electron transfer in the reduction of iodate in alkaline solution on a mercury electrode is studied. The rate constant for electron transfer at the potential corresponding to the maximum of the electrocapillary curve (the difference of potential at the interface is *very approximately* equal to zero) is essentially proportional to the cation concentration. Comparison with data obtained on the effect of foreign salts on the rate of isotopic exchange is made, and Libby's interpretation is applied to the electrochemical reduction of iodate. It is shown that in general cations and anions may influence the rate of electron transfer depending on the electrode potential. The effect of foreign salt on the polarographic half-wave potential for irreversible electrode processes is discussed. The influence of temperature on the reduction of iodate, Ni(II), Cr(III) and oxygen on a mercury cathode is studied experimentally. Variations of the rate constant for electron transfer with temperature result from the dependence of the free energy of activation on temperature and from several other factors (variations of the transfer coefficient; variations of the potential (*vs.* N.H.E.) at which the difference of potential at the interface is equal to zero; complications resulting from consecutive reactions and from variations in the composition of the solution). Experimental rates were obtained by conventional polarography and voltammetry at constant current.

Part I. Influence of Foreign Salts

Introduction

The rate of electrochemical reactions is influenced by the presence of foreign electrolytes,[1-4] *i.e.*, electrolytes which are not involved in the stoichiometric equation of the electrode reaction. It is generally assumed that the nature of the anion is determinative, although the effect of cation has been reported.[3,5] The effect of foreign electrolytes has also been observed in polarography: in the case of reversible waves the shift in half-wave potential results from complexation and variations of activities[6]; however, these effects do not account for the shift in half-wave potential in the case of irreversible waves.[7] The present study will throw, it is hoped, some light on this subject and will show how the effect of foreign electrolytes in electrochemical kinetics can be measured and interpreted quantitatively.

Great care should be taken in the selection of a suitable electrode process in such a study, and the following conditions should preferably be fulfilled. (1) The substances involved in the electrode reaction should not form stable complexes with the electrolyte being studied. (2) The kinetic characteristics of the electrode process should not be affected by a change in the hydrogen ion activity, since the addition of foreign electrolyte obviously causes a change in the activity of this ion. (3) The electrode process should preferably be totally irreversible at the current densities being used; the influence of the backward reaction can then be neglected, and the interpretation of experimental data is simplified. Furthermore, the kinetics of the electrode reaction should essentially be controlled by a single rate-determining step. (4) Mercury electrodes should be preferred to solid electrodes because of better reproducibility of data.

The previous requirements are fulfilled in the reduction of iodate on mercury in alkaline solution

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