Fluorine-19 Nuclear Magnetic Resonance Chemical Shift of Hydrofluoric Acid in H_2O and D_2O Solutions[1]

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Abstract: Values of the ^{19}F chemical shift in aqueous solutions containing HF in the presence of varying amounts of potassium fluoride are reported. Both $HF-KF-H_2O$ and $HF-KF-D_2O$ systems have been investigated. The chemical shifts of the species $F^-(H_2O)_x$, HF, HF_2^-, $F^-(D_2O)_x$, DF, and DF_2^- are derived from the concentration dependence of the exchange averaged ^{19}F shift. The results obtained show that isotopic substitution of hydrogen by deuterium produces high-field shifts of several parts per million for the F^- ion and HF molecule resonances in solution.

Several recent papers[4-6] have discussed the ^{19}F nuclear magnetic shielding of the fluorine nucleus present as fluoride ion,[7] $F^-(H_2O)_x$, hydrogen fluoride, HF, and bifluoride ion, HF_2^-, in aqueous solutions of alkali bifluorides[4] and hydrofluoric acid.[5,6] Only a single fluorine resonance is observed in these solutions because of the rapid exchange of fluorine between the different species. Nevertheless, it is still possible to derive values for the magnetic shielding in each of the fluorine-containing species by studying the behavior of the exchange averaged ^{19}F chemical shift as the solution composition is altered. Previous studies[8] of the thermodynamic properties of aqueous hydrofluoric acid solutions provide the essential information, describing the equilibria between the different species, required for the interpretation of the nuclear magnetic resonance results.

The sets of shifts for F^-, HF, and HF_2^- in aqueous solution obtained by earlier workers[4-6] show several inconsistencies (see Table I). Not only are there discrepancies in the magnitudes of the shifts, but there are also variations in the actual sequence of increased shielding for these species. In order to resolve this problem, we have undertaken an investigation of the ^{19}F chemical shift in aqueous solutions containing hydrofluoric acid in the presence of varying amounts of potassium fluoride. Our calculated values for the chemical shifts of the species F^-, HF, and HF_2^- are similar to those obtained by Borodin and Sventitskii[6] in their studies of aqueous hydrofluoric acid solutions but are in disagreement with values given by Haque and Reeves.[4]

Table I. ^{19}F Chemical Shifts of the Species $F^-(H_2O)_x$, HF, and HF_2^- in Aqueous Solution

Chemical shift[a]			
δ_{F^-}	δ_{HF}	$\delta_{HF_2^-}$	Reference
0	20.5	36.4	3
0	55	33	4
0	44.1 ± 0.6	32.5 ± 7	5
0	42.6 ± 0.5	33.0 ± 1	This work

[a] Relative to $F^-(H_2O)_x$. $\delta^0_{F^-(H_2O)_x} - \delta_{CF_3COOH} = 40.6$ ppm; $\delta_{F^-} - \delta_{F_2} = 548$ ppm.

Although there have been several investigations of the ^{19}F nmr spectra of solutions of hydrofluoric acid and alkali bifluorides in ordinary water, there have been no reports of similar studies on systems containing heavy water as a solvent. We have repeated the experiments outlined above using D_2O as solvent and determined the chemical shifts of the species $F^-(D_2O)_x$, DF, and DF_2^-. The isotope shifts are significant, being of the order of several parts per million. As an extension of previous studies[9,10] of isotope effects upon the ^{19}F chemical shift in alkali fluoride solutions, we have examined the dependence of the fluorine magnetic shielding in hydrofluoric acid solutions upon the isotopic composition of the solvent water. It has been found that the data can be satisfactorily interpreted in terms of the chemical shifts of the species present.

Experimental Section

Solutions were prepared from analytical grade 49% w/w hydrofluoric acid and analytical grade potassium fluoride. The latter was dried at 300° and stored in a desiccator. All solutions were prepared gravimetrically with an accuracy of ±0.1% and were kept in polyethylene containers. Samples under investigation were kept in polyethylene inserts within the ordinary 5-mm nmr sample tubes. A capillary standard of CF_3COOH in a 1-mm o.d. polyethylene tube was used.

Spectra were obtained with a Varian HA-60 spectrometer at 56.4 MHz using an internal lock and frequency sweep. A voltage-controlled oscillator was employed to obtain high manual oscillator frequencies as described elsewhere.[11] Measurements were made at 32 ± 2°. In the most dilute solutions, generally those of approximately 0.5 *m* HF, a Varian C1024 computer was employed to average several spectra and improve the signal-to-noise ratio.

Results

The resonance frequency of the single peak in the ^{19}F nmr spectrum of aqueous solutions containing 0.445 mole of HF in 55.55 moles of water in the presence of varying concentrations, m_2, of potassium fluoride was measured relative to the external standard of CF_3-

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(3) NRC Postdoctorate Fellow, 1966–1968.

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(7) The species F^-, HF, and HF_2^- all are undoubtedly solvated by water molecules to varying degrees. We have shown the fluoride ion in ordinary water as $F^-(H_2O)_x$ as a means of distinguishing it from the analogous species, $F^-(D_2O)_x$, present in heavy water.

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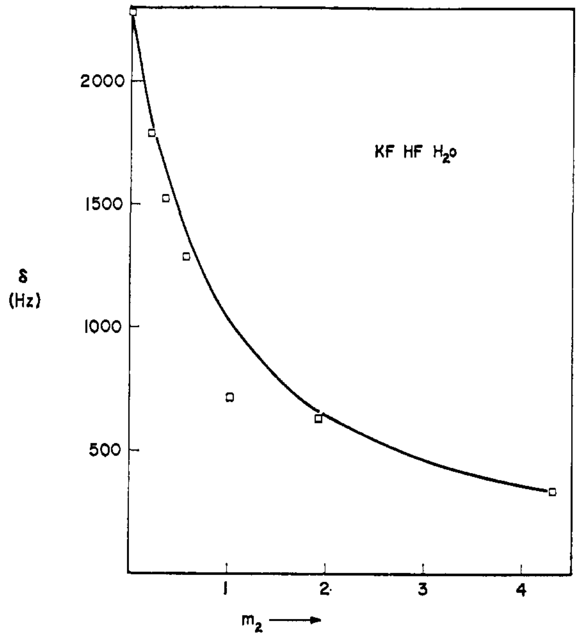

Figure 1. ^{19}F chemical shift in solutions containing 0.445 mole of HF, m_2 moles of KF, and 55.51 moles of H_2O: ——, calculated dependence with $K_1 = 5.91 \times 10^{-4}$ mole and $K_2 = 4.23$ mole^{-1}.

COOH. The results are listed in Table II and shown graphically in Figure 1. A parallel series of experiments with a solution containing 0.525 mole of HF in 55.51 moles of deuterium oxide gave the results shown in Table III and Figure 2.

Table II. ^{19}F Chemical Shift in Solutions Containing 0.445 Mole of HF, m_2 Moles of KF, and 55.51 Moles of H_2O

m_2	δ_{CF_3COOH}	$\delta_{F^-(H_2O)}$[a]	$\delta_{K^+F^-}$[b]	δ_{susc}[c]	δ[d]
0	4572.2	2283.2	...	...	2283.2
0.215	4077.5	1788.5	3.2	0.2	1791.9
0.360	3805.6	1516.6	5.4	0.4	1522.4
0.574	3566.2	1277.2	9.7	0.7	1287.6
1.024	2095.9	706.9	11.5	1.2	719.6
1.925	2894.9	605.9	24.4	2.3	632.6
4.315	2589.8	300.8	35.2	5.1	341.1

[a] ^{19}F chemical shift relative to fluoride ion at infinite dilution in water; $\delta_{F^-(H_2O)} - \delta_{CF_3COOH} = 2289.0$ Hz. [b] Correction for influence of potassium ion upon ^{19}F chemical shift. [c] Bulk diamagnetic susceptibility correction. [d] Corrected ^{19}F chemical shift.

Table III. ^{19}F Chemical Shift in Solutions Containing 0.525 Mole of HF, m_2 Moles of KF, and 55.51 Moles of 99.75% D_2O

m_2	δ_{CF_3COOH}	$\delta_{F^-(D_2O)}$[a]	$\delta_{K^+F^-}$[b]	δ_{susc}[c]	δ[d]
0	4884.9	2428.6	...	...	2428.6
0.097	4646.6	2189.8	1.5	0.1	2191.4
0.188	4436.9	1980.1	2.9	0.2	1983.7
0.246	4320.0	1863.2	3.7	0.2	1867.6
0.323	4183.8	1727.0	4.7	0.4	1732.6
0.429	4022.5	1565.7	6.2	0.5	1572.9
0.548	4884.0	1427.7	8.1	0.6	1436.4
0.667	3757.1	1300.8	9.6	0.8	1311.2
0.991	3511.5	1055.2	11.1	1.2	1067.5
1.413	3291.6	835.3	19.4	1.7	856.7
1.930	3128.9	672.6	24.4	2.3	699.3
2.314	3038.8	582.5	27.6	2.7	612.8
2.857	2942.5	486.2	31.1	3.4	520.7
3.371	2875.8	419.5	33.5	4.0	457.0
4.382	2782.0	325.7	35.2	5.8	366.7

[a] ^{19}F chemical shift relative to fluoride ion at infinite dilution in heavy water, $\delta_{F^-(D_2O)} - \delta_{CF_3COOH} = 2456.3$ Hz. [b] Correction for influence of potassium ion upon ^{19}F chemical shift. [c] Bulk diamagnetic susceptibility correction. [d] Corrected ^{19}F chemical shift.

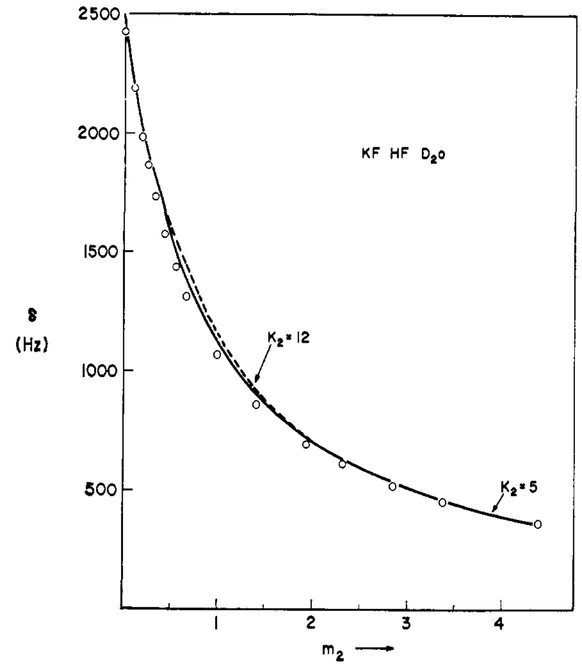

Figure 2. ^{19}F chemical shift in solutions containing 0.525 mole of HF, m_2 moles of KF, and 55.51 moles of 99.75% D_2O: ——, calculated dependence with $K_1 = 2 \times 10^{-4}$ mole and $K_2 = 5$ mole^{-1}; - - - -, calculated with $K_2 = 12$.

Calculation

The principal equilibria present in a solution of hydrofluoric acid and potassium fluoride can be represented by the following equations

$$\underset{(m_1 - q - r)}{\mathrm{HF}} \overset{K_1}{\rightleftharpoons} \underset{q}{\mathrm{H}^+} + \underset{(m_2 + q - r)}{\mathrm{F}^-}$$

$$\underset{(m_1 - q - r)}{\mathrm{HF}} + \underset{(m_2 + q - r)}{\mathrm{F}^-} \overset{K_2}{\rightleftharpoons} \underset{r}{\mathrm{HF}^{2-}}$$

$$K_1 = \frac{q(m_2 + q - r)}{(m_1 - q - r)} \frac{\gamma_{H^+}\gamma_{F^-}}{\gamma_{HF}} \tag{1}$$

$$K_2 = \frac{r}{(m_1 - q - r)(m_2 + q - r)} \frac{\gamma_{HF_2^-}}{\gamma_{HF}\gamma_{F^-}} \tag{2}$$

where m_1 and m_2 are the initial stoichiometric concentrations of HF and KF, respectively; γ_{H^+}, γ_{F^-}, γ_{HF}, and $\gamma_{HF_2^-}$ are the molal activity coefficients of the various species in solution.

Because of the rapid fluorine exchange between the different species, only one ^{19}F resonance signal is observed, and this corresponds to a weighted average[12] of the chemical shifts, δ_{F^-}, δ_{HF}, and $_{HF_2^-}$ characteristic of F^-, HF, and HF_2^-. This may be expressed as

$$\delta = \frac{m_1 - q - r}{m_1 + m_2}\delta_{HF} + \frac{m_2 + q - r}{m_1 + m_2}\delta_{F^-} + \frac{2r}{m_1 + m_2}\delta_{HF_2^-} \tag{3}$$

It is convenient to express the chemical shifts relative to that of the fluoride ion at infinite dilution, $\delta^0_{F^-}$. This latter quantity is found to have the value $\delta^0_{F^-(H_2O)} - \delta_{CF_3COOH} = 2289.0$ Hz for solutions in ordinary water,

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(12) The formula used in ref 4 to relate δ to δ_{F^-}, δ_{HF}, and $\delta_{HF_2^-}$ is in error since no allowance has been made for the presence of two fluorines in the species HF_2^-.

and when 99.75% D_2O is the solvent the corresponding value $\delta^0_{F^-(D_2O)} - \delta_{CF_3COOH} = 2456.3$ Hz. Shifts adjusted to these reference points are shown in Tables II and III. It is also necessary to make two small corrections to experimental data in order to allow for the effects produced firstly by the variation in bulk susceptibility of the solutions and secondly by the presence of potassium ion. Bulk diamagnetic susceptibility corrections were calculated[13] with the aid of ion susceptibilities given by Selwood.[14] Measurements in aqueous potassium fluoride solutions[3,15–17] indicate a chemical shift to low fields of the ^{19}F resonance up to salt concentrations of about 5 m. We have employed these results[16] to correct for the influence of potassium ion upon the ^{19}F chemical shifts in the HF–KF solutions. In the absence of any detailed studies of the concentration dependence in heavy water solutions of potassium fluoride, we have used the data obtained for solutions in ordinary water to correct our results for the system HF–KF–D_2O. Some preliminary measurements we have made indicate that there are only very small differences in the concentration dependence of the ^{19}F chemical shift for solutions of potassium fluoride in light or heavy water. Corrected values, δ, for the ^{19}F chemical shifts in HF–KF solutions are given in Tables II and III.

In order to determine the individual chemical shifts of the three fluorine-containing species F^-, HF, and HF_2^- in these solutions, it is necessary to have information about the equilibrium constants, K_1 and K_2, and the molal activity coefficients of the ions. We consider first the system HF-KF-H_2O. Broene and De Vries[8] have measured the equilibrium constants for solutions of hydrofluoric acid in ordinary water, and their data give the interpolated values $K_1 = 5.91 \times 10^{-4}$ mole and $K_2 = 4.23$ mole^{-1} at 32°. These are the values used in our calculations. We have adopted two procedures to determine appropriate values for the molal ionic activity coefficients, γ, occurring in eq 1 and 2. Firstly, in the case where the solutions contain only hydrofluoric acid, we have followed the procedure given by Broene and De Vries.[8] Since the concentrations of ionic species in such solutions are extremely small, the activity coefficients can be represented by the Debye–Hückel expression

$$\log \gamma = -0.516\sqrt{\mu}/(1 + \sqrt{\mu}) \qquad (4)$$

where μ is the ionic strength. It is assumed that the activity coefficients are the same for all the ions, *i.e.*, $\gamma_{F^-} = \gamma_{HF_2^-} = \gamma_{H^+} = \gamma$ and that for the uncharged hydrogen fluoride molecule $\gamma_{HF} = 1$. The value of γ was approximated until a value was found that satisfied eq 1, 2, and 4. We obtain the values $\gamma = 0.830$, $q = [H^+] = 3.41 \times 10^{-2}$, and $r = [HF_2^-] = 2.22 \times 10^{-2}$ for the 0.445 m solution of HF. Substitution in eq 3 gives

$$\delta = 0.874\delta_{HF} + 0.0999\delta_{HF_2^-} + 0.0269\delta_{F^-} \qquad (5)$$

Since we have already adjusted our experimental data so that $\delta_{F^-} = 0$, the above expression contains two unknowns, δ_{HF} and $\delta_{HF_2^-}$. It is therefore necessary to estimate the concentrations of the various species in at least one other solution in order to obtain a second equation relating the chemical shifts of the HF molecule and the HF_2^- ion.

Consider the other extreme case when there is a large excess of potassium fluoride present. Then we have the condition $m_2 \gg q$, so that from eq 1

$$\frac{q(m_2 - r)\gamma^2}{(m_1 - q - r)} = K_1$$

and from eq 2

$$\frac{r}{(m_1 - q - r)(m_2 - r)} = K_2$$

We have taken the activity coefficient, γ, in this case to be identical with that of a potassium fluoride solution of concentration m_2.[18,19] The calculations are not very sensitive to the magnitude of the activity coefficient since this quantity only occurs in the expression for K_1. Calculations for the solution of composition $m_2 = 4.315$ and $m_1 = 0.445$ with $\gamma = 0.803$ give the values $r = 0.420$ and $q = 6 \times 10^{-6}$. Substitution in eq 3 gives

$$\delta = 0.00525\delta_{HF} + 0.1764\delta_{HF_2^-} + 0.8185\delta_{F^-} \qquad (6)$$

Combination of eq 5 and 6 yields the following values for the chemical shifts of the hydrogen fluoride molecule, δ_{HF}, and the bifluoride ion, $\delta_{HF_2^-}$, in aqueous solution relative to that of the fluoride ion: $\delta_{HF} = 2402$ Hz $= 42.6$ ppm; $\delta_{HF_2^-} = 1862$ Hz $= 33.0$ ppm.

By using the procedure outlined above for the solution containing 4.315 moles of KF, it is possible to calculate the composition expected for the other KF–HF–H_2O solutions. Substitution of estimated values for the parameters q and r together with the values for the chemical shifts δ_{HF} and $\delta_{HF_2^-}$ given above allows estimates of the resultant ^{19}F chemical shifts to be made using eq 3. Figure 1 compares shifts calculated in this way with those observed experimentally, and Figure 3 shows the estimated concentrations of the species $F^-(H_2O)_x$, HF, and HF_2^- in these solutions.

Calculations similar to those described in the preceding paragraphs may be made for solutions of hydrofluoric acid and potassium fluoride in 99.75% D_2O. However, it is necessary to employ different values for the equilibrium constants K_1 and K_2 when heavy water is the solvent. Generally acid dissociation constants are reduced by a factor of 3 in D_2O compared to their value in ordinary water.[20] For example, acetic acid has dissociation constants of 1.76×10^{-5} and 0.55×10^{-5} in light and heavy water at 25°. We have used a value of $K_1 = 2 \times 10^{-4}$ mole for the system KF–HF–D_2O. In the absence of any data on comparable systems we have chosen a value of $K_2 = 5$ mole^{-1}.

Using the approach described previously, we obtain for the solution containing 0.525 mole of HF in D_2O with $\gamma = 0.857$, $q = 0.0220$, and $r = 0.0159$

$$\delta = 0.9279\delta_{DF} + 0.06056\delta_{DF_2^-} + 0.0116\delta_{F^-} \qquad (7)$$

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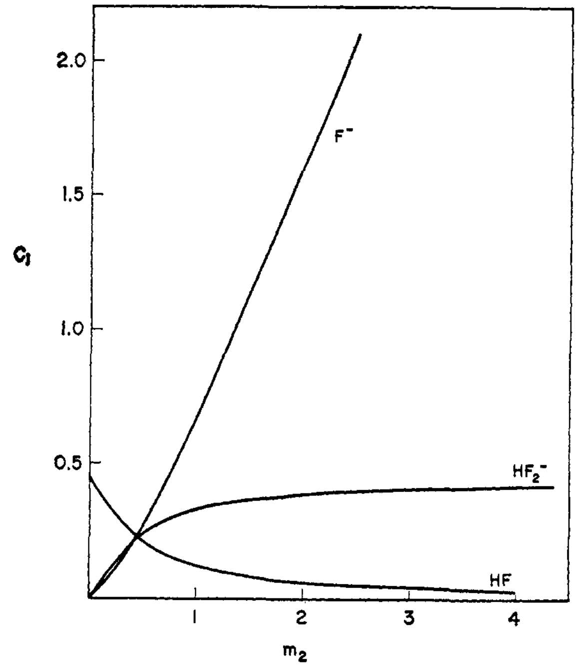

Figure 3. Estimated concentrations of F^-, HF, and HF_2^- in the system 0.445 mole of HF, m_2 moles of KF, and 55.51 moles of H_2O.

and when $m_2 = 4.382$, $m_1 = 0.525$, and $\gamma = 0.808$, we have

$$\delta = 0.005096\delta_{DF} + 0.2038\delta_{DF_2^-} + 0.791\delta_{F^-} \quad (8)$$

Combination of eq 7 and 8 gives the chemical shifts δ_{DF} and $\delta_{DF_2^-}$ relative to the shift of the fluoride ion in heavy water, $\delta_{F^-}(D_2O)$: $\delta_{DF} = 2503$ Hz = 44.4 ppm; $\delta_{DF_2^-} = 1736$ Hz = 30.8 ppm. In Figure 2 chemical shifts calculated using these values are compared with the experimental data.

Chemical shifts of the species HF, DF, HF_2^-, and DF_2^- relative to the shift of the fluoride ion in ordinary water are listed below.

	δ, ppm		δ, ppm
HF	42.6	DF	47.3
HF_2^-	33.0	DF_2^-	33.7
$F^-(H_2O)_x$	0	$F^-(D_2O)_x$	2.96

Discussion

Uncertainties in the calculation of ^{19}F chemical shifts are introduced mainly by the limited accuracy of the equilibrium constants, K_1 and K_2. We have employed values given in the literature[8] for ordinary water solutions and assumed values for corresponding data in heavy water solutions. Determination of activity coefficients from the Debye–Hückel expression is generally reliable for low ionic concentrations and should not lead to any serious errors. If we allow a 100% variation in the values of $K_1(\gamma_{HF}/\gamma_{H^+}\gamma_{F^-})$ and $K_2(\gamma_{HF}\cdot\gamma_{F^-}/\gamma_{HF_2^-})$, the corresponding variation in the values of the chemical shifts δ_{HF} and δ_{DF} is calculated to be ±0.3 ppm. The magnitude of the chemical shifts $\delta_{HF_2^-}$ and $\delta_{DF_2^-}$ of the bifluoride ions is mainly determined by the magnitude of K_2, and an error of 100% in this quantity would correspond to a variation of 1 ppm. A variation of this order in the equilibrium constant K_2 is not to be expected in the solutions for the system KF–HF–H_2O, but for the corresponding system in heavy water our assumed value of K_2 may well be in error by 100%.

It has been implicitly assumed in our calculations that the quantities δ_{HF}, δ_{DF}, $\delta_{HF_2^-}$, $\delta_{DF_2^-}$, $\delta_{F^-(H_2O)_x}$, and $\delta_{F^-(D_2O)_x}$ are constants independent of the solution concentration. The reasonable agreement between the calculated variation in ^{19}F chemical shift with concentration and the experimental data suggests that there is no significant concentration dependence of the chemical shifts assigned to the different species. However, a more detailed treatment of these systems would have to take into account the possibility of such a dependence. Such a treatment is not necessary within the accuracy of our calculations.

The observed increase in ^{19}F magnetic shielding for DF compared to HF is in agreement with results of other investigations,[21] where substitution of a lighter by a heavier isotope always produces an increase in shielding. These effects are generally interpreted in terms of differences in zero-point vibrational amplitudes. In the absence of any reliable data about the state of HF and DF molecules in solution, no quantitative interpretation can be given.

Raman studies[22] of solutions containing bifluoride ions, HF_2^-, suggest a highly ionized structure for this ion with the proton only loosely attached to the fluorines. If this is so it would be expected that the sensitivity of the ^{19}F chemical shift of the HF_2^- ion to isotopic substitution should be lower than that of the HF molecule. The small isotope effect observed experimentally for HF_2^- and DF_2^-, only 0.7 ppm, compared with the large difference between HF and DF is in agreement with the behavior indicated by Raman data. It must be remembered, however, that other changes in magnetic shielding resulting from differences in solvation cannot be predicted although they might make important contributions.

The sequence of increased ^{19}F magnetic shielding $F^-(H_2O)_x < HF_2^- < HF$ appears reasonable since we might expect the bifluoride ion to be intermediate in character between the fluoride ion and hydrogen fluoride molecule. The observation of an averaged ^{19}F signal indicates that the lifetime of these species in solution is less than 10^{-4} sec.

It is evident that some explanation must exist for the discrepancy between the data in ref 4 and values obtained by other workers (see Table I). These results were derived from studies of the concentration dependence of the ^{19}F chemical shift in aqueous KHF_2 solutions. The most obvious reason is the extrapolation to concentrated solutions used to derive a value for the shift of the HF_2^- ion. Jones and Penneman[23] have shown from infrared spectra of bifluoride solutions that polymeric species are already present in significant amounts at a concentration of about 3 *M*. Since these polymers are known to give a high-field ^{19}F chemical shift with respect to the species studied here,[6] this explains in part the rather high value obtained for the chemical shift of HF_2^-.

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Inaccuracies also arise in the extrapolation to infinite dilution used[4] to obtain a value for the chemical shift of the HF molecule due to the steep slope of the curve in this region.

We have tried to interpret the experimental data given by Haque and Reeves[4] in terms of our derived chemical shifts values, δ_{HF} and $\delta_{HF_2^-}$. The equilibrium can be described by

$$\underset{(1-\alpha)}{HF_2^-} \rightleftharpoons \underset{\alpha}{HF} + \underset{\alpha}{F^-} \tag{9}$$

where α is the degree of dissociation. This quantity can be expressed in terms of the observed chemical shift, δ, and the shifts of the three fluorine-containing species as

$$\alpha = 2\frac{\delta_{HF_2^-} - \delta}{(2\delta_{HF_2^-} - \delta_{HF} - \delta_{F^-})} \tag{10}$$

By inserting our derived values for the chemical shifts δ_{F^-}, δ_{HF}, and $\delta_{HF_2^-}$ together with the experimental values for the resultant chemical shift obtained by Haque and Reeves[4] into eq 10, we find that the calculated values for the degree of dissociation, α, are greater than 1 at concentrations below 0.5 *M*. We have repeated the determination of the ^{19}F chemical shift for a number of KHF_2 solutions in the concentration range 0.5–2.0 *M*. Using our experimental technique we obtain values approximately 1 ppm to high field of those reported by Haque and Reeves.[4] A change of this magnitude reduces calculated values of the degree of dissociation, α, to less than 1.

A possible explanation for the discrepancy between our results and those of Haque and Reeves[4] might arise from their use of glass tubes. Both fluoride[16,24] and bifluoride solutions readily attack glass to produce complex fluoride ions including SiF_6^{2-}. The ^{19}F resonance of the SiF_6^{2-} ion occurs approximately 30 ppm to low field of that for HF_2^- in solution,[25] and, if significant amounts are present in the KHF_2 solutions, this will lower the value of the observed average signal below that expected solely from exchange between HF_2^-, HF, and F^-.

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Mechanism of the Metal-Ion-Catalyzed Hydrolysis of Ethyl Valinate- and Ethyl Leucinate-N,N-diacetic Acids

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Abstract: Ethyl valinate-N,N-diacetic acid (EVDA) was prepared by the reaction of iodoacetic acid and valine ethyl ester in basic solution and was identified by elemental analysis, nmr, and infrared spectra. Ethyl leucinate-N,N-diacetic acid (ELDA) was prepared analogously and identified by nmr. Formation constants were determined with the metal ions copper(II), cobalt(II), nickel(II), lead(II), and samarium(III) which indicate that EVDA coordinates strongly to these metal ions as a tridentate ligand; *i.e.*, the extent of ester carbonyl coordination to these metals is small. Hydroxo-complex, M(EVDA)(OH), formation constants were determined at several temperatures so that ΔH and ΔS could be calculated. The rate of ester hydrolysis in M(EVDA) and M(ELDA) in the pH range 7.0–9.0 which includes the range of hydroxo-complex formation was studied and found to obey the rate law: rate = k[M(EVDA)][OH^-]. Enthalpies and entropies of activation were also determined for the hydrolysis reaction of the copper(II) complex of ethyl glycinate-N,N-diacetic acid, Cu(EGDA). Nitrite ion, 4-picoline, pyridine, acetate ion, and phosphate dianion exhibited general nucleophilic catalysis with the order of nucleophilicity being roughly the same as observed for simple organic esters which undergo hydrolysis by external nucleophilic attack. The most probable mechanism for the ester hydrolysis of M(EVDA) and M(ELDA), which is consistent with all observations, involves external hydroxide ion attack on the carbonyl carbon of the ester which has coordinated to the metal ion in a rapid prior equilibrium.

A number of mechanisms have been proposed for the metal-ion-promoted hydrolysis of α-amino acid esters.[1–7] Most explain the promoted hydrolysis by assuming polarization of the carbonyl group by the metal ion. The most difficult problem has been to identify the nucleophile and particularly to distinguish between external hydroxide ion attack (mechanism A) and internal attack by a hydroxo group bound to the metal ion (mechanism B). Both mechanisms obey the same rate law.

The present investigation utilizes metal complexes of ethyl valinate-N,N-diacetic acid and ethyl leucinate-N,N-diacetic acid which undergo slow ester hydrolysis even at pH 7–9 in the region where hydroxo complexes

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