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CHEMICAL SHIFTS OF FLUORINE IN HYDROGEN FLUORIDE AND FLUORIDE ION

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SUMMARY

Chemical shifts of fluorine in solutions of hydrogen fluoride, sodium fluoride, potassium fluoride, cesium fluoride, silver fluoride, silver bifluoride, ammonium bifluoride, and tetraethylammonium fluoride have been measured. Hydrogen fluoride was dissolved in water and in aqueous and anhydrous organic solvents (methanol, ethylene glycol, dimethoxyethane, carbitol (diethyleneglycol monoethyl ether), tetrahydrofuran, dioxane, dimethylformamide, acetonitrile, dimethylsulfoxide, and sulfolane (tetramethylene sulfone); all other fluorides were dissolved in water and aqueous organic solvents. The effects of fluoride concentration in water and in aqueous organic solvents on chemical shifts of fluorine were investigated.

INTRODUCTION

In the syntheses of organic fluorine compounds, the reaction mixtures often contain hydrogen fluoride and inorganic fluorides, either as reactants or as by-products. It is of advantage to use ^{19}F NMR for the analysis of such mixtures. However, the literature data on chemical shifts of hydrogen fluoride and fluorides differ considerably, depending on the source and on the conditions of measurement.

Some confusion has been generated by the different usage of positive or negative values of chemical shifts in higher magnetic fields. The value of the chemical shift of hydrogen fluoride (-40 ppm) as quoted in Volume 7 of Progress in Nuclear Magnetic Resonance Spectroscopy [1] is evidently a victim of an error in the sign. If the reported chemical shift -116.55 ppm

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from trifluoroacetic acid were used as a positive value, the chemical shift of hydrogen fluoride would be 193.55 (not far away from 204 ppm, quoted in Compilation of Reported F^{19} NMR Chemical Shifts [2], and quite in agreement with chemical shifts reported by other authors. Examples of variations in reported chemical shifts are shown in Table 1.

The purpose of the present work is to verify some of the literature data and to report chemical shifts of hydrogen fluoride and fluoride ions obtained under various but well-defined conditions. In order to avoid the confusion of signs, all values reported in this paper are chemical shifts with respect to the internal standard of fluorotrichloromethane (F_{11}). As a consequence, all appear to the right (east) of F_{11}.

EXPERIMENTAL

Fluorine NMR spectra were taken at a temperature of 21° on a Varian EM 390 NMR spectrometer at 84.6 MHz in standard 5 mm glass tubes or 4 mm polytetrafluoroethylene inserts. Trifluoroacetic acid (TFA) or hexafluorobenzene (HFB), or both, were used as internal standards. All the measurements were repeated immediately, and some measurements were repeated both immediately and then after certain intervals. Average values were taken in cases where slight differences occurred owing to the momentary instability of the instrument's magnetic field. The majority of the measurements were preceded by taking spectra of a standard solution containing fluorotrichloromethane (F_{11}), TFA, and HFB in carbon tetrachloride. The values of chemical shifts of TFA and HFB thus found were used as references for calculations of the chemical shifts of the samples. Average values of 77.2 ppm for TFA and 163.8 ppm for HFB were obtained as a result of many measurements of the standard solution. (Literature values are 77 and 163 ppm [1], or 76.55 and 164.9 [2], respectively.)

Chemicals

Anhydrous hydrogen fluoride was distilled from a commercial cylinder, condensed in a 75 ml stainless steel container, and pipeted from the container, which was cooled with a dry ice-acetone bath. Aqueous hydrogen fluoride was reagent grade 48-51% hydrofluoric acid. Sodium and cesium fluorides were reagent grade, while the potassium fluoride was certified grade. Potassium fluoride was dried at 180° for 24 h; cesium fluoride at 200° for 36 h. Ammonium bifluoride was crystalline of technical grade.

TABLE 1

Survey of literature data on chemical shift of fluorine in hydrogen fluoride, fluoride ion and bifluoride ion*

Ref.	HF	HF_2^-	F^-	Standard	Conditions of Measurements
1	-40			TFA ext.	
2	204		124.8	F_2 ext. (-422.9)	HF aq.; KF aq.
4	196		119.2	F_2 ext.	HF anhyd.; room temp.; KF aq., room temp.
5	167.9			TFA ext.	HF aq., 48-51%
			118.7	TFA ext.	NaF, KF aq., dilute
			120.2	TFA ext.	KF aq., 13.3M
			121	TFA	AgF aq., 1M, 2M
6	161.7	150.1			HF aq.; KF aq.
7	196		96,221		HF; KF, and NaF aq., respec.
8	193.55			TFA ext.	TFA -116.55 ppm
9	138.1	154.0		F^- (117.6)	HF aq.; KHF_2 aq. (see ref. 10)
10			117.5	TFA ext.	KF aq., 32°
11	160.2	150.6	117.6	TFA ext.	HF aq., KF, KHF_2 aq., 32°
			119.6	F_2 ext.	
12	166.0			TFA ext.	HF aq., 48%
13	190.53			SiF_4 ext.	HF anhyd., liq.
14		167.9			$Bu_4N^+ HF_2^-$ aq., 30°;
			128.3		$Bu_4N^+ F^-$ aq., 30°
15		144.0		TFA ext.	$Bu_4N^+ HF_2^-$, MeCN, -20°
		148.0		TFA ext.	$Bu_4N^+ HF_2^-$, MeCN, 70°
16	170				HF aq., 49%, in MeCN-CH_2Cl_2 1:1
		149.4			$Pr_4N^+ HF_2^-$, CH_2Cl_2, 0.1M
			114.6		$Pr_4N^+ F^-$, CH_2Cl_2, 0.96M
17	188.1			HF (76.1)	HF-C_5H_5N 7:3

* Chemical shifts are given in positive values of ppm east of F_{11} (fluorotrichloromethane): TFA = 77.0, HFB = 163.0, F_2 = -429 ppm [1].

Silver fluoride (Ozark Mahoning) and silver bifluoride (Ventron) were of reagent grade. Tetraethylammonium fluoride contained water which was removed by evaporation at 30° at 0.05 mm.

The solvents used were of the following qualities: methanol, analytically pure; ether, anhydrous; benzene, certified; ethylene glycol, certified; dimethoxyethane, 99% minimum assay; carbitol, purified; tetrahydrofuran, distilled from lithium aluminum hydride; dioxane, certified; acetone, analytical; dimethylformamide, distilled at 50°C at 13 mm; acetonitrile, certified; dimethylsulfoxide, certified; tetramethylenesulfone, distilled at 173°C at 30 mm, m.p. 24.5°.

Preparation of Samples

Stock solutions of the fluorides in distilled water were of 10% w/w concentration and were stored in polyethylene bottles. Solutions of fluorides in aqueous organic solvents were prepared by mixing equal volumes of the 10% aqueous solutions of the fluorides and of organic solvents. Solutions of hydrogen fluoride in organic solvents (10%) were prepared by adding weighed amounts of precooled anhydrous hydrogen fluoride to the weighed amounts of the solution in polyethylene bottles. Solutions of hydrogen fluoride in aqueous organic solvents were prepared by diluting the solutions in anhydrous solvents by the same weight of distilled water. A solution of hydrogen fluoride in a mixture of ether and benzene was prepared by extraction with the mixture of the solvents of aqueous (48-51%) hydrofluoric acid. Aqueous solutions of hydrogen fluoride of various concentrations were prepared by dilution of certified 48-51% hydrofluoric acid with distilled water. Solutions of anhydrous hydrogen fluoride of various concentrations were obtained by dilution of the stock solution of anhydrous hydrogen fluoride in dimethylformamide (40%) with dimethylformamide. Solutions of various concentration of some fluorides in water were prepared by dilution of the stock solutions (50%) with water.

RESULTS AND DISCUSSION

In order to check how much storage of the solutions of the fluorides in water affected the chemical shift, samples of aqueous fluorides were measured at one day intervals. Data in Table 2 show that no significant variations occurred after up to 8 days of storage. Also, with the exception of cesium fluoride, chemical shift did not change noticeably whether the samples were kept in polytetrafluoroethylene or glass tubes.

TABLE 2

Effect of storage on the chemical shift of fluorine in aqueous solution of alkali fluorides

	^{19}F Chemical Shift					
	Same Day	After One Day*	After 2 Days	After 7 Days	After 8 Days	Average
NaF	125.0	125.5, 124.7	122.4	122.3	125.0	124.2 ± 1.43%
KF	123.0	123.1, 122.5	121.5	121.7	122.5	122.4 ± 0.66%
CsF	124.2	124.7, 122.4	121.0	121.2	122.3	122.6 ± 1.52%

* Measurements done in polytetrafluoroethylene inserts and in glass tubes, respectively.

TABLE 3

Effect of concentration on the fluorine chemical shift in solutions of hydrogen fluoride and some fluorides

%	HF in H_2O	HF in DMF	HF in DMF/H_2O	Et$_4$NF in* DMF/H_2O	KF in H_2O	CsF in H_2O
5	163.1	182.3		169.7	122.5	
10	163.4	181.7		159.2	124.3	126.5
13.3			164.6			
16.7				150.6		
20	164.4	181.2	170.1		126.2	128.6
25	164.6			139.3		
26.6		179.2	168.4			
30	165.8	178.4			125.3	127.5
33				136.2		
40	167.1	177.7			126.1	125.3
50	169.8			124.4	124.4	

* Water contents were 6, 10, 17, 25, 33, and 50%, respectively.

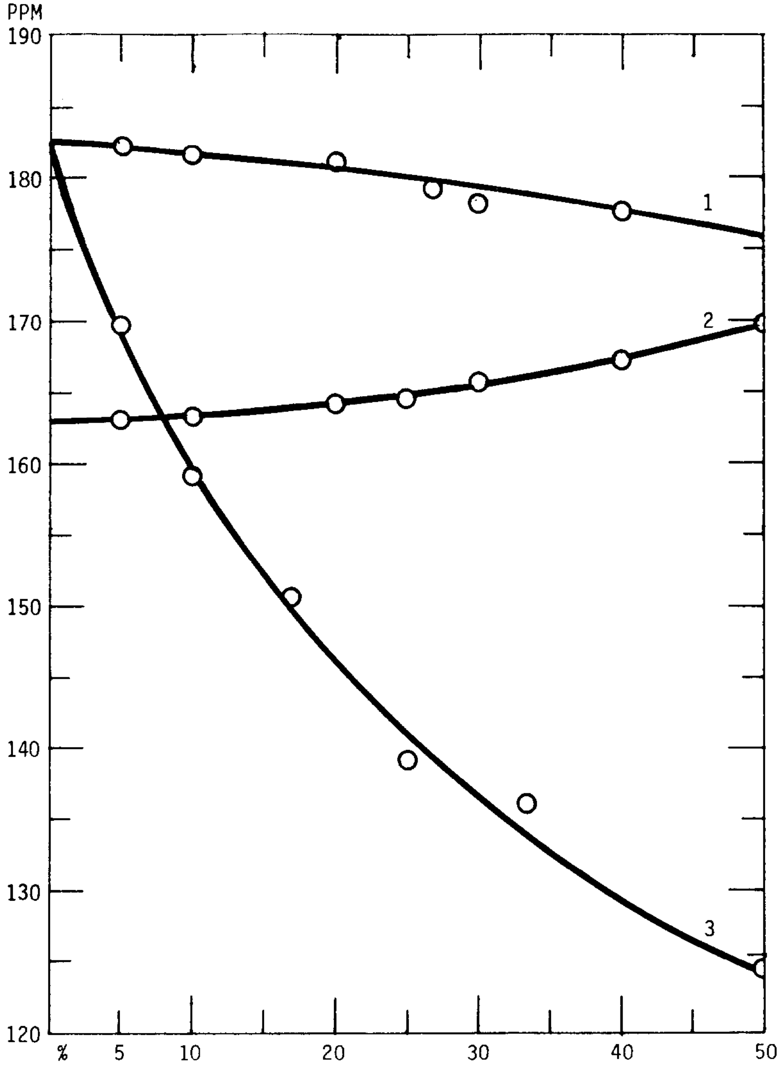


Fig. 1. Change of Chemical Shift of Fluorine on Concentration of Solutions of Hydrogen Fluoride and Tetraethylammonium Fluoride.

Curve 1. Solutions of hydrogen fluoride in anhydrous dimethylformamide.

Curve 2. Solutions of hydrogen fluoride in water.

Curve 3. Solutions of tetraethylammonium fluoride in aqueous dimethylformamide (1:1).

TABLE 4

Chemical shifts of fluorine in hydrogen fluoride in anhydrous and aqueous organic solvents

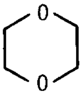
Solution	10% HF Same Day	10% HF After 8 Days	5% HF, 45% organic solvent, 50% water
CH_3OH	184.9	184.9	167.9
CH_2OH CH_2OH	177.5	177.6	164.8
CH_2OMe CH_2OMe	186.8	183.1	166.0
C_2H_4OH O C_2H_4OEt	178.8	179.2	165.1
$(C_2H_5)_2O$	184.7	183.5	
	192.1	181.3	165.6
	192.9	182.0	166.2
$(CH_3)_2CO$	185.6	185.6	166.3
$HCONMe_2$	182.0	182.3	166.0
CH_3CN	183.1	183.4	167.0
$(CH_3)_2SO$	168.0	168.3	163.5
$(CH_2)_4SO_2$	187.2	187.0	165.2
$(C_2H_5)_2O + C_6H_5$	175.6	175.5	

TABLE 5

Chemical shifts of fluorine in fluorides and bifluorides in water and aqueous organic solvents*

Fluoride:	NaF	KF	CsF	AgF	AgF•HF	NH_4F•HF	Et_4NF
Solvent							
H_2O	124.8	122.8	124.0	153.9 (132.1)	149.2 (132.0)	148.6 (130.7)	148.6 (132.4)
$(CH_2OH)2$	137.5	131.2	129.3	168.4	153.3 (132.7)	151.5 (131.2)	151.2 (132.5)
$(CH_2OMe)_2$	161.4	139.6	143.7	167.2 (132.2)	159.3 (132.2)	151.5 (130.3)	160.8 (132.0)
Carbitol	146.7	138.5	145.4	168.7	156.9 (131.6)	150.3 (131.0)	159.9 (132.0)
THF				151.4 (132.2)			154.7 (131.7)
Dioxane	156.3	143.1	143.2	169.2 (153.3)	162.9 (132.4)	149.8 (130.8)	161.5 (131.7)
Me_2CO							
DMF	139.2	126.4	125.4	169.3	152.0 (132.2)	150.2 (130.2)	152.0 (131.6)
MeCN	146.5	123.7	121.6	166.3	151.7 (131.7)	144.2 (130.2)	150.6 (131.7)
DMSO	153.2	124.5	123.1	160.0	150.2 (131.7)	148.4 (129.9)	143.6 (131.3)
$(CH_2)_4SO_2$	139.1	126.2	124.4	169.6	151.2 (132.7)	150.1 (131.0)	150.5 (132.2)

* Numbers in parentheses are chemical shifts of the satellite peaks.

The chemical shifts of fluorine in aqueous hydrofluoric acid (163.1-169.8 ppm) agree with the literature values listed in Table 1 (160.2-170 ppm). The chemical shifts of fluorine in solutions of anhydrous hydrogen fluoride in anhydrous organic solvents (168.0-192.9) approach the shifts found for anhydrous hydrogen fluoride (190.5-196) (Table I).

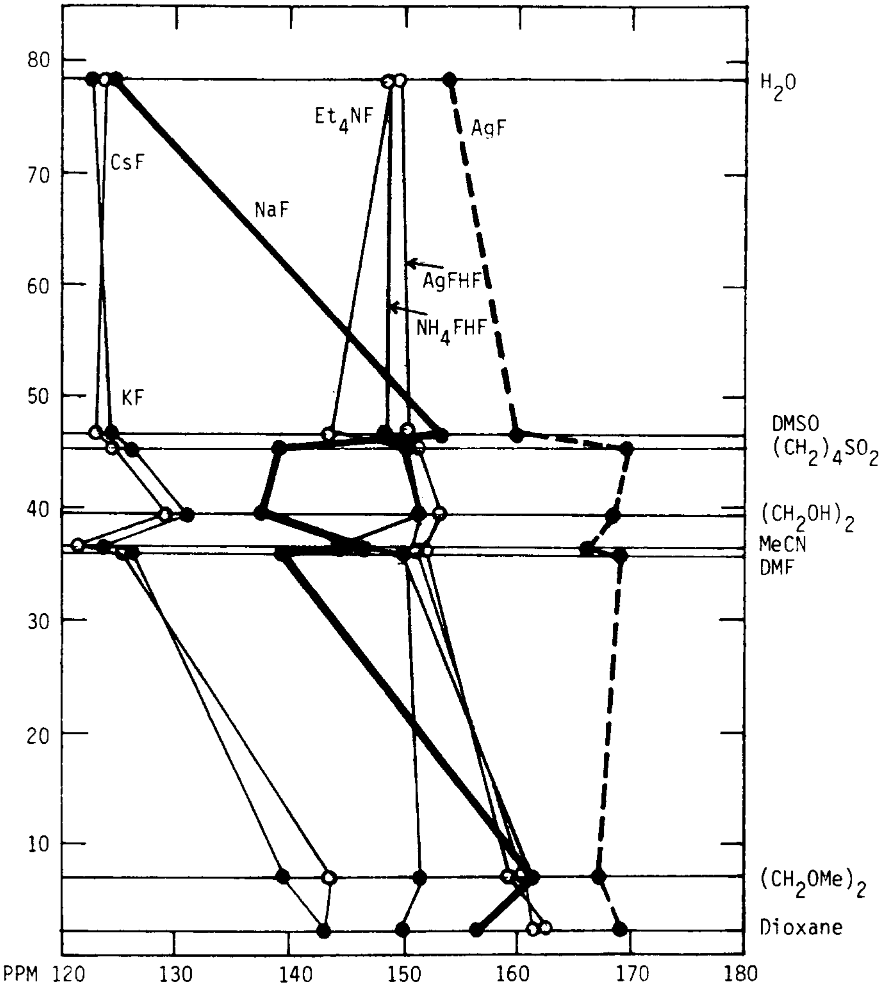


Fig. 2. Plot of Fluorine Chemical Shifts of Fluorides in Aqueous Organic Solvents versus Dielectric Constant of the Organic Solvents.

The effect of dilution on the chemical shifts of fluorine in hydrogen fluoride and some fluorides is shown in Table 3. Chemical shifts of fluorine in aqueous solutions of hydrogen fluoride increase, and in solutions of anhydrous hydrogen fluoride in dimethylformamide decrease with increasing concentrations. A very strong decrease in chemical shifts in solutions of tetraethylammonium fluoride in aqueous dimethylformamide reveals a change in solvation of the fluoride ion (Fig. 1).

The effect of organic solvents on chemical shifts of fluorine in anhydrous hydrogen fluoride is demonstrated in Table 4. A variation over as much as 25 ppm was observed. On the other hand, chemical shifts in aqueous organic solvents do not differ more than 4.4 ppm and resemble the chemical shifts of fluorine in aqueous hydrofluoric acid. Large decreases in chemical shifts on storage of solutions of hydrogen fluoride in anhydrous diglyme (dimethyl ether of ethylene glycol) and especially in tetrahydrofuran and dioxane indicate chemical reactions occurring between the solvents and hydrogen fluoride. In tetrahydrofuran and in dioxane indeed additional signals of hydrogen were found.

Aqueous solutions of sodium, potassium, and cesium fluorides gave chemical shifts of 124.8, 122.8, and 124.0 ppm, respectively (Table 5). These values approach the literature values listed in Table 1 (117.5-124.8). On the other hand, chemical shifts of fluorine in aqueous solutions of silver fluoride and tetraethylammonium fluoride (153.9 and 148.6, respectively) are considerably higher and resemble more literature chemical shifts found for bifluoride ion HF_2^-(144-167.9) (Table 1). Chemical shifts of silver bifluoride and ammonium bifluoride (149.2 and 148.6, respectively, Table 5) are, not surprisingly, in the same range.

Addition of organic solvents to aqueous solutions of the fluorides resulted in dramatic increases of chemical shifts of fluorine compared to the chemical shifts in aqueous solutions. Some of the present findings approach the data reported in the literature; some differ considerably [3]. With the exception of ammonium bifluoride where the maximum increase was only 2%, the other fluorides showed increases of 8.7 through 29.3% (Table 5)

The main signals of ammonium and silver bifluorides and of silver and tetraethylammonium fluorides in water and in aqueous organic solvents were accompanied by very small satellite signals of chemical shifts of 129.9-132.7 with very small variations. There is no apparent explanation of what species gives the small signals of little variation of the chemical shift with the solvent. Nor is there any explanation of the wide variation of chemical shifts shown by the major peaks.

In order to find out if there is any correlation of the fluorine chemical shifts of the solutions of fluorides in aqueous organic solvents and the nature of the solvents, the fluorine chemical shifts versus the dielectric constants of the solvents were plotted. Fig. 2 shows that there is no apparent correlation. The only feature that can be read from the graphs is a close resemblance between potassium and cesium fluoride, and among silver bifluoride, ammonium bifluoride and tetraethylammonium fluoride. Silver fluoride and especially sodium fluoride differ strongly from each other and from all the rest of the fluorides and bifluorides.

CONCLUSIONS

Measurements of chemical shifts of hydrogen fluoride and fluorides in water, anhydrous, and aqueous organic solvents gave the following results:

1. Chemical shifts of fluorine in aqueous hydrofluoric acid increased from 163.1 to 169.8 ppm with increasing concentrations of hydrogen fluoride from 5% to 50%.
2. Chemical shifts of fluorine in solutions of anhydrous hydrogen fluoride in dry dimethylformamide decreased from 182.3 to 177.7 ppm with increasing concentrations of hydrogen fluoride from 5% to 40%.
3. Chemical shifts of fluorine in solutions of hydrogen fluoride in aqueous organic solvents showed little variation over the range of 163.5 to 167.9 ppm.
4. Chemical shifts of fluorine in aqueous 10% solutions of sodium fluoride, potassium fluoride, cesium fluoride, silver fluoride, silver bifluoride, ammonium bifluoride, and tetraethylammonium fluoride were found to be 124.8, 122.8, 124.0, 153.9, 149.2, 148.6, and 148.6, respectively.
5. Chemical shifts of fluorine in solutions of the above fluorides in aqueous organic solvents are considerably higher than those found in aqueous solutions (up to 30%).
6. No correlation was found between the values of chemical shift of fluorine in aqueous organic solvent and physical or chemical nature of the solvents.

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