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NUCLEAR MAGNETIC RESONANCE SPECTRUM OF THE FLUORIDE ANION

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SUMMARY

The fluorine NMR shift of the fluoride anion in CH_3CN solution has been recorded. The observed shift of -74 ppm significantly differs from the value of -150.6 ppm recently reported. The previously observed signal is attributed to the HF_2^- anion. It is also shown that the previously reported and unexplained satellite at about -131 ppm is due to the SiF_6^{2-} anion. The chemical shifts of F^- in isopropanol, ethanol and CH_2Cl_2 have also been recorded and suggest that the F^- shifts are strongly solvent dependent.

INTRODUCTION

During a recent ^{19}F NMR study of the tetramethylammonium salts of the ClF_4^-, BrF_4^- and BrF_6^- anions in CH_3CN solution [1], we have also measured the chemical shift of the fluoride anion in this solvent. To our surprise, the observed shift dramatically deviated from the values given in a recent paper [2]. Furthermore, in that same paper a mysterious satellite had been reported for F^- which could not be explained. The purpose of this note is to explain these inconsistencies.

RESULTS AND DISCUSSION

The ^{19}F NMR chemical shifts of the F^-, HF_2^-, and SiF_6^{2-} anions were measured at 84.6 MHz on a Varian Model EM390 spectrometer using either 5 mm glass or Teflon-FEP tubes (Wilmad Glass Co.) and $CFCl_3$ as an external standard with negative shifts being upfield from the standard. The observed chemical shifts are summarized in the Table.

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TABLE

^{19}F NMR Data for HF and $[N(CH_3)_4]^+$ or Na^+ Salts of F^-, HF_2^- and SiF_6^{2-} in either dry CH_3CN, $(CH_3)_2CHOH$, CH_3CH_2OH, CH_2Cl_2 or H_2O at Ambient Temperature

Solute	Solvent	Chemical Shift (ppm)*	Multiplicity of Peak and line width (ppm) at half height	Coupling Constant (Hz)
$[N(CH_3)_4]F$	CH_3CN	-73.2	singlet (2)	--
	$(CH_3)_2CHOH$	-122.4	singlet (4)	--
	CH_3CH_2OH	-136.7	singlet (4)	--
	CH_2Cl_2	-97.0	singlet (2)	--
$[N(CH_3)_4]HF_2$	CH_3CN	-145.6	doublet (3)	$J_{HF} = 122$
HF	CH_3CN	-184	singlet (4)	--
NaF	H_2O	-119.2	singlet (30)	--
$NaHF_2$	H_2O	-146.0	singlet (80)	--
$NaF/NaHF_2$	H_2O	-119 to -146**	singlet (80)	--
HF	H_2O	-160 to -170***	singlet	--
Na_2SiF_6	H_2O	-130	singlet (5) with ^{29}Si satellites	$J_{^{29}SiF} = 110$

* All chemical shifts are relative to the external standard $CFCl_3$ with negative values being upfield from the standard.

** Shifts depend on the mole ratio of NaF to $NaHF_2$.

*** Data from ref. 2; shifts depend on the concentration of the HF.

As can be seen from the Table, the fluoride anion in a saturated solution of $[N(CH_3)_4]F$ (prepared in our laboratory) in CH_3CN (Baker, Bioanalyzed, having an initial H_2O content of 40 ppm which was reduced to 4 ppm by distillation from P_2O_5) exhibits a chemical shift of -73 ppm. This value deviates greatly from the value of -150.6 ppm, recently reported [2]. Furthermore, it is far outside the range of -121 to -166 ppm, given in the same paper for the fluoride anion of other salts in CH_3CN. Since the previously reported values were measured for aqueous CH_3CN solutions (the water content of the CH_3CN was unfortunately not specified), we have added 10% water to our solution of $[N(CH_3)_4]F$ in CH_3CN. Two immiscible layers formed, and only the aqueous layer exhibited a ^{19}F NMR signal. Its chemical shift value (-118 ppm) is in excellent agreement with previous reports for aqueous fluoride solutions [3-6] and our own observation for an aqueous NaF solution. It appears that the large upfield shifts observed in [2] for NaF (-146.5), AgF (-166.3) and $[N(C_2H_5)_4]F$ (-150.6) are probably due to the presence of HF_2^-, HF or a combination of the two. The HF_2^- anion has a chemical shift of about -146 ppm, both in CH_3CN and aqueous solution. Whereas for the HF_2^- and F^- anions well separated signals with an H-F spin-spin coupling for HF_2^- are observed in CH_3CN solution (see the Table and [7]), a single peak with a line width of about 80Hz results for HF_2^-, F^- and HF in aqueous solution due to rapid exchange. The chemical shift of this peak depends on the mole ratios of the three species and, therefore, can vary from -118 to -170 ppm.

We have also measured the chemical shifts of F^- for solutions of $N(CH_3)_4F$ in anhydrous isopropanol ($\emptyset$ = -122.6), ethanol ($\emptyset$ = -136.7) and CH_2Cl_2 ($\emptyset$ = -97.0). Our data show that the chemical shifts of the F^- anion are strongly solvent dependent and span a chemical shift range of at least -73 to -137 ppm. This is also supported by a previously published [8] plot of $^{19}F^-$ shifts versus those of $^{35}Cl^-$ in various solvents. Based on this plot, a chemical shift range from about -75 to -150 ppm can be deduced for the F^- anion.

Another mystery in [2] was the observation of a satellite peak at about -131 ppm in the spectra of the HF_2^- salts and those fluorides which, based on their unusually high chemical shifts, probably also were bifluorides. In our study, a similar signal was observed for all samples containing either HF_2^- or HF, but only when recorded in glass tubes and in aqueous solvents. These observations strongly suggested that this signal might be generated by attack on the glass by HF. Therefore, the most likely candidate for this signal was the SiF_6^{2-} anion. The identity of the -131 ppm signal as SiF_6^{2-} was confirmed by comparison with the spectrum of Na_2SiF_6 in H_2O (see the Table) and the observation of ^{29}Si satellite peaks with a coupling constant $J_{^{29}Si\text{-}F}$ = 110Hz, which are characteristic for SiF_6^{2-} [9].

In conclusion, the chemical shifts previously reported in [2] for the F^- anion have been flawed by the presence of HF_2^-, HF or both in some of the samples. Furthermore, our measurements show that the chemical shift range of F^- extends over a much wider range than previously reported [2], and that the unexplained satellite at about -131 ppm is due to SiF_6^{2-}.

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