

'Naked Fluoride' Masked: N.M.R. Evidence for Tight Ion Pairs in KF-Crown Ether

Jack M. Miller*^a and James H. Clark*^b

^a Department of Chemistry, Brock University, St. Catharines, Ontario, Canada L2S 3A1

^b Department of Chemistry, University of York, York YO1 5DD, U.K.

¹⁹F N.m.r. spectra of solutions of KF-18-crown-6 in a variety of organic solvents show *ca.* 6 kHz line widths essentially indistinguishable from those of solid KF suggesting tight ion pairs or higher aggregates in solution.

The use of crown ethers to solubilise alkali metal salts in organic solvents, so as to enhance the reactivity of the anion, is a major area of research.¹ Similarly, the structures of many crown ether complexes have been determined by *X*-ray crystallography.¹ There are, however, few reported studies of the nature of the solutions formed, these usually involving formation constants for the complexes² with the anions being described as 'naked'.^{3,4} Recent ³⁵Cl n.m.r. studies on the KCl-18-crown-6 complex in various solvents suggests ion pair formation involving the complexed potassium.⁵ Our recent n.m.r. studies on F⁻ in strongly hydrogen bonding systems⁶ and on analytical applications of KF-18-crown-6 solutions⁷ suggest that the F⁻ systems may be anomalous. It has also become apparent that, despite the popularity of KF-18-crown-6 as a synthetic reagent, the reactivity of the F⁻ in this system is not enhanced to an extent that would be suggested by the presence of 'naked' fluoride.^{1,4,8}

The ¹⁹F n.m.r. spectra of samples saturated with KF in 0.2 molal 18-crown-6 solutions are summarised in Table 1. Basically, for aprotic organic solvents broad lines are observed, widths at half-peak height usually being greater than 6000 Hz with line shapes and chemical shifts very similar to those of powdered solid KF. The line widths of the benzene solutions are reduced by only a factor of two on raising the temperature from 303 to 373 K. RbF and CsF gave similar spectra to KF. As the important isotopes of these nuclei have spins of 3/2, 5/2, or 7/2 the possibility of line broadening due specifically to coupling by these quadrupoles had to be considered. Thus TlF was examined and yielded the same results even though thallium is a spin-1/2 species.

In aqueous solutions containing an excess of crown ether over KF (10:1) we observed two lines, a sharp signal that one would expect for aqueous solutions of KF, and a broad signal similar to those observed above. When the crown ether: KF

Table 1. ^{19}F N.m.r. of KF-18-crown-6 and related systems.

MF	Solvent ^a (0.2 molal in 18-crown-6)	$\Delta\nu_1^b$ / kHz	δ^b /p.p.m. (CFCl_3)
KF (solid)	—	> 6	-140
KF	H_2O (crown:F ⁻ 1:1)	< 0.01	-116.6
KF	H_2O (crown:F ⁻ 10:1)	< 0.01	-120.3
KF	C_6H_6 (303 K)	> 6	-135
KF	C_6H_6 (323 K)	> 5	-135
KF	C_6H_6 (343 K)	≥ 3.5	-135
KF	C_6H_6 (363 K)	≥ 3	-135
KF	C_6H_6 (373 K)	≥ 3	-135
RbF	C_6H_6	> 5	-143
CsF	C_6H_6	> 6	-140
KF	CCl_4	> 7	-136
KF	MeCN	> 6	-134
KF	PhNO_2	> 6	-142
KF	PhNO_2 (sat. with H_2O)	> 6	-134
KF	$\text{PhNO}_2 + \text{MeOH}$ (4:1)	> 6	-139
		< 0.01	-148
TlF	CCl_4	> 6	-128
Bu_4NF	C_6H_6	0.01	-142
Bu_4NF	H_2O	< 0.01	

^a Unless otherwise indicated solutions were 0.2 molal in 18-crown-6 and then were saturated with KF. ^b Errors in line width are ± 0.5 kHz and in chemical shift of the broad peaks ± 10 p.p.m. All spectra were recorded at 303 K, 56.4 MHz unless otherwise noted.

ratio was reduced to 1:1, the broad line was less apparent. Saturating a nitrobenzene solution with water did not show any sign of a peak due to aqueous F⁻, but a 4:1 solution of nitrobenzene and methanol did show the sharp peak expected for the solvated F⁻. These observations are in contrast to the fast ion-pair-solvated anion exchange observed for Cl⁻ in similar solutions.⁵

In the case of tetra-n-butylammonium fluoride, with a cation too large for the cavity of the crown, benzene and

aqueous solutions gave sharp lines only, suggesting that crown complexed cations are necessary for line broadening to be observed.

Very preliminary ^{39}K n.m.r. studies show appreciable line broadening on going from aqueous KF to solutions containing an excess of crown. Line widths for aqueous solutions of the complex are comparable to those observed with solid KF (ca. 250 Hz).

It is clear from these data that we are not dealing with a 'naked' fluoride ion or even a simple solvated ion, but rather with a fluoride ion which is interacting strongly with the K⁺-crown complex, possibly to a greater extent than a simple ion pair, since the line widths so closely resemble that of solid KF. This almost suggests a complex of more than one KF with external molecules of crown ether.

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