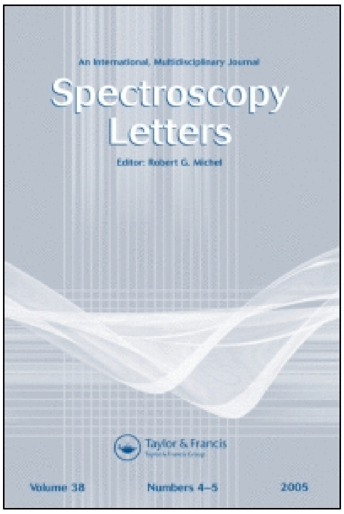

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V. A. Shcherbakov[a]; B. N. Chernyshov[a]; R. L. Davidovich[a]
[a] Institute of Chemistry, Far East Research Center, Academy of Sciences of the USSR, Vladivostok-22, USSR

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AN NMR STUDY OF OUTER-SPHERE INTERACTIONS OF BF_4^- ANIONS WITH PARAMAGNETIC IONS

KEY WORDS: outer-sphere associates, NMR spectra, fluoroborates

V.A. Shcherbakov, B.N. Chernyshov and R.L. Davidovich

Institute of Chemistry, Far East Research Center, Academy of Sciences of the USSR, Vladivostok-22, USSR.

The significance and role of outer-sphere interactions for the chemistry of complex compounds and solutions have been discussed in the literature time and again.[1,2] The existence of the complexes per se in solutions is determined not only by the interactions of the central ion with the near-by ligands, but also with the particles of the outer or secondary coordination sphere. Now, while "intra-sphere" complexes may be both labile and inert with respect to their kinetic behavior in solutions, outer-sphere compounds are predominantly labile. Inasmuch as the majority of outer-sphere compounds cannot be isolated from solutions, NMR-spectroscopy is essentially one of the most convenient methods for their study. Naturally, such investigations are complicated by an exchange of particles constituting associate compositions, and this exchange may be sufficiently rapid to present interest in itself.

In this communication, the investigation results on ammonium tetrafluoroborate solutions containing a series of paramagnetic ions Co^{2+}, Ni^{2+}, Cu^{2+}, Mn^{2+} and Cr^{3+} are reported. Solutions of fluoroboric acid diamagnetic salts were studied by various methods.[3-9] It was shown that the BF_4^- anion, considered similar to perchlorate[3], forms various ionic pairs whose stability depends on the nature of the cation and solvent.[4-6] Paramagnetic solutions of tetrafluoroborate have not been studied; meanwhile, due to the electronic-nuclear Fermi AIS-interaction, precisely these solutions provide valuable data on outer-sphere associates.

Paramagnetic ions in aqueous solutions lead to a shift and broadening of ^{19}F and ^{1}H NMR lines of BF_4^- anions and H_2O molecules, respectively. The concentrational dependencies of the paramagnetic shift of fluorine and proton NMR spectra, δ_F and δ_H, as well as the widths of the lines, ΔH_F and ΔH_H, are linear and practically do not depend on the presence of ammonium ions (see Table). These dependencies indicate to the formation of labile compounds of hydrated cations and BF_4^- and are essentially caused by processes of rapid anion and water molecule exchange between free and coordinated states. Their linearity in the concentration range studied indicates to a constancy in the composition of the compounds formed.

To determine the compound composition, the water molecule and anion exchange rates and dissociation degrees were decreased to the utmost by introducing acetone.[10] The position of the signal of coordinated water molecules in an acetone solution of cobalt tetrafluoroborate hexahydrate is in good agreement with the δ_H value of cobalt perchlorate hexahydrate in aqueous[11] and acetone[10] solutions, as well as with the value obtained for an aqueous 3.4 molal solution

TABLE

Chemical shifts, line widths and isotropic hyperfine interaction constants of ^{I9}F in ammonium tetrafluoroborate aqueous solutions containing paramagnetic ions (I Mole/l).

	Co^{2+}	Ni^{2+}	Cu^{2+}	Mn^{2+}	Cr^{3+}
$\overset{*}{\delta}\ I9_F$ (p.p.m.)	-I0.5	-8.0	-I.5	-I.0**	-4.5
ΔH_{I9_F} (Hz)	60	64	75	60**	200
(A/h) x IO^5	+0.37	+0.40	+0.64	+0.70	+0.20

* all shifts are given in relation to aqueous solution of ammonium tetrafluoroborate (I.5 Mole/l).

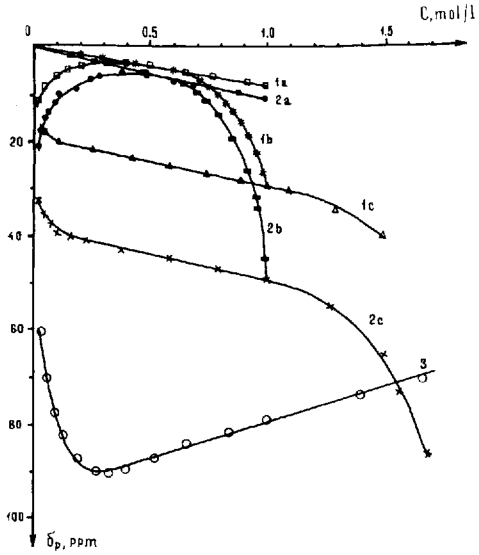
** at Mn^{2+} concentration equal to 0.04 Mole/l.

of $Co(H_2O)_6BF_4$ equal to -98 ± 3 p.p.m. at $-65^{\circ}C$. This signifies that, in an acetone solution, coordination of BF_4^- anions occurs in the outer sphere of Co^{2+} without apparent violations of the aquacomplex structure. It is equally important that the ratio $\Delta H_H/\Delta H_F$ is greater than the unity for all the ions studied, i.e. the distance between fluorine atoms and paramagnetic ions is somewhat larger than the distance between the ions and protons of coordinated water molecules. The $\Delta H_H/\Delta H_F$ ratios are equal to I.6; 2.3; 3.2; 8.0 and I0 for Co^{2+}, Ni^{2+}, Cu^{2+}, Mn^{2+} and Cr^{3+}, respectively. Furthermore, it should be noted that the constants of the hyperfine isotropic interaction A/h for ^{I9}F measured in aqueous solutions of ammonium tetrafluoroborate with various paramagnetic ions and given in the Table for a I mole/l concentration, are almostequal to the A/h value of ^{I}H for free water molecules present in the second coordination sphere of the paramagnetic ions. The latter equals 0.3×10^{2} with Co^{2+} solutions. Hence, in aqueous solutions of the paramagnetic salts studied, BF_4^- anions form labile outer-sphere associates whose compositions include essentially unchanged cation hexaquacomplexes.

Dilution with acetone of aqueous solutions of paramagnetic metal salts, as well as dissolution of their hexahydrates in acetone, leads to δ_F and ΔH_F increase (see Figure). In both cases, this is caused by a sharp change in the solvent dielectric constant and a drop in the exchange rate, which, in turn, increase the association degree of aquaions and BF_4^- anions.

There are several contradictory assumptions in the literature[4-7,9] concerning the nature of the $M(H_2O)_n(BF_4)_q$ ionic pairs, where M is the metal, $n=4-6$ and $q=1-2$. At the same time, basing on the results obtained, the authors of the above papers have quite convincingly indicated to the slight probability of intraspheric ionic pairs being present in such systems, i.e. to the absence of direct contact of the BF_4^- ions with the metal ions. However, the outer-sphere associate model cannot fully explain neither the $J_{^{11}B-^{19}F}$ variation, nor the changes in the ^{19}F NMR chemical shifts of BF_4^- in different solutions of tetrafluoroborate salts. A consideration of the B-F...H-O hydrogen bond could partially explain some of the data so far obtained. Yet, this bond is too weak and, apparently, cannot cause the existence of associates; this circumstance was previously discussed by Gillespie et al.[4]

The said associates are most probably outer-sphere ionic pairs with complex dynamic bonds depending on the cation na-



FIGURE

Concentrational dependencies δ_p^F and δ_C^H in water-acetone solutions of cobalt and nickel tetrafluoroborate at 25°C.

δ_p^F: Ia and 2a - dilution with acetone of aqueous solutions of Ni^{2+} and Co^{2+} salts;

Ib and 2b - dilution with water of acetone solutions of Ni^{2+} and Co^{2+} salts;

Ic and 2c - dilution with acetone of acetone solutions of Ni^{2+} and Co^{2+} salts.

δ_C^H: 3 - **dilution with** acetone of acetone solution of Co^{2+} salt.

ture and its solvation, as well as on the mobility of BF_4^- near the metal ion, i.e. on the solvent composition. Indeed, on diluting the salts studied, the proton and fluorine resonance line widths decrease, and the corresponding shifts display reverse changes(see Figure). These results unambiguously indicate to a dissociation of unstable ionic pairs in the concentration range studied, where rise $(\delta_p^H)_C$ and fall δ_p^F

correspond to changes in the composition of the second coordination sphere of the paramagnetic ions, this being quite apparent on diluting acetone solutions with water (dependencies Ib and 2b). Dilution with acetone of both acetone and aqueous solutions (dependencies Ic and 2c; Ia and 2a), though leading to dissociation, nevertheless is insignificant in the first case, and is comparable to the second with continuous dilution. Consequently, unlike in aqueous solutions, a decrease in steric obstacles in acetone solutions does not lead to complete dissociation of ionic pairs at room temperature. On the contrary, it creates favorable conditions for their existence. In this case, both the chemical shift and the constant $J_{^{11}B-^{19}F}$ would probably be determined by a BF_4^- exchange not between free and bounded states, but between pseudo-free (outer-sphere) and coordinated states; the same process ostensibly takes place in concentrated ($>$ 2.5 molal) aqueous solutions. Now, the question arises as to the nature of the coordinated state. Apparently, the weak dissociation $BF_4^-(\rightleftarrows [BF_3F] \rightleftarrows BF_3 + F^-)$ sharply increases when BF_4^- is situated near the hydrate shell of multicharged metal ions tending towards hydrolysis, since one of the B-F and O-H bonds weakens at BF_4^- and coordinated water molecules.[8] As a result of such instantaneous disturbance, formation of a species similar to BF_3OH^- is possible, the said species being more inclined towards coordination. Such a rapid process would slightly disturb the first coordination sphere (the proton shift of coordinated water molecules is equal to -96 p.p.m.), though it could give rise to considerable fluorine shifts in BF_4^- (approx. -50 p.p.m.). It is noteworthy that the paramagnetic shifts of ^{19}F in the system KBF_3OH - Co^{2+}, which we measured beforehand, are high enough (-60 and -185 p.p.m. in concentrated aqueous and acetone solutions at 30°C, respectively). At the same time, it should be noted that direct exchange between BF_4^- and BF_3OH^- is very weak.[4,7] However, exchange in accord with the mechanism accompanied by formation of $B_2F_7^-$ as an intermediary stage is quite probable.[4]

In conclusion, we would like to point out that the structures of the associates formed are to be the topic of our future communications, the starting data being the temperature dependencies of ^1H and ^{19}F spectra, as well as of ^{11}B in different solutions.

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