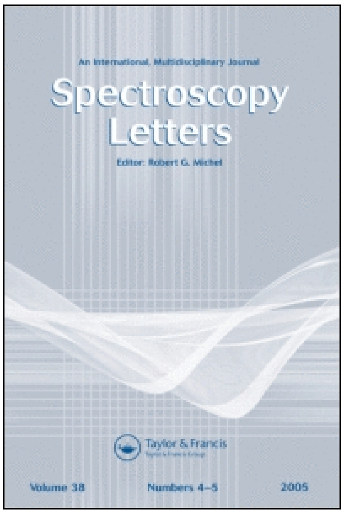

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TEMPERATURE DEPENDENCIES OF ^{19}F NMR SPECTRA PARAMETERS IN BF_4^- SOLUTIONS

KEY WORDS: NMR spectrum, temperature dependencies, fluoroborates

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Despite numerous studies on the BF_4^- anion [1-6] indicating to its complex behavior in different solutions in the presence of different cations, it is still quite difficult to explain this unambiguously. This is ostensibly due to the incompleteness of experimental data both for temperature dependencies and for solution compositions[3]. Taking this into account, we measured the dependencies of ^{19}F NMR spectra in a broad range of temperatures and concentrations in aqueous and water-acetone solutions of Co^{2+}, Ni^{2+} and Zn^{2+} tetrafluoroborate salts on "RYA-2305" and "SWL 2-31/10" instruments in spherical and cylindrical ampoules. The said dependencies were recorded both for BF_4^- and BF_3OH^- signals, the latter forming in insignificant quantities due to the hydrolysis of the tetrafluoroborate anion in positively hydrated cation solutions[1].

The contact chemical shift δ_p of the BF_4^- anion in the acetone solutions of paramagnetic salts is rather large at 30°C[6], being approximately -45 p.p.m. for Co^{2+} and -25 p.p.m. for Ni^{2+} salts, respectively; it changes slightly in the region of concentrations less than 1 Mole/l (δ_p of BF_3OH^- being equal to −180 p.p.m. and −100 p.p.m. for the salts of Co^{2+} and Ni^{2+}, respectively). The introduction of small amounts of water sharply increases the dissociation of the forming complexes, as well as the exchange of water molecules between the hydrate ion shell and the solution per se. This,in turn, affects the δ_p value, which essentially tends towards an "arbitrary zero" (position of the ^{19}F NMR signal for an aqueous 1 mole/l NH_4BF_4 solution) at infinite dilution. Our and other studies indicate to the predominant formation in the solutions of outer-sphere associates of the $M(H_2O)_6(BF_4)_2$ type, even though this does not explain the anomalous behavior of δ_p and $J(^{11}B - ^{19}F)$.

Fig.1 shows the temperature dependencies of the paramagnetic shifts δ_p of BF_4^- in the water-acetone solutions of Co^{2+} and Ni^{2+} salts in the range between room temperature and freezing point. All the plots are almost linear with a small curvature depending on salt concentration and water molecule content whose relationship is expressed as $P = \frac{[m_{H_2O}]}{[m_{M^{2+}}]}$.

A comparison of curves 1, 5 and 7 (Fig. 1) shows that at P = 6.6 with slowed-down exchange of BF_4^- anions between free and coordinated states, the curvature of the plots increases at low temperatures and lesser salt concentrations; however, at temperatures of from −60 to −110° the curves are all linear. It is noteworthy that the temperature dependencies are similar to the concentration dependencies[6], the only difference being that they do not reach "zero" by 2 to 5 p.p.m.

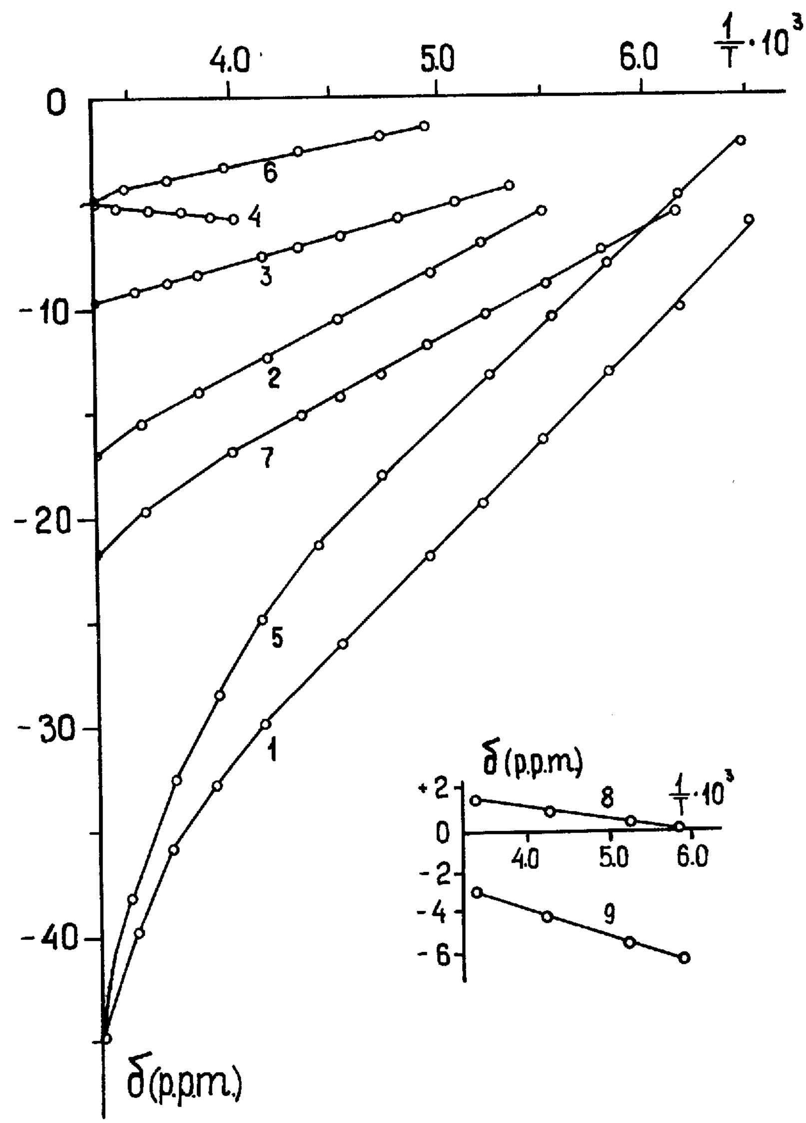

FIG. 1

Temperature dependencies of the ^{19}F chemical shift in water-acetone solutions of Co^{2+} and Ni^{2+} tetrafluoroborates (curves 1-7, see Table) and in the acetone (0.3 mole/l) solution of $Zn(BF_4)_2\cdot 6H_2O$ (curves 8 and 9 for BF_4^- and BF_3OH^-, respectively). The shifts were recorded in relation to an aqueous (1 mole/l) NH_4BF_4 solution.

Taking into consideration the slow exchange of water molecules[6] at temperatures below −40°C, we calculated the effective AJS interaction constants for ^{19}F in the BF_4^- ion. The A/h values obtained are shown in the Table.

TABLE.- Constant values of isotropic hyperfine interaction A/h for ^{19}F in water-acetone solutions of Co^{2+} and Ni^{2+} tetrafluoroborates.

Curve	Compound	Concentration, mole/l	$P=\frac{[m_{H_2O}]}{[m_{M^{2+}}]}$	$\frac{A}{h}{}^{19}F\cdot 10^5$ Hz
1	$Co(BF_4)_2\cdot 6H_2O$	0.5	6.6	-2.4 ± 0.1
2	$Co(BF_4)_2\cdot 6H_2O$	0.5	12	-1.2 ± 0.1
3	$Co(BF_4)_2\cdot 6H_2O$	0.5	18	-0.64 ± 0.05
4	$Co(BF_4)_2\cdot 6H_2O$	0.5	aq.	$+0.18\pm0.03$
5	$Co(BF_4)_2\cdot 6H_2O$	0.25	6.6	-2.3 ± 0.1
6	$Co(BF_4)_2\cdot 6H_2O$	0.25	18	-0.48 ± 0.05
7	$Ni(BF_4)_2\cdot 6H_2O$	0.25	6.6	-2.6 ± 0.1

In the figure, curves 2,3 and 6 show the temperature dependencies of δ_p when $P > 6$. In such solutions, the dissociation increases greatly[3,6], and the residence time of BF_4^- at the hydration shell of the 3d-ions becomes less, this being indicated by the linearity of the curves. In this case, with salt concentration decrease and P increase, the "residual shift" is only 1 p.p.m. The effective value of A/h also decreases sharply and drops below the zero mark, since in aqueous solutions (curve 4, see Figure) A/h is always positive. Similar dependencies were likewise observed for water-acetone solutions of nickel tetrafluoroborate.

The behavior of A/h in mixed solutions resembles $J(^{11}B-^{19}F)$ changes and is, ostensibly, due to the properties of the solvent. The low values of the "residual shifts" at low temperatures show that both contact and pseudocontact interactions (if the latter exist at all, they should be maximum under these conditions) are essentially insignificant for outer-sphere complexes.

All the results so far obtained for the BF_4^- ion should, apparently, be treated on the basis of the various forms of its existence in the solution and near the c ation, taking into account the nature of the latter. It is common knowledge that for aqueous solutions of tetrafluoroborate salts with negatively hydrated NH_4^+, $(CH_3)_4N^+$ and Ag^+ cations, $J(^{11}B - ^{19}F)$ lies in the range of 1.5 ± 0.05 Hz[1,3]. No significant amounts of BF_3OH^- were observed in the solutions (even after boiling them for several hours); this indicates to the stability of the BF_4^- anion. However, for salts with positively hydrated cations changes were observed for both $J(^{11}B - ^{19}F)$ and [1,2,3]. For aqueous solutions of lithium and sodium tetrafluoroborates, a BF_3OH^- quartet was recorded in the ^{19}F spectrum with $J(^{11}B - ^{19}F) = 12.7 \pm 0.3$ Hz, located at -6.2 p.p.m. from the BF_4^- signal. More detailed studies of BF_3OH^- in the presence of BF_4^- were not conducted because the BF_3OH^- quantities observed were too insignificant.

We have studied the water-acetone solutions of zinc tetrafluoroborate recording the ^{19}F NMR spectra for both BF_4^- and BF_3OH^-, in which $BF_4^-/BF_3OH^- = 28$. In the concentration range of 0.4 to 3.1 mole/l in aqueous solutions, $J(^{11}B-^{19}F)$

change in a linear manner from 1.27±0.03 Hz to 2.0±0.05 Hz for BF_4^- and from 15.7±0.5 Hz to 11.5±0.5 Hz for BF_3OH^- ($J(^{10}B-^{19}F)$ = 0.4±0.05 Hz and isotopic shift δ'=0.055 p.p.m. for intermediate concentrations of the ^{19}F spectra for BF_4^- anions). The ^{19}F NMR signal for BF_4^- in acetone solutions (0.1–0.7 mole/l) at temperatures of +30 to −115°C consists of two lines caused by an isotope shift of 0.055 p.p.m. in ^{10}B and ^{11}B. With temperature fall, the line widths decreased from 4 to 1 Hz. The BF_3OH^- signal was recorded as a quartet with J=9.5±0.3 Hz in a temperature range of from +42 to +10°C. On lowering the temperature, the spectrum multiplicity collapsed so that in the range of from −30 to 100°C a single line was observed, its width being from 10 to 16 Hz. Temperature dependencies of δ for BF_4^- and BF_3OH^- signals for acetone solutions of 0.3 mole/l zinc tetrafluoroborate are linear and have different slopes. At low temperatures, the difference between the δ value of BF_4^- and BF_3OH^- in acetone solutions is comparable with that in concentrated aqueous solutions[1]. It should be noted that the ^{19}F NMR signal in acetone solutions is shifted to a high field relative to NH_4BF_4 for concentrations less than 1.5 mole/l at 30°C.

Even though the distinct BF_4^- and BF_3OH^- signals testify to a slow fluorine exchange between BF_4^- and BF_4^- and between BF_4^- and BF_3OH^-, the changes in shifts, line widths and constants $J(^{11}B-^{19}F)$ and A/h nevertheless indicate to the existence of another more rapid exchange process caused by the following reaction suggested by R. Haque et al.[3]:

$$BF_4^- \rightleftharpoons BF_3 + F^- \qquad (I)$$

This reaction is promoted by positively hydrated cations, and its equilibrium is shifted on changing the solvent; as a result, various alterations in the parameters of the NMR spectra are observed. The shift of (I) to the right and subsequent developments are determined by the residence time of BF_4^- near the cation, the said time depending on the composition, concentration and temperature of the solutions used. For acetone solutions, where the dissociation of ion pairs is weak and BF_4^- exchange is quenched, (I) leads to the formation of BF_3OH^- and HF. This, in turn, causes a rapid process in the outer sphere:

$$BF_4^- + H\dot{F} \rightleftharpoons BF_3\dot{F}^- + HF \qquad (2),$$

which results in a BF_4^- signal shift to a high field, since $\delta_{HF} > \delta_{BF_4^-}$. On the other hand, the presence of non-dissociated HF molecules facilitates the recombination of BF_3OH^- and restoration of the status quo.

Now, in water-acetone solutions with rapid BF_4^- exchange between free and bound states, HF molecules dissociate and (2) plays no role. In this case, the following different exchange process prevails on the border of the first and second coordination spheres:

$$HBF_3\dot{F} + BF_3OH^- \rightleftharpoons HBF_4 + \dot{F}BF_2OH^- \qquad (3),$$

whose rate is less than that of (2). The equilibrium (3) shifts the BF_4^- signal to a low field and increases the $J(^{11}B-^{19}F)$ value in BF_4^-, since the same value in BF_3OH^- is approximately 13-15 Hz. The constant A/h in the water-acetone solutions of paramagnetic salts decreases and changes its sign when the P value increases; this process takes place along with J alterations in diamagnetic salt solutions containing various mixed solvents. Both developments are ostensibly due to different reaction (I) conditions and correspondingly different fluorine exchange processes.

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