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Abstract

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CONCENTRATION DEPENDENCE OF THE MAGNETIC SHIELDING OF F^{19} NUCLEI IN THE SYSTEMS KHF_2—H_2O AND KHF_2—KF—H_2O

(Presented by Academician A. N. Terenin, 18 VII 1960)

In 1956 P. M. Borodin, together with one of the authors of the present work, investigated the chemical shifts of the nuclear magnetic resonance line of F^{19} in the system HF—H_2O ($^{1-3}$); the concentration of HF was varied in the range $1 \div 99$ wt. %. As is known (^{4}), dilute solutions contain fluorine in single molecules HF and in the ions F^- and HF_2^-. The equilibrium constants at 20° (^{5}) are:

$$k' = \frac{[H^+][F^-]}{[HF]} = 7.32 \cdot 10^{-4}; \tag{1}$$

$$k'' = \frac{[HF][F^-]}{[HF_2^-]} = 0.25, \tag{2}$$

where $[H^+]$, $[F^-]$, $\cdots$are molar concentrations. The experimentally measured chemical shift is

$$\xi = \frac{[HF]\xi_{HF} + [F^-]\xi_{F^-} + 2[HF_2^-]\xi_{HF_2^-}}{[HF] + [F^-] + 2[HF_2^-]}. \tag{3}$$

(ξ_{HF}, ξ_{F^-}, $\xi_{HF_2^-}$ are the chemical shifts of the individual fluorine-containing components in an aqueous medium.) On the basis of data for KF solutions (^{3}), $\xi_{F^-} = 5.48 \cdot 10^{-4}$ relative to elemental fluorine. The two other constants remained unknown; however, since $2[HF_2^-] \ll [HF]$, a very rough estimate $\xi_{HF_2^-} \sim 5.4 \cdot 10^{-4}$* made it possible to carry out a sufficiently accurate determination of $\xi_{HF} = (6.06 \pm 0.05) \cdot 10^{-4}$. From the values of ξ at higher concentrations it was concluded that in this case other molecular forms also take part in the equilibrium, characterized by higher shielding of the F^{19} nuclei (apparently, complexes of molecules formed through hydrogen bonding).

E. Z. Utyanskaya, A. U. Stepanyants, M. I. Vinnik, and N. M. Chirkov (^{6}), after again investigating the same system at HF concentrations up to 42.5 wt.

Fig. 1

Figure 1: Fig. 1

%, used the results obtained to calculate the acidity function and the molecular composition of hydrofluoric acid. However, the interpretation of the nuclear-resonance data in (6) differs strongly from that adopted by us in (3) and raises objections. Thus, for ξ_{HF} the experimentally observed chemical shift for 100% hydrogen fluoride ($6.25 \cdot 10^{-4}$) was adopted, although by its meaning in the subsequent analysis ξ_{HF} characterizes the shielding of fluorine in a molecule surrounded by water. In this connection, from the analysis of the experi- experimental data in (6) yielded the value $\xi_{\mathrm{HF}_2^-} = 3.4 \cdot 10^{-4}$, which is unlikely from the standpoint of the general regularities of magnetic shielding of fluorine nuclei.

In order to obtain additional possibilities for interpreting the nuclear-resonance spectra of such systems and, in particular, to choose between the two above-mentioned variants of interpreting the experimental data for hydrofluoric acid, we carried out a study of the chemical shifts of the F^{19} nuclear magnetic resonance line in the systems $\mathrm{KHF_2}$—$\mathrm{H_2O}$ and $\mathrm{KHF_2}$—KF—$\mathrm{H_2O}$ at various concentrations of the components. The experimental procedure was analogous to that described in (3), and the error of measuring ξ was approximately $2 \cdot 10^{-6}$. The samples were contained in polystyrene ampoules. Freon 11 ($\mathrm{CCl_3F}$) served as the standard, but the chemical shifts were then recalculated relative to elemental fluorine. The results obtained are presented in Fig. 1.

Fig. 1. Concentration dependences of the chemical shift of the F^{19} nuclear magnetic resonance line in the systems $\mathrm{KHF_2}$—$\mathrm{H_2O}$ and $\mathrm{KHF_2}$—KF—$\mathrm{H_2O}$. Points are experimental data; lines are values calculated using (4). Total molar concentrations of substances in the solution: a –[KF] = 0 ($\xi_{\mathrm{HF}_2^-} = 5.81$); b – $[\mathrm{KHF_2}] = 1.95$;

v –$[\mathrm{KHF_2}] = 1.00$

At low concentrations in the indicated systems, the dissociation of salts may be regarded as complete, and the equilibrium $\mathrm{HF_2^-} \rightleftarrows \mathrm{HF} + \mathrm{F^-}$ is still described by relation (2). As for the further decomposition of HF into $\mathrm{H^+}$ and $\mathrm{F^-}$ according to (1), in the present case it plays a completely secondary role. The experimental data for aqueous solutions of $\mathrm{KHF_2}$ (Fig. 1a) at low concentrations supplement the results of work (3) in such a way that, for determining ξ_{HF} and $\xi_{\mathrm{HF}_2^-}$, it is now possible to set up two equations. Their solution gives

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* In choosing this figure, experimental data on the position of the nuclear-resonance signal in a concentrated solution of NH_4HF_2 were used without detailed analysis.

$$\xi_{\mathrm{HF}} = (6.03 \pm 0.03) \cdot 10^{-4}, \qquad \xi_{\mathrm{HF}_2^-} = (5.81 \pm 0.03) \cdot 10^{-4}, \qquad (4)$$

The course of the concentration dependence of ξ, expected on the basis of (3) and (4), is shown in Fig. 1a by the solid line. The small discrepancy between the calculated and experimental values at high concentrations (i.e., where the initial assumptions of the calculation, apparently, already become inapplicable) has the same sign as for HF in water (^{3}). It is not excluded that in both cases these discrepancies are due to one and the same cause.

In exactly the same way, from (2), (3), and (4), one can calculate the expected values of ξ in the ternary system KHF_2—KF—H_2O at various concentrations of the components. Comparison of these values with those observed experimentally (Figs. 1b and 1v) is a good independent test of the correctness of the conclusions drawn above. The agreement is quite satisfactory in all cases, so that further variation of the parameters ξ_{HF} and $\xi_{\mathrm{HF}_2^-}$ is hardly justified.

Thus, with respect to the value of ξ_{HF}, the present work has led to only a very small change in the numerical value, not exceeding the previously indicated error limits. The value of $\xi_{\mathrm{HF}_2^-}$ has proved to be even larger than was assumed. The value $\xi_{\mathrm{HF}_2^-} = 3.4 \cdot 10^{-4}$, adopted in (^{6}), now

can be considered excluded; it is sufficient to say that it would lead to calculated values of the chemical shift lying far outside the range shown in Fig. 1.*

At present we are completing analogous studies of systems containing ammonium salts.

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REFERENCES

1. P. M. Borodin, *Investigation of chemical shifts and fine structure of the signals of nuclear magnetic resonance of fluorine in a number of compounds*, Author' s abstract of candidate' s dissertation, LSU, 1956.

2. P. M. Borodin, F. I. Skripov, Materials of the 10th All-Union Conference on Spectroscopy, 1, Publishing House of Lviv State University, 1957, p. 78.

3. P. M. Borodin, F. I. Skripov, *Izv. vyssh. uchebn. zaved.*, Radiophysics, 1, No. 3, 37 (1958).

4. *Fluorine and Its Compounds*, ed. by D. Saimons, 1, 1953.

5. H. H. Broene, T. De Vries, *J. Am. Chem. Soc.*, 69, 1644 (1947).

6. E. Z. Utyanskaya, A. U. Stepanian, M. I. Vinnik, N. M. Chirkov, *DAN*, 124, 1095 (1959).

7. A. Carrington, F. Dravnieks, M. C. R. Symons, *Mol. Phys.*, 3, 174 (1960).

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* In a recently published work (7), the authors, on the basis of indirect data, come to the conclusion that $\xi_{\mathrm{HF2}^-} < \xi_{\mathrm{F}^-}$. This conclusion also cannot be reconciled with the results of the present investigation.

Note: Figure translations are in progress. See original paper for figures.

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