INVESTIGATION OF AQUEOUS SOLUTIONS OF ELECTROLYTES BY MEANS OF NUCLEAR MAGNETIC RESONANCE OF THE NUCLEI OF THEIR CATIONS

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The cations of gallium and indium salts in aqueous solution are surrounded by six molecules of water. According to Eigen [1] the rate constant for the exchange of water molecules is about 10^1 sec^{-1} for $Ga(H_2O)_6^{3+}$, while in the case of $In(H_2O)_6^{3+}$ it has a value of about 10^3 sec^{-1}. In aqueous solution the aquocations undergo hydrolysis. The hydrolysis constants are equal to $\sim 10^{-3}$ and 10^{-4} for gallium and indium, respectively [2].

In concentrated solutions of the halogen acids, Ga(III) and In(III) tend to form complex anions with a coordination number of four. It has been established by means of Raman spectroscopy that the ion $GaCl_4^-$ exists in the form of a right tetrahedron [3] in a solution containing 1.5 M $GaCl_3$ and 6.3 M HCl. Indium is not transformed in significant quantities into the species $InHal_4^-$ either in solutions saturated with HCl or in a 6 M solution of HBr. However, in 4 M HI the predominant species is InI_4^- [4]. The formation of $Ga(H_2O)_6^{3+}$, $GaCl_4^-$, $GaBr_4^-$, and GaI_4^- has been confirmed by $Ga^{69,71}$ NMR [5, 6]. Scandium (III), which has an ionic radius of 0.83 Å lying at a position intermediate between the ionic radii of Ga(III) (0.62 Å) and In(III) (0.92 Å) [7], differs noticeably, as the first member of the 3d series of transition elements, in its chemical behavior from gallium and indium. In aqueous solutions Sc(III) apparently is present as the hexaaquocation. The hydrolysis constant for this cation is equal to about 10^{-5} [2].

The complexes formed between scandium and oxygen-containing ligands are the most stable. However, there is some indication in the literature that the chlorocomplexes $ScCl^{2+}$, $ScCl_4^-$, etc. are formed [8]. In analogy with Ti(III), V(III), and Cr(III) a series of salts with the composition M_3ScHal_6 (M = Na^+, K^+, Rb^+, and Cs^+, and Hal = Cl^-, Br^-) are known in the case of Sc(III) in which the scandium atom is probably octahedrally coordinated [8]. A PMR investigation of aqueous–acetone solutions of $Sc(NO_3)_3$ and $Sc(ClO_4)_3$ has shown that the Sc(III) ion is associated with 3.9 and 5.1 molecules of water, respectively [9, 10]. The differences in the degrees of hydration are due to the predominating formation of contact ion pairs in scandium nitrate solutions.

The present paper concerns itself with the study of complex formation in aqueous solutions by the Group III elements Sc, Ga, and In. For this purpose the magnetic resonances of Sc^{45}, $Ga^{69,71}$, and $In^{113,115}$ nuclei have been studied as a function of the concentration of salt dissolved and the nature of the anion (Cl^-, NO_3^-, and ClO_4^-). The NMR spectra of the above-mentioned isotopes were recorded at 25 ± 2°C at a frequency of 6 MHz using phase-sensitive detection. The modulation frequency was 15 Hz, and the modulation amplitude varied from 0.05 to 1.5 G (depending on the linewidth). The derivative of the dispersion signal was recorded. In the case of the gallium chloride solutions the intensity of the signals was measured using a planimeter. The salts were synthesized using standard techniques The concentrations are quoted in terms of moles of salt per 1000 g of water (m).

Investigations on the rate of magnetic relaxation T_2^{-1} of quadrupolar nuclei in aqueous solutions have shown [11, 12] that T_2^{-1} substantially depends on the fact that, when interactions of the ion–ion or ion–dipole type are

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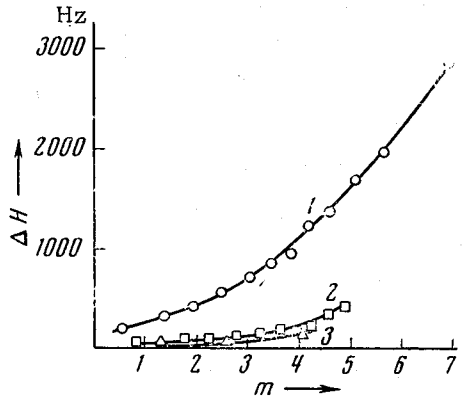

Fig. 1

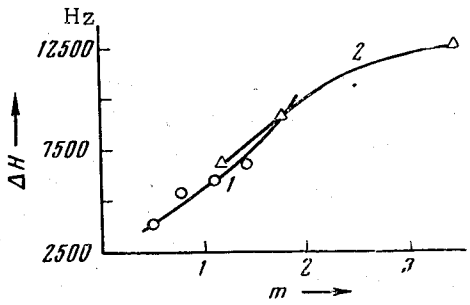

Fig. 2

Fig. 1. The dependence of the linewidth ΔH for the resonance of the Sc^{45} nuclei on the concentration of the salt m: 1) $Sc(NO_3)_3$; 2) $ScCl_3$; 3) $Sc(ClO_4)_3$.

Fig. 2. The dependence of the linewidth ΔH for the resonance of the In^{115} nuclei on the concentration of the salt m: 1) $In(NO_3)_3$; 2) $In(ClO_4)_3$.

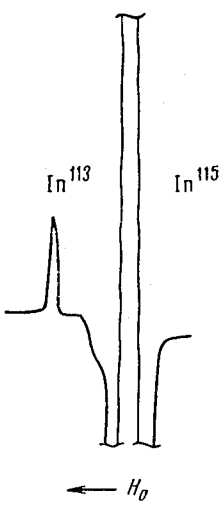

Fig. 3

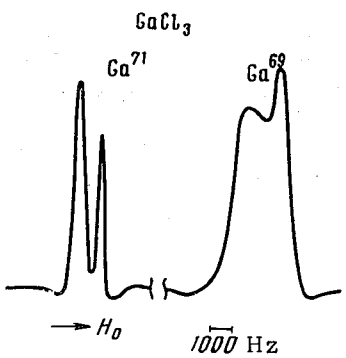

Fig. 3

Fig. 3. The NMR spectrum of an acidic aqueous solution of $In(ClO_4)_3$.

Fig. 4. The $Ga^{69,71}$ NMR spectrum of an aqueous solution of $GaCl_3$ (concentration of salt 5.82 m).

operative, an electric field gradient is created at the resonating nucleus. In the case of ionic relaxation $T_2^{-1} \sim m^2$, while in the case of dipole relaxation $T_2^{-1} \sim m$.

The dependence of the linewidth of the Sc^{45} and In^{115} resonances as a function of the concentrations of the solutions that were studied is shown in Figs. 1 and 2. It can be seen from Fig. 1 that the two relaxation domains, ionic and dipolar, are included in the concentration range from 0.5 to 6.8 m; that is, in the concentrated solutions the field gradient increases due to the formation of ion pairs. In the case of solutions of the indium salts, no signals were observed at concentrations greater than 1.8 m. When the concentration of the electrolyte was reduced, a signal was registered which was however extremely broad (12.5 kHz). The significant linewidth for the indium nitrate solutions is associated with the formation of ion pairs $[In(NO_3)_n(H_2O)_m]^{(3-n)+}$. In the case of the indium perchlorate solutions, the larger linewidth can be explained by the fact that complex formation $[In(OH)_n(H_2O)_m]^{(3-n)+}$ occurs as the result of hydrolysis together with the formation of ion pairs. Hence, for an acidic solution of $In(ClO_4)_3$ the linewidth narrows down to about 2000 Hz. At the same time a signal from the second indium isotope In^{113} is observed at higher field (Fig. 3).

The widths of the Sc^{45} lines are significantly narrower than the In^{115} lines in the corresponding solutions. In the case of scandium nitrate, the linewidth at all concentrations is greater than the linewidths for the chloride and perchlorate (Fig. 1). This corresponds to the following order for the complexing ability of the anions:

$$NO_3^- > Cl^- \geqslant ClO_4^-.$$

The quadrupole moment of the scandium nucleus $Q_{Sc} \simeq 0.35 \cdot 10^{-24}$ cm^2 was estimated from the values of the linewidths for the Sc^{45} (40 Hz) and Ga^{69} (170 Hz) resonances in the perchlorate solutions after they had been extrapolated to infinite dilution. Two lines with a chemical shift between them equal to 1200 Hz (Fig. 4) were observed in the $Ga^{69,71}$ NMR spectra of an aqueous solution of gallium chloride with a concentration of 5.82 m without any added HCl. The line at higher field belongs to $Ga(H_2O)_6^{3+}$, while the second line belongs to $GaCl_4^-$, which is in agreement with the data given in [5, 6]. An estimation of the intensities of the signals from the areas under the curves allows one to represent the equilibrium in solution in the form of the scheme:

$$4GaCl_3 + H_2O = 3GaCl_4^- + Ga(H_2O)_6^{3+}.$$

The coordination number of the gallium in the anion is four, while in the cation it is six.

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