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A Proton Magnetic Resonance Cation Co-ordination Study of Gallium Trichloride in Water-Acetone Mixtures†

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WE report direct evidence for the formation of contact ion-pairs in solutions of GaCl_3 in acetone-water solvent mixtures. Using the low-temperature ^1H n.m.r. method previously described,¹⁻⁹ separate signals are observed for the protons of bulk water and water molecules in the Ga^{III} solvation shell. An evaluation of these peak areas provides an accurate measure of the number of water molecules co-ordinated to the Ga^{III} .

The results of several of these measurements carried out on a Varian A60 Spectrometer, in the temperature range, -60° to -80° , are summarized in the Table, with the

can solvate a cation only when the water concentration is insufficient to saturate the ion-solvation shell.⁷ In the spectra of these solutions only one signal was observed for acetone, reflecting this lack of solvating ability. Thus, it may be assumed that the co-ordination results in the last column of the Table represent the total number of solvent molecules in the Ga^{III} solvation shell.

This number decreases from six in a pure aqueous solution of GaCl_3 ,⁶ to about one in mixtures containing large amounts of acetone. These results are a strong indication of contact ion-pairing and they are in marked contrast to those obtained with nitrate and perchlorate solutions of Ga^{III} and other cations,³⁻⁷ wherein the hydration numbers remain constant over a wide range of acetone concentration. This ion-pair postulate is consistent with the observed decrease in the Ga^{III} hydration number with decreasing bulk dielectric constant and with increasing salt concentration for systems of the same dielectric constant. Further confirmation of this phenomenon was provided by the solutions of low water content, which exhibited multiple complexed-water molecule signals in ^1H n.m.r. spectra. The spectrum substantiates the presence of differently hydrated cationic species in solution. Thus, it appears that water molecules of hexahydrated Ga^{III} are replaced by chloride ions as acetone is added to the solution, resulting in the eventual appearance of $(\text{H}_2\text{O})\text{Ga}^{\text{III}}\text{Cl}_3$ as the dominant species in solutions of high acetone content.

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Cation hydration numbers of GaCl_3 in water-acetone mixtures

GaCl_3 molality	Ga^{III} water/acetone (mole ratios)	Dielectric constant	Ga^{III} hydration no.
0.84	1:40:8	53	5.5
1.10	1:30:6	53	4.4
1.30	1:20:7	46	3.1
1.12	1:20:10	41	2.8
1.43	1:17:8	41	2.7
1.08	1:17:10	36	2.6
0.89	1:17:14	32	2.0
0.63	1:17:22	28	1.5
0.26	1:8:64	20	1.3

dielectric constants of the pure solvent mixtures at 25° ,⁹ listed in column 3, and the contributions of water molecules to the Ga^{III} solvation shell in column 4. Previous solvation studies in water-acetone mixtures³⁻⁸ have demonstrated the inability of acetone to displace water from an ion-solvation shell. In fact, in the systems studied, acetone apparently

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