CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
CALIFORNIA STATE COLLEGE, LOS ANGELES, CALIFORNIA 90032

Hydrogen-1 and Gallium-69 Nuclear Magnetic Resonance Cation Hydration Study of Gallium Halide Solutions in Water–Acetone Mixtures

BY ANTHONY FRATIELLO, ROBERT E. LEE, AND RONALD E. SCHUSTER

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A ^1H and ^{69}Ga nuclear magnetic resonance cation hydration study of gallium halide solutions has been completed. At low temperatures, separate pmr signals were observed for bulk water and water molecules in the Ga^{3+} solvation shell. A minimum hydration number of 4 was obtained for solutions of high acetone content and low dielectric constant, containing a 1:1 mole ratio of halide to Ga^{3+}. From pmr chemical shift data, signal intensities, and other spectral considerations, the dominant species were concluded to be $Ga(H_2O)_6^{3+}$ and GaX_4^-. This conclusion was supported by the ^{69}Ga nmr spectra of these solutions which revealed two signals in all cases, with chemical shifts analogous to reference samples known to contain only $Ga(H_2O)_6^{3+}$ or the particular tetrahalide.

Introduction

The utility of the direct proton magnetic resonance (pmr) method in the study of cation hydration in water and aqueous solvent mixtures has been amply demonstrated.[1–17] At low temperatures, proton and ligand exchange can be slowed sufficiently to permit the observation of resonance signals for bulk ligand and ligand molecules in the primary coordination shell of the cation. Such an observation aids the identification of the species present in systems in which contact ion pairing is occurring.[12–17] This process, which involves the replacement of water molecules in the cation solvation shell by the anion, has been investigated in aqueous acetone solutions of $Sc(NO_3)_3$, $Y(NO_3)_3$, and $Th(NO_3)_4$,[12,15] the gallium halides,[13,14] $SnCl_4$,[16] and uranyl nitrate and uranyl halides.[17] Although the previous pmr study of $GaCl_3$, $GaBr_3$, and GaI_3 solutions revealed extensive ion pairing and evidence for the presence of both octahedrally and tetrahedrally complexed cations, the data were not sufficient for an unambiguous identification of the species. The present work represents an attempt to place the measurements of gallium halide ion pairing in water–acetone mixtures on a more quantitative basis using pmr and gallium-69 nmr methods.

Experimental Methods

The gallium salts (99.99% purity; Alfa) and spectroquality acetone were used as received. Samples were prepared by adding demineralized water and acetone to the gallium salt. The halide ion concentration was regulated by addition of the particular hydrogen acid to a $Ga(ClO_4)_3$ solution or, to avoid increasing the water concentration, by precipitation of a portion of the halide with the addition of $AgClO_4$ to a gallium trihalide solution.

The pmr measurements were made on a Varian A-60 and a Varian HA-100 nmr spectrometer each equipped with a variable-temperature device for measurements from −150 to +200°. The technique involved cooling the sample in the spectrometer probe until the rate of water proton exchange decreased sufficiently to permit the observation of the cation solvation shell signal. The separate water resonance signals were integrated electronically directly on the spectrometer.

The ^{69}Ga nmr experiments were carried out at the Varian Associates Applications Laboratories, Palo Alto, Calif., using a Varian WL-12 wide-line spectrometer, operating at 15.65 kG and 16 MHz.

Results

The pmr hydration number results are summarized in Table I for water–acetone mixtures containing various halide:Ga^{3+} mole ratios. All integrations were made at −50°, the temperature at which the water signals were sharpest. $Ga(ClO_4)_3$ was used in solutions containing a 6:1 mole ratio or greater of water to Ga^{3+}. In the remaining systems, the particular trihalide was used and the solution was treated with $AgClO_4$ to adjust the halide concentration. The salt molalities ranged from 0.2 to 0.8 depending on the solvent composition. The systems were studied at least twice at each concentration and the hydration numbers were measured with a 5–10% precision. The water pmr spectrum of a Ga^{3+}–Cl^- solution is shown in Figure 1, and the spectrum arising from a Ga^{3+}–I^- solution is given in Figure 2.

Typical ^{69}Ga nmr spectra are shown in Figures 3–6, for aqueous acetone solutions at several Ga^{3+} : halide mole ratios. The spectra were recorded at modulation levels which prevented signal distortion and the chemical shifts indicated in the figures were measured with a precision of 1%. The Ga^{3+}–Br^- solution spectra were analogous to those shown in Figures 3–6, but signal overlap and broadening prevented accurate chemical shift

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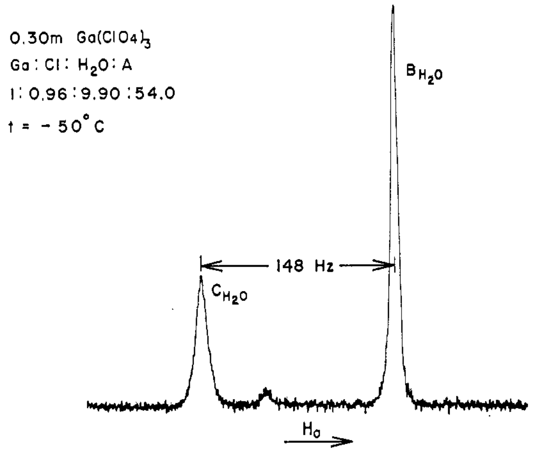

Figure 1.—The water proton magnetic resonance (pmr) spectrum of a $Ga(ClO_4)_3$ solution in a water–acetone mixture containing a 1:1 mole ratio of HCl to $Ga(ClO_4)_3$. The spectrum was recorded at −50° on a Varian A-60 nmr spectrometer. The signals arising from bulk water (B_{H_2O}) and water molecules in the Ga^{3+} solvation shell (C_{H_2O}) are labeled in the diagram, as are the mole ratios of all species.

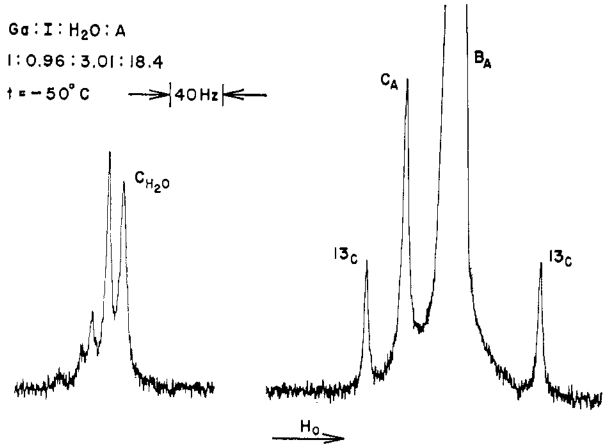

Figure 2.—The water pmr spectrum of a GaI_3 solution in a water–acetone mixture. The I^- to Ga^{3+} mole ratio was reduced to 1:1 by addition of $AgClO_4$. The spectrum was recorded on a Varian A-60 nmr spectrometer. The signals arising from bulk water (B_{H_2O}) and water molecules in the Ga^{3+} solvation shell (C_{H_2O}) and bulk and complexed acetone (B_A and C_A) are labeled in the diagram, as are the mole ratios of all species.

measurements. The peak corresponding to $GaBr_4^-$ is only 0.5 G downfield from that due to $Ga(H_2O)_6^{3+}$.

Discussion

Evidence for the existence of contact ion pairs in pure, concentrated aqueous solutions has been provided by a variety of electrochemical and spectroscopic methods, with Raman spectroscopy being the most widely used in the latter category. Measurements in aqueous solvent mixtures are frequently limited to low concentrations and require the use of the more sensitive conductance and transference number techniques. These methods are extremely precise, but they provide only indirect information about a cation solvation shell, and they cannot distinguish between contact and solvent-separated ion pairs. The principal advantage of the pmr method is the ability to study the cation solvation shell directly and, thereby, to measure quantitatively any changes occurring with salt or solvent composition. The formation of a contact ion pair involves a replacement of one or more water molecules in the solvation shell, with a subsequent decrease in the measured hydration number.

Previous studies indicated that the addition of acetone to aqueous solutions of the gallium trihalides

TABLE I

Ga^{3+} HYDRATION NUMBERS IN AQUEOUS ACETONE SOLUTIONS OF GALLIUM HALIDES AT −50°

$Ga^{3+}:X^-:H_2O:A$ (mole ratios)	Ga^{3+} hy no.	$Ga^{3+}:X^-:H_2O:A$ (mole ratios)	Ga^{3+} hy no.
$X^- = Cl^-$		$X^- = Br^-$	
1.00:0.55:8.61:23.1	4.9	1.00:1.05:10.5:31.6	4.0
1.00:1.02:15.0:15.8	4.0	1.00:0.99:4.80:10.2	3.8
1.00:0.98:10.0:53.3	4.1	1.00:1.01:3.47:14.3	3.5
1.00:1.05:4.68:29.5	4.0	1.00:0.92.3:18:9.7	3.2
1.00:1.05:3.20:14.8	3.2	1.00:3.00:4.07:42.8	1.4
1.00:0.99:3.20:35.2	3.2		
1.00:2.00:23.4:23.4	3.0	$X^- = I^-$	
1.00:2.13:14.6:106	2.6	1.00:1.12:11.7:35.2	4.2
1.00:2.50:15.4:100	2.0	1.00:0.98:4.77:26.4	4.0
1.00:3.00:8.02:64.1	1.5	1.00:1.00:3.58:56.0	3.6
1.00:4.08:3.80:25.6	0	1.00:1.00:3.44:27.4	3.4
		1.00:0.96:3.01:18.4	3.0
		1.00:0.99:2.74:24.5	2.7
		1.00:1.98:4.73:37.3	2.9
		1.00:3.00:4.05:43.8	1.8

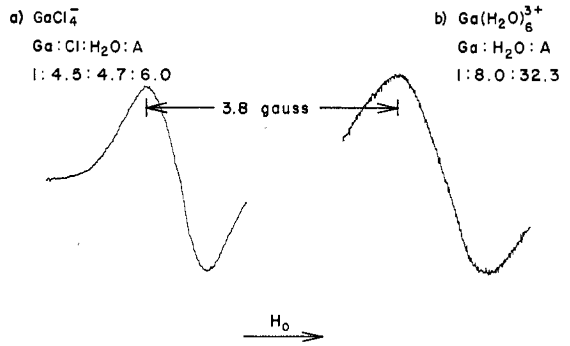

Figure 3.—The ${}^{69}Ga$ nmr spectra of solutions of (a) $GaCl_3$ acidified with HCl and (b) $Ga(ClO_4)_3$ in water–acetone mixtures recorded on a Varian WL-12 wide-line spectrometer at +35°. The signals are identified and the mole ratios are given in the diagram.

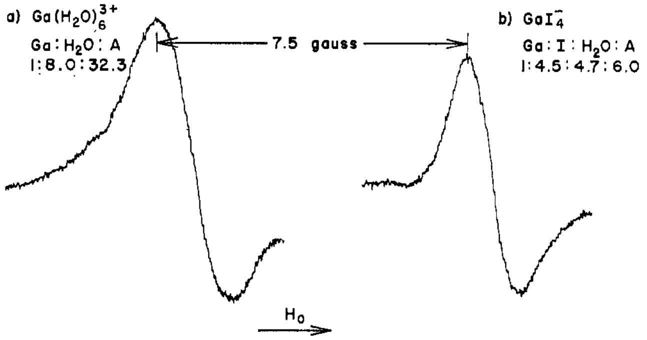

Figure 4.—The ${}^{69}Ga$ nmr spectra of solutions of (a) $Ga(ClO_4)_3$ and (b) GaI_3 acidified with HI in water–acetone mixtures recorded on a Varian WL-12 wide-line spectrometer at +35°. The signals are identified and the mole ratios are given in the diagram.

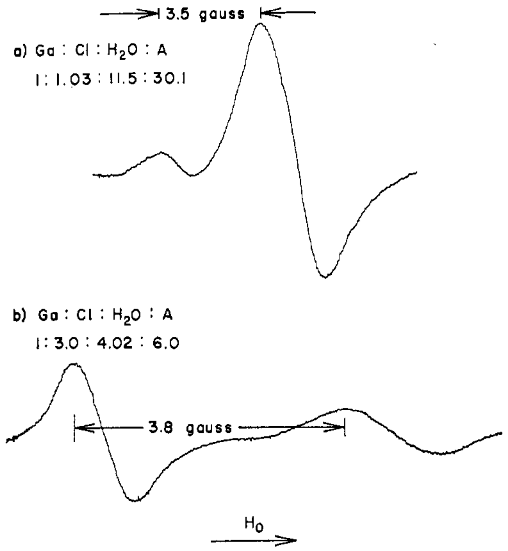

Figure 5.—The ^{69}Ga nmr spectra of solutions of (a) $Ga(ClO_4)_3$ and HCl in a 1:1 mole ratio and (b) unacidified $GaCl_3$ in water–acetone mixtures recorded on a Varian WL-12 wide-line spectrometer at +35° and at different sweep fields. The mole ratios of all species are given in the diagram

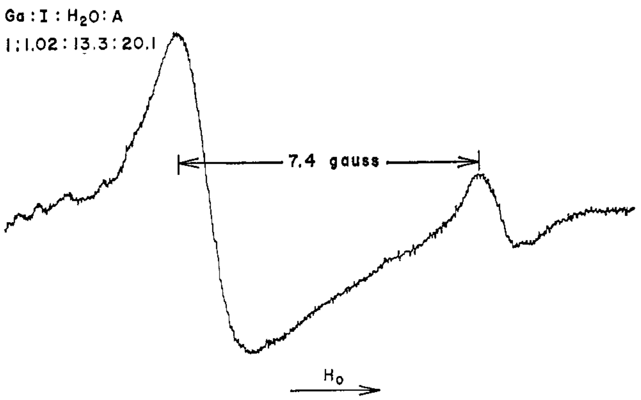

Figure 6.—The ^{69}Ga nmr spectrum of a solution of $Ga(ClO_4)_3$ and HI in a 1:1 mole ratio in a water–acetone mixture recorded on a Varian WL-12 wide-line spectrometer at +35°. The mole ratios of all species are given in the diagram.

produced a hydration number decrease from a value of 6 in pure water to values of 1.5, 1.6, and 2.5 for the Cl^-, Br^-, and I^- solutions, respectively, in 1:8 mole ratio, water to acetone, solvent mixtures.[13,14] Since inner-shell solvation by acetone in the presence of water at the concentrations used has been ruled out as a possibility by other studies,[3,6,11] the hydration number decrease can be attributed only to contact ion pairing. Furthermore, the relative hydration number changes showed that the ion-pairing ability of the anions decreased in the order $Cl^- > Br^- > I^-$, and they demonstrated the probable existence of tetrahedrally complexed Ga^{3+} in solution.

In the present study, an attempt was made to measure equilibrium quotients for ion pairing, in particular, for the process

$$Ga(H_2O)_6{}^{3+} + X^- \rightleftarrows (H_2O)_5GaX^{2+} + H_2O$$

From the data of Table I, it can be seen that in solutions containing Ga^{3+} and halide ion in a 1:1 mole ratio, the hydration number decreases to 4 rather than 5. Also, the equilibrium for the ion-pairing process which is occurring is displaced far to the right as manifested by the hydration number of 4 obtained over a range of water–acetone concentration, varying from about 1:1 to 1:6 mole ratios in these halide systems. This result precluded the calculation of equilibrium quotients for ion pairing since mixtures more concentrated in water could not be cooled to the low temperatures required in these studies.

An equally important aspect of this study, however, is the identification of the species present in these solutions. The hydration number of 4 could be explained by the presence of $(H_2O)_4GaX^{2+}$ or its dimer as the dominant component. The addition of a halide ion to the tightly packed hexahydrated Ga^{3+} might displace two water molecules rather than one, and the resultant pentacoordinated ion could dimerize to form a more stable entity. The formation of roughly equal amounts of $(H_2O)_3GaX^{2+}$ and $(H_2O)_5GaX^{2+}$ as the dominant species also would give an average hydration number of 4. This is a more likely possibility since Ga^{3+} is known to undergo tetrahedral and octahedral coordination. Although these possibilities cannot be completely discounted, the results of the present study strongly indicate that $Ga(H_2O)_6{}^{3+}$ and $GaX_4{}^-$ are the dominant species in all solutions studied, with the presence of a small amount of a third species also being noted in the Cl^- solutions.

The pmr spectra of all solutions in Table I containing a 1:1 Ga^{3+} to X^- mole ratio and at least a 4:1 water to Ga^{3+} mole ratio showed two water signals separated by about 150 Hz, with the peak at higher field corresponding to bulk water and that at lower field to water molecules in the Ga^{3+} solvation shell. This is illustrated by the spectrum of Figure 1 for a 1:1 Ga^{3+} to Cl^- solution. The small signal approximately 50 Hz upfield from the complexed water peak appears only in the Cl^- solutions, and it remains essentially unchanged in intensity in all solutions, even those containing different amounts of Cl^-. The appearance of only one principal signal in the complexed water regions of these halide solution spectra minimizes the possibility that a variety of Ga^{3+} species are present. Such species almost certainly would give rise to individual water resonance signals displaced from each other. For instance, from Table I and Figure 2, it can be seen that when the water to Ga^{3+} mole ratio is decreased to less than 4:1 in the 1:1 halide to Ga^{3+} solutions, all the water is complexed and the water proton spectrum is a multiple pattern. Notice that a signal for complexed acetone also is apparent in Figure 2 at this low water concentration. When the water to Ga^{3+} mole ratio increases to 4:1, only one signal appears at low field in the Br^- and I^- solution spectra, and a spectrum similar to that in Figure 1 is obtained for the Cl^- system. In view of the spectral evidence of Figure 2, it seems improbable that the electronic environments which the water molecules would experience in a variety of

Ga^{3+}–X^- species in these solutions would give rise to only one signal.

The chemical shift of the complexed water signal in all spectra also points to a common species, namely, $Ga(H_2O)_6{}^{3+}$. The average chemical shifts of this signal from acetone, for all solutions containing at least a 4:1 water to Ga^{3+} mole ratio, were 498 ± 2, 495 ± 4, and 498 ± 2 Hz for the Cl^-, Br^-, and I^- systems, respectively. For comparison, the complexed water proton signal of $Ga(ClO_4)_3$ solutions in water–acetone mixtures of comparable concentrations is about 500 Hz at $-50°$, a value which agrees closely with those obtained in the halide systems. In the $ClO_4{}^-$ solutions, the species is known to be $Ga(H_2O)_6{}^{3+}$.[6] Thus, the remarkable similarity of the chemical shifts indicates that this is one of the dominant species in all solutions.

The existence of tetrahedrally coordinated Ga^{3+} is manifested by the low hydration numbers obtained with higher mole ratios of halide to cation. With a 2:1 or 3:1 halide to Ga^{3+} mole ratio, the hydration number decreases to values as low as 1.5. These low values could be interpreted in terms of species such as $(H_2O)_{4-n}GaX_n{}^{3-n+}$. However, the presence of $GaX_4{}^-$ as the dominant tetrahedrally coordinated species may be reflected by the disappearance of the signal for water of hydration when the ratio of Cl^- to Ga^{3+} was increased to 4:1 (see Table I).

The ^{69}Ga nmr measurements were initiated by comparing the relative positions of the signals arising from $Ga(H_2O)_6{}^{3+}$, in a $Ga(ClO_4)_3$ solution, and $GaX_4{}^-$, prepared by acidifying the trihalide solution. These species were confirmed by pmr measurements as described above. The ^{69}Ga chemical shifts of $GaCl_4{}^-$ and $GaI_4{}^-$, each with respect to $Ga(H_2O)_6{}^{3+}$, are shown in Figures 3 and 4, respectively. The results were obtained by recording the spectrum of the $Ga(H_2O)_6{}^{3+}$ solution, changing samples, and recording the $GaX_4{}^-$ solution spectrum. Field drift errors introduced by this method amount to ±1% in the measured chemical shifts. The trend in increased ^{69}Ga shielding observed in the tetrahalides, that is, $GaCl_4{}^- < GaBr_4{}^- < GaI_4{}^-$, agrees with the results of a previous nmr study.[18]

The spectra of Figure 5 were obtained from aqueous acetone solutions of a 1:1 $Ga(ClO_4)_3$–HCl mixture (Figure 5a) and unacidified $GaCl_3$ (Figure 5b). Two signals are apparent in each spectrum of Figure 5, and they are separated by about 3.8 and 3.5 G, respectively. This corresponds closely to the 3.8 G observed for the signal separation of the $Ga(H_2O)_6{}^{3+}$ and $GaCl_4{}^-$ reference peaks of Figure 3. Although the signals were not integrated, a qualitative consideration of the peak intensities indicates a preponderance of an octahedral species in the 1:1 Ga^{3+}–Cl^- solution (Figure 5a) and a tetrahedral species in the $GaCl_3$ system (Figure 5b).

The same considerations apply to the spectrum of Figure 6 for a solution containing a 1:1 mole ratio of Ga^{3+} to I^-. The two distinct signals observed for this solution are separated by about 7.4 G, a value which may be compared to the 7.5-G separation of the $Ga(H_2O)_6{}^{3+}$ and $GaI_4{}^-$ reference signals of Figure 4. Qualitative support for the presence of these species in the solution of Figure 6 is provided by intensity considerations.

The Ga^{3+} hydration number value of 4 in the 1:1 halide solutions can be rationalized in terms of the presence of primarily $Ga(H_2O)_6{}^{3+}$ and $GaX_4{}^-$. If these were the only species present, the hydration number would be 4.5. However, as seen in Figure 1, another species is definitely present in the Cl^- solutions, and the presence of a similar species in the Br^- and I^- solutions cannot be precluded from the spectral observation of only one complexed water peak in their pmr spectra. The structure of this species could not be deduced unambiguously from the pmr data and a signal was not observed in the ^{69}Ga nmr spectra. Although the data do not support the existence of the several Ga^{3+}–X^- ion pairs which are theoretically possible, one may be stable in addition to $GaX_4{}^-$. As mentioned below, the species may be GaX^{2+}, hydrated by 3 or 5 water molecules. At a 2:1 and 3:1 mole ratio of anion to Ga^{3+}, hydration numbers of 3.0 and 1.5, respectively, are predicted if only $Ga(H_2O)_6{}^{3+}$ and $GaX_4{}^-$ are present, in excellent agreement with the results of Table I.

The conclusions drawn here also are consistent with those of other studies of cation complexes. For example, a pmr and ^{27}Al nmr study of $AlCl_3$ in acetonitrile provided evidence for $Al(AN)_6{}^{3+}$ and $AlCl_4{}^-$ as the dominant species in solution.[19] Even more pertinent are Raman spectral studies of aqueous $GaCl_3$ solutions containing various amounts of excess Cl^-.[20,21] In these solutions, lines which could be unambiguously attributed to $GaCl_4{}^-$ were detected at Cl^-:Ga^{3+} mole ratios of about 8:1. In addition, an anion-exchange study of acidified aqueous $GaCl_3$ solutions clearly confirmed the Raman spectral result for the existence of $GaCl_4{}^-$, and, more importantly, established Ga^{3+}, $GaCl_4{}^-$, and possibly $GaCl^{2+}$ as the dominant species in solution.[22] Admittedly, the salt and Cl^- concentrations are much higher in the Raman and anion-exchange experiments, but the presence of large amounts of acetone in the systems described here would enhance ion pairing by reducing the dielectric constant of the solution.

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