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On the Hydration of the Lutetium(III) Ion in Water Acetone Mixtures. A ^{1}H and ^{35}Cl NMR Study

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Abstract

The hydration of the Lu^{3+} ion was studied by ^{1}H- and ^{35}Cl-NMR spectroscopic methods in water-acetone mixtures at low temperatures. The observed hydration number obtained by the 'NMR peak-area' method is not constant, but decreases with increasing $Lu(ClO_4)_3$ and ClO_4^- ion concentrations, as well as with rising acetone-to-water ratio. The hydration number obtained for 2.92 M, 2.00 M, 1.17 M, 0.82 M and 0.49 M $Lu(ClO_4)_3$ solutions are 6.3 ± 0.12, 6.5 ± 0.12, 7.2 ± 0.2, 7.9 ± 0.17 and 8.7 ± 0.45, respectively. From these data, a primary hydration number $n_h \geqslant 9$ can be deduced for dilute solutions. The decrease of the hydration number with increasing $Lu(ClO_4)_3$ and acetone concentration can be explained assuming the coordination of the ClO_4^- ions in the inner shell of Lu^{3+} and/or the decrease of the coordination number of Lu^{3+} in more concentrated solutions, mainly due to water activity changes. The relaxation rate of the ^{35}Cl nucleus of the perchlorate ion increases with the increase of the Lu^{3+} concentration, consistent with the assumption of the perchlorate ion coordination.

Introduction

The coordination number of lanthanide(III) ions in solution, which is of primary importance in the interpretation of thermodynamic and kinetic properties of lanthanide complexes, has been disputed for a long time. In solid state compounds, according to the results of X-ray diffraction studies the coordination number CN of the lanthanide(III) ions, Ln^{3+}, varies between 6 and 12 depending mainly on the properties of the ligands [1, 2]. In some crystalline salt hydrates containing non-coordinating anions, the Ln^{3+} ions are ennea-hydrated (*e.g.* $Ln(BrO_3)_3 \cdot 9H_2O$ and $Ln(C_2H_5OSO_3)_3 \cdot 9H_2O$ [3]). In spite of the results of the X-ray diffraction studies of solids, the CN of the Ln^{3+} ions in solution was thought for a long time to be 6. In 1963, Thompson [4] assumed a CN of 8 or 9 to explain the formation of Ln(III) aminopolycarboxylate mixed ligand complexes. This assumption has been accepted and successfully applied in the interpretation of the stability constants of Ln(III) complexes [5, 6].

Two main viewpoints are known regarding the CN or the 'primary hydration number' of the Ln^{3+} ions along the lanthanide series in dilute aqueous solution. One of them was forwarded by Spedding and co-workers [7–9], who interpreted a detailed investigation of thermodynamic and transport properties of Ln(III) chloride, nitrate and perchlorate solutions, assuming a change of CN in the middle of the lanthanide series. According to this assumption, the CN is 9 for the lighter elements (La to Nd) and 8 for the heavier ones (Tb to Lu), while in the same of Sm, Eu and Gd an equilibrium exists between the $Ln(H_2O)_9^{3+}$ and $Ln(H_2O)_8^{3+}$ ions. On the other hand, this assumption has been criticized by other workers, who could interpret similar experimental results assuming a constant CN of 9 for the whole series [10–13].

Solution X-ray diffraction studies are a more direct method for the determination of hydration numbers, but the results obtained by different authors for the same Ln^{3+} ions often differ considerably. The hydration numbers obtained in concentrated solutions by Habenschuss and Spedding [14] confirm their assumption [7–9] on the change of the CN in the middle of the series. However, Wertz *et al.* reported a CN of 8 for the lighter elements [15–18], while Russ *et al.* obtained a value of 9.9 for Sm and Gd [3, 19]. Studying the hydration of the Ce^{3+} ion in nitrate solution, Caminiti *et al.* have stated [20] that 'it is very difficult to give unambiguously an answer with X-ray diffraction technique'. This point is nicely exemplified in a recent X-ray study of yttrium and erbium perchlorate solutions performed by Johansson *et al.* [21].

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Neutron diffraction has also been used [22] to determine the CN of the Nd^{3+} ion in chloride solutions, which was found to be 8.5 ± 0.2.

The results of a study of glassy Ln(III) chloride solutions with Raman spectroscopy [23] seem to be in agreement with the statements of Spedding *et al.* [7–9, 14], although the increase of the hydration number of Eu and Gd with increasing concentration is surprising.

The measurement of the fluorescence life time of Ln^{3+} ions can also be used to determine hydration numbers [24, 25]. From the similar fluorescence life-time values for the solid $Eu(CF_3COO)_3 \cdot 9H_2O$ and Eu^{3+}(aq), as well as for $Tb(CF_3COO)_3 \cdot 9H_2O$ and Tb^{3+}(aq), Sinha deduced a CN of 9 for both ions in aqueous solution [26].

However, the most direct values of the number of water molecules coordinated in the inner sphere of metal ions, can often be obtained with the NMR-spectroscopy 'peak-area' method [27]. The hydration number determined in this way is equal to the CN or to the 'primary hydration number', if there is no complex formation between the metal ion and the anion; otherwise, the observed hydration number is lower than the CN. However, studying lanthanide ions with ^{1}H-NMR or ^{17}O-NMR is difficult, because the water molecules coordinated in the 'primary hydration sphere' exchange very rapidly with those of the bulk solvent. Fratiello *et al.* have carried out ^{1}H-NMR measurements at low temperatures in water-acetone mixtures [28, 29] in order to slow down the rate of water exchange (and also the rate of proton exchange). They obtained hydration numbers of about 6 for the La^{3+} and Lu^{3+} ions in perchlorate solutions, much lower than the CN values obtained by other methods. Hydration numbers of about 6 or lower were also obtained for some paramagnetic Ln^{3+} ions [28, 29]. These relatively low values, obtained by the ^{1}H-NMR 'peak-area' method, have not been explained although the possibility of the formation of Ln(III) perchlorate complexes was not ruled out [28, 29]. The hydration number of the Lu^{3+} and Yb^{3+} ions was found to be 6 [30] and 8 [31], respectively, applying a similar ^{1}H-NMR technique. The results of a ^{139}La-NMR study of La(III) perchlorate solutions have been interpreted by assuming a decrease in the hydration number from 9 to 8 with increasing concentration [32]. This assumption has been criticized by Reuben, who suggested a constant hydration number of 9 [33].

The present study was undertaken in order to obtain more information on the hydration of the Ln^{3+} ions, and to find an explanation for the contradictory hydration number values obtained by the ^{1}H-NMR 'peak-area' and by other methods.

The ion studied was the diamagnetic Lu^{3+}. This ion is the last member of the lanthanide series and has the smallest ionic radius. Thus, if any decrease of the hydration number occurs along the series, it should be possible to detect it by determining the hydration number of Lu^{3+}.

The use of an improved spectrometer in connection with a higher magnetic field ought to provide more accurate results than those obtained by previous investigators [28–31].

Experimental

The $Lu(ClO_4)_3$ stock solution was prepared from Lu_2O_3 (99.9%, Ventron), using a slight $HClO_4$ excess to avoid hydrolysis. The concentration of the stock solution was determined by complexometric titration with the use of xylenol orange as indicator, and dilutions from this solution were carried out by weighing. For the determination of the solution densities, an Anton Paar KG model DMA 35 digital instrument was used. The $Lu(ClO_4)_3$ concentrations in the aqueous solution – (acetone-d_6) mixtures are given as $[Lu^{3+}]$ of the original aqueous solution, *i.e.* before mixing with acetone-d_6.

For the preparation of the $Lu(ClO_4)_3$ solution–acetone mixtures, 99.5% and 99.95% acetone-d_6 (Ciba-Geigy) were used. Both acetone-d_6 samples contained some impurities in small amounts. At low temperatures the proton signal of the impurities appeared under the broad signal of the bulk water. The amount of the impurities was determined comparing the integral values of the signals of the impurities with those of the methyl protons of the acetone-d_6. The effect of the impurities on the intensity of the signals was taken into account when the hydration numbers were calculated. The amount of protons in the acetone-d_6 was also determined by comparing the signal intensities of samples containing known amounts of acetone-d_6 and water or chloroform.

For the proton- and ^{35}Cl-NMR measurements Bruker WP200 and Bruker CXP100 instruments, respectively, were used. In order to obtain separate signals for coordinated and bulk water, the measurements were carried out at about –95 °C (using a Bruker VT1000 variable temperature control unit). The temperature in the probe head was controlled applying the 'methanol thermometer' method [34].

The parameters used to record the FT-NMR spectra were chosen with the aim of obtaining optimal values of the signal integrals [35, 36]. The longitudinal relaxation rates of the protons of the coordinated and bulk water molecules were determined by using the 'inversion recovery' method applying $180^\circ - \tau - 90^\circ$ pulse sequence [37]. In order to determine the hydration number (n_h) the 'peak-area' of the signal of the coordinated water molecules (A_c) was compared with the total amount

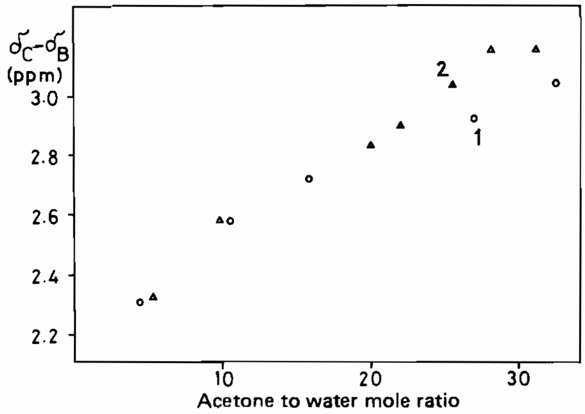

Fig. 1. The chemical shift differences between the ^1H signals of the coordinated and bulk water molecules, obtained for 2.92 M (1) and 1.17 M (2) $Lu(ClO_4)_3$.

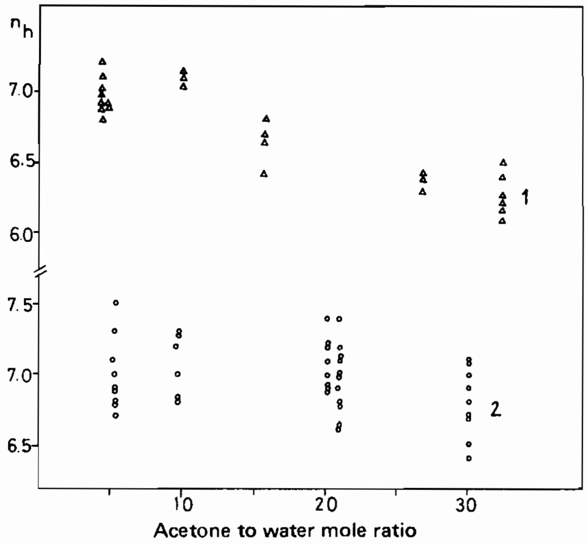

Fig. 2. The observed hydration numbers obtained for 2.92 M (1) and 1.17 M (2) $Lu(ClO_4)_3$. The points shown for the same acetone/water ratio represent spectra obtained at different temperatures.

of water present ($A_c + A_b$, where A_b is the 'peak area' of the signal of the bulk water). To calculate the hydration number, the following equation was used: $A_c/(A_c + A_b) = n_h m_{Lu}/m_w$, where m_{Lu} and m_w are the amounts of Lu and water in mol.

Results

The signal of the water molecules coordinated to the Lu^{3+} ion and the signal of the bulk water are well separated at about −95 °C in water–acetone mixtures. The signal separation increases with the acetone to water mole ratio (Fig. 1), mainly due to the upfield shift of the bulk water signal.

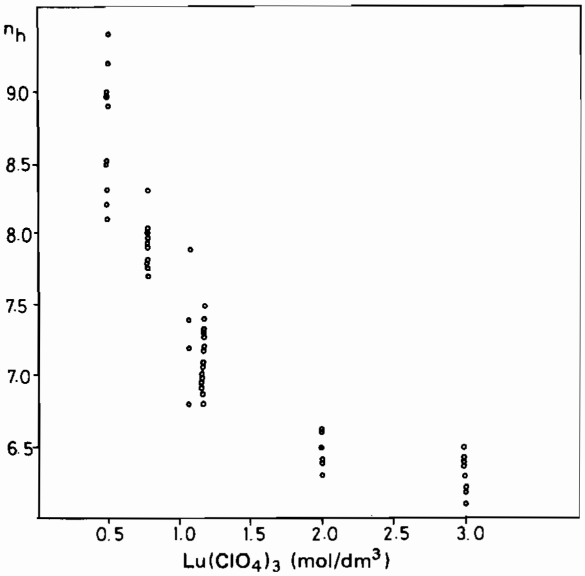

Fig. 3. The dependence of the observed hydration number on the concentration of $Lu(ClO_4)_3$ (the acetone to water mole ratio is 22 ± 1.5).

The hydration number of the Lu^{3+} ion was determined in water–acetone mixtures, where both the concentration of $Lu(ClO_4)_3$ and the ratio acetone to water were varied. Figure 2 shows the observed hydration number as a function of the acetone-water mole ratio at two $Lu(ClO_4)_3$ concentrations.

The value of the observed hydration number decreases slightly with increasing acetone content of the solution (*cf.* Fig. 2). This variation is larger in more concentrated $Lu(ClO_4)_3$ solutions. Hence, we have studied the hydration numbers as a function of $Lu(ClO_4)_3$ concentration in solutions of practically constant acetone to water mole ratio. The results of these experiments are shown in Fig. 3. The acetone-water mole ratios were kept between 20.5 and 23.5, except for a 0.82 M $Lu(ClO_4)_3$ solution where the ratio was 14. However, at such low Lu^{3+} concentrations the observed hydration number depends only very slightly on the acetone-water mole ratio (see Fig. 2).

According to the data presented in Fig. 3, the value of the observed hydration number decreases very significantly with the increase of the $Lu(ClO_4)_3$ concentration. We tried to decide whether or not this phenomenon is due to the coordination of the ClO_4^- ions into the inner shell of the Lu^{3+} ion by using the following technique.

The hydration numbers were determined in solutions where the $Lu(ClO_4)_3$ concentration as well as the acetone to water mole ratio were constant (1.17 M and 20.5 ± 0.4) and the excess of ClO_4^- was varied by adding solid $NaClO_4$. The results are shown in Fig. 4.

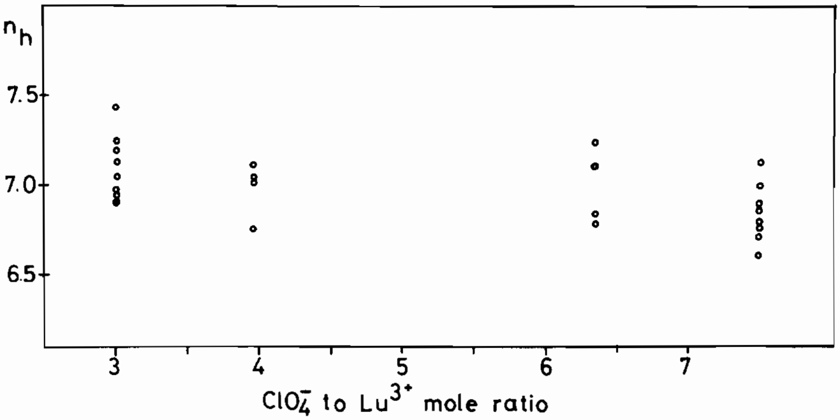

Fig. 4. The observed hydration number, obtained for the solution of 1.17 M $Lu(ClO_4)_3$ and varying amounts of added solid $NaClO_4$.

^{35}Cl-NMR studies were performed in solutions where the concentration of the ClO_4^- ion and the acetone-water mole ratio were constant (6.0 M and 10 ± 1), while the Lu^{3+} ion concentration was varied. The change in the chemical shift of the ^{35}Cl nucleus was insignificant. At room temperature, the chemical shift difference between a 6.0 M $NaClO_4$ and a 2.0 M $Lu(ClO_4)_3$ was found to be 1.4 ppm. From the line width values measured at half height of the signals ($w_{1/2}$), the relaxation rate of the ^{35}Cl nuclei ($1/T_2^*$) was determined at different temperatures ($w_{1/2} = 1/\pi T_2^*$, where T_2^* is somewhat longer than the transverse relaxation time as a result of the inhomogeneity of the magnetic field). The results are shown in Fig. 5.

The longitudinal relaxation time (T_1) of the protons of the coordinated and free water molecules, determined by the "inversion recovery" method, were found to be 0.051 s and 0.049 s. These values are identical, within the error of the method.

Discussion

The results presented in Figs. 2 and 3 clearly show that the number of the water molecules coordinated in the inner shell of the Lu^{3+} ion is not constant, but depends both on the acetone/water mole ratio and on the concentration of $Lu(ClO_4)_3$, with a stronger dependence on the latter. The average values of the observed hydration numbers obtained from the data in Fig. 3 in $Lu(ClO_4)_3$ solutions of concentration 2.92 M, 2.00 M, 1.17 M, 0.82 M, and 0.49 M are 6.3 ± 0.12, 6.5 ± 0.12, 7.2 ± 0.2, 7.9 ± 0.17, and 8.7 ± 0.45, respectively (the errors given are experimental standard deviations).

At the highest $Lu(ClO_4)_3$ concentration, where the experimental conditions are very similar to those used by Fratiello *et al.* [29], the observed hydration number is 6.3, which agrees well with the value of about 6 obtained by them. However, a decrease in $Lu(ClO_4)_3$ concentration results in a definite increase in the observed hydration numbers. From the trend of the data in Fig. 3, a primary hydration number ≥ 9 is indicated in more dilute solutions.

There are several possible explanations to the observed variations in the hydration number of Lu^{3+}:

–a replacement of coordinated water by inner-sphere coordination of acetone or ClO_4^- ions

– a change in the coordination/hydration number as a result of changes in the water activity of the solution. The water activity may change either as a result of changes in the water/$Lu(ClO_4)_3$ ratio, and/or because of varying water/acetone hydrogen bonding at different water/acetone mole ratios.

Coordination of acetone in the inner coordination sphere of the Lu^{3+} ion has previously been assumed not to take place [29] on the basis of an unchanged hydration number determined in solutions of different acetone/water ratios.

The interaction between ClO_4^- and several metal ions has recently been studied in organic and mixed solvents using ^{35}Cl-NMR techniques [39–43]. This method seems to be relatively sensitive to indicate the coordination of the ClO_4^- ion. The NMR signal of the free $^{35}ClO_4^-$ ion in solution is quite narrow, because the relaxation rate of the ^{35}Cl nucleus is proportional to the second power of the electric field gradient at the nucleus, and the tetrahedral symmetry of the ClO_4^- ion is only very slightly distorted due to the interaction of solvent molecules. The formation of outer sphere complexes also results in only a small change in the relaxation rate, because the effect of the electric field of the metal ion drops by the sixth power of the distance between the metal and the ^{35}Cl nucleus [40, 41]. The coordination of the ClO_4^- ion into the inner shell of the metal ion yields an efficient distortion

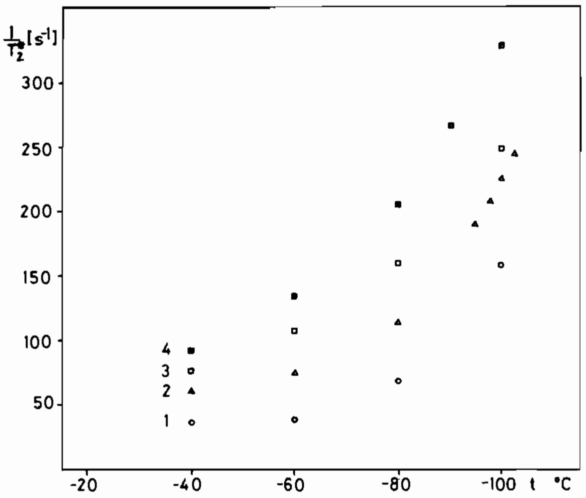

Fig. 5. The relaxation rate of the ^{35}Cl nuclei. The concentrations of the $NaClO_4$ and $Lu(ClO_4)_3$ is respectively 6 M and 0 M (1), 3.0 M and 1.0 M (2), 1.5 M and 1.5 M (3), and 0 M and 2 M (4). The acetone to water mole ratio is 10 ± 1.

of its symmetry that gives rise to a significant increase in the relaxation rate.

Inner sphere complexes with ClO_4^- are rare, and evidence in the literature concerning possible rare earth–ClO_4^- inner sphere complex formation is contradictory. The La^{3+} and Ce^{3+}–ClO_4^- systems have been investigated by using Raman and ^{35}Cl-NMR spectroscopy [38, 39], but no evidence for perchlorate coordination was observed. On the other hand, in a ^{1}H- and ^{35}Cl-NMR investigation [31] of the Yb^{3+}–ClO_4^- system in water–acetone at −100 °C, three separate bound water peaks were observed in concentrated solutions and attributed to the formation of complexes with 1, 2 and 3 perchlorate ions. The ^{35}Cl signal was extremely broad, a fact which was also interpreted as ClO_4^- coordination to the paramagnetic Yb^{3+} ion.

The data in Fig. 4 show a slight decrease in the observed hydration number values with the increase of the ClO_4^- excess present. The reduction of the hydration numbers can be explained assuming the coordination of the perchlorate ions into the inner sphere of the Lu^{3+}, but the change is quite small at this concentration and is not convincing evidence.

The data in Fig. 5 show that the relaxation rate of ^{35}Cl in the perchlorate ion is higher in the $Lu(ClO_4)_3$ solutions than in the $NaClO_4$ solutions. There is also an increase in the relaxation rate with increasing Lu^{3+} concentration, a fact which may indicate the formation of inner sphere perchlorate complex. At about −100 °C, the dielectric constant of the water/acetone mixtures is very low, which is favourable to perchlorate complex formation. However, the data do not allow any quantitative estimation either of the composition of the complexes, or of their stability constants.

The relatively large decrease in the hydration number of Lu^{3+} with increasing metal ion concentration can also be interpreted as a result of a decrease in coordination number, caused by water activity changes. Similar assumption was also made by others, *e.g.* to interpret the change in the visible spectra of the Nd^{3+} in concentrated HCl, $HClO_4$ and LiCl [44] and in other cases [32]. The decrease in the CN can be the consequence of the interaction between the acetone and water molecules through hydrogen-bond formation. Such interaction has been detected by ^{1}H-NMR spectroscopy in water–acetone mixtures at very low water content [45]. In this interaction, the water molecule acts as a proton donor, and can interact with one (HOH···· A) or two acetone molecules (A····HOH····A). The equilibrium constant, expressed in mole fractions, characterizing the formation of the A···· HOH····A species from the HOH····A species, was found to be 2.0 at −14 °C. The enthalpy change for this process is −10.0 kJ/mole, that is, the association is favoured by lowering the temperature [45]. In our samples, prepared from the more concentrated $Lu(ClO_4)_3$ solutions, the water to Lu^{3+} mole ratio is quite low (about 12 in a 3 M and 21 in a 2 M solution), while the acetone to water mole ratio is very high. Hence, large water activity changes are expected. A decrease of the CN of Lu^{3+}, as a result of a lowering of the water activity with a decrease in the mole ratio water/Lu^{3+}, may contribute to the variations in hydration number shown in Fig. 3.

The results of this ^{1}H-NMR study show a variable hydration number for the Lu^{3+} ion, thus resolving the contradiction between the results of previous X-ray diffraction [14–19], and ^{1}H NMR studies [27–30]. In purely aqueous solutions at room temperature, the hydration numbers obtained by X-ray diffraction and other methods are between eight and nine and only slightly dependent on the solution concentration. In water–acetone mixtures at low temperatures, the variation of the hydration number is larger. This is a consequence of a more extensive ClO_4^- complex formation and/or of the change in the water activity. Moreover, our data indicate that there is no change of the hydration number from nine to eight along the lanthanide series, as has previously been postulated.

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