Interactions of La(III) with Anions in Aqueous Solutions. A $^{139}$La NMR Study

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The interactions of the La(III) cations with three anions (X), nitrate, chloride and perchlorate, in aqueous solutions in the pH range 4.0-6.5, were studied by $^{139}$La NMR spectroscopy. A single model, involving the formation of the contact ion-pair (inner-sphere complex) (LaX)$_2^{2+}$ was successfully and quantitatively applied to the chemical shift and the transverse relaxation rate data. Both measurements gave values for the thermodynamic equilibrium constants of formation of (LaX)$_2^{2+}$ ($K_{th}$) in good agreement (average $K_{th} = 0.45 \pm 0.05$; 0.15 $\pm$ 0.09; 0.03 $\pm$ 0.01, respectively for nitrate, chloride and perchlorate). The complexes are characterized by chemical shifts of -25, 22 and -3.1 ppm and by transverse relaxation rates of 11.2, 5 and 1.65 kHz respectively for nitrate, chloride and perchlorate. The $^{139}$La quadrupolar relaxation rate is not controlled by the reorientational correlation time. This finding is discussed, and it is suggested that the very fast exchange of water molecules in the first coordination sphere of La(III) is responsible for the time fluctuation of the electric field gradient at the $^{139}$La nucleus site.

KEY WORDS: $^{139}$La NMR; lanthanide coordination; ion pairing; aqueous solutions; quadrupolar relaxation; solvation dynamics.

1. Introduction

With the increasing use of lanthanoid ions as probes in biochemical systems,$^{(1)}$ their properties of complexation by specific ligands in solution are of considerable interest.$^{(2)}$ However, the nature and the structure of the chemical species present in the aqueous solutions of their salts are not yet fully understood. More particularly, two questions have not yet been fully resolved: the coordination number of the lanthanoid cations and the nature of their ion pairs, contact (inner-sphere complex), or solvent-separated (outer-sphere complex).

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941
Several techniques have been used to characterize the coordination properties of lanthanoid cations in aqueous, aqueous-nonaqueous mixtures, and nonaqueous solvents. X-ray measurements in concentrated solutions have given coordination numbers of 8 (heavy lanthanoids) or 9 (lighter ones), in agreement with the decrease of the ionic radii along the series. This description is far from being fully accepted since, for example, a constant coordination number of 8 along the series was found when the formation of chlorocomplexes was taken into consideration. Moreover, a \( ^{17}O \) NMR chemical shift study was consistent with a constant hydration number along the series. This controversy has been reviewed by Cossy and Merbach. More recently the same group measured by neutron scattering coordination numbers of 8 for Dy(III) and Yb(III) and of 9 for Nd(III).

Several spectroscopies and techniques, including UV-visible, luminescence and ultrasonic relaxation, have characterized the nature of the complexes formed between lanthanoid cations and various anions in aqueous solutions. While, generally, no inner-sphere complexes were detected with perchlorate, the experimental data indicate the formation of a 1:1 complex \([\text{Ln(NO}_3\text{)})^2+\) in the case of nitrate. The presence of mono- and dinitrate complexes was deduced from \(^{15}\text{NO}_3\) NMR spectra in solutions of Lu(III) in water-acetone-\(d_6\)-freon-12 mixtures. In the same ternary mixtures, a similar conclusion was reached from the \(^1H\) and \(^{89}\text{Y}\) NMR spectra of Y(III) solutions, and direct evidence for inner sphere complex formation was provided in the case of \(\text{La(NO}_3\text{)}_3\).

Metal cation NMR of quadrupolar nuclei in solution is a powerful probe of the nature of the immediate environment of the metal cation. Among the lanthanoid series, only a very limited number of nuclides are amenable to NMR studies, the most sensitive one being \(^{139}\text{La}\), a spin 7/2 nuclide, with a natural abundance of 99.91% and a receptivity of 342 relative to \(^{13}\text{C}\). These characteristics, coupled with the diamagnetic nature of the La(III) cation, led to a number of solution NMR studies of lanthanum salts, despite the large quadrupole moment of \(^{139}\text{La}\) \((0.22 \times 10^{-28} \text{ m}^2)\). The formation of inner-sphere complexes in the case of \(\text{NO}_3\), which was detected by several other techniques, was confirmed by the strong variation with concentration of both \(^{139}\text{La}\) linewidths and chemical shifts of aqueous \(\text{La(NO}_3\text{)}_3\) solutions. Such a strong variation was not observed for chloride and perchlorate, and it was concluded that outer-sphere complexes were formed in these two cases. However, no quantitative interpretation of the \(^{139}\text{La}(III)\) NMR chemical shifts and linewidths in