A Direct Nitrogen-15 NMR Study of Neodymium(III)-Nitrate Complex Formation in Aqueous Solvent Mixtures

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A study of contact ion-pair formation between the neodymium (III) and nitrate ions in aqueous solvent mixtures has been carried out by a direct, low temperature, nitrogen-15 ($^{15}$N) nuclear magnetic resonance (NMR) technique. At low temperatures, -90 to -120°C, ligand exchange is slow enough to permit the observation of $^{15}$N NMR signals for uncomplexed nitrate ion, and this anion in the primary solvation shell of Nd(III). In aqueous mixtures with inert acetone and Freon-12, resonance signals for Nd(NO$_3$)$_2$$^+$, Nd(NO$_3$)$_3$$^+$, and two higher complexes are observed. Signal areas indicate these additional species are possibly a combination of the tetra-, penta-, and hexanitrato complexes, but not the trinitrato. In water-methanol, a medium of higher dielectric constant, complexation is much less and signals only for the mono-and dinitrato complexes are observed. The effect of solvent on complexation is demonstrated more clearly by a series of measurements in water-methanol-acetone mixtures.

KEY WORDS: Nitrogen-15 NMR; neodymium-nitrate complexes; aqueous solvent mixtures.

1. Introduction

In view of the continually expanding utilization of the lanthanide metal-ions in chemical and physiological systems, the need for quantitative information concerning their binding properties has stimulated studies by a variety of techniques. Among these, spectroscopic methods provide the most detailed evaluation of coordination numbers, binding preferences with different molecular and ionic ligands, and changes in complexing behavior across the lanthanide series. Much at-
tention has been directed toward the evaluation of the extent of contact, inner-shell, ion-pair formation, and the dependence of this process on the nature of the anion, solvent properties, particularly basic strength and dielectric constant, and temperature. Contact ion-pairing can be induced with most anions, including perchlorate and trifluoromethanesulfonate (triflate), if the measurements are made in anhydrous inert solvents, such as acetonitrile, nitromethane and sulfolane.\(^2\) However, in more basic solvents, such as alcohols, dimethylformamide (DMF), dimethylsulfoxide (DMSO), or their aqueous mixtures, this process can occur only with more competitive anions, for example, chloride at high concentrations,\(^9\) and nitrate.\(^16\)

Of the various methods, nuclear magnetic resonance (NMR) has been a valuable tool for evaluating the coordination properties of the lanthanides, including the extent of contact ion-pair formation, by chemical shift and relaxation time perturbations for nuclei at or near the ligand binding site, in the anion, or the metal-ion itself. The NMR method also can lead to the direct observation of nuclides in coordinated and uncomplexed electronic environments, if the particular exchange can be slowed sufficiently. With the use of inert solvents whose aqueous mixtures could be cooled to -120°C, our early studies of the lanthanide ions and "lanthanide-like" yttrium relied primarily on \(^1\)H NMR experiments of water in these systems.\(^31\) Using multinuclear magnetic resonance methods, these studies recently were expanded to solutions of La(III) \((^{1}\text{H}, ^{35}\text{Cl}, ^{139}\text{La})\),\(^35\) Y(III) \((^{1}\text{H}, ^{35}\text{Cl}, ^{89}\text{Y})\),\(^36\) Lu(III) \((^{1}\text{H}, ^{15}\text{N}, ^{35}\text{Cl})\),\(^37\) Er(III) \((^{15}\text{N}, ^{35}\text{Cl})\),\(^38\) and Ce(III) \((^{15}\text{N}, ^{35}\text{Cl})\).\(^39\) The observation of multiple \(^1\)H NMR signals for bound water peaks and inordinately low hydration numbers provided evidence of ligand displacement by nitrate contact ion-pair formation. In the Y(III) study, this was confirmed by the presence of \(^{89}\text{Y}\) NMR signals for two nitrate complexes. However, the best evidence for this process was provided by the appearance of \(^{15}\text{N}\) NMR signals for the nitrate ion in different complexes in these ionic systems.\(^37\)\(^39\) The difficulties presented by \(^{15}\text{N}\) NMR have resulted in only a few studies of metal-ion nitrate solutions\(^40\)\(^42\) by this nuclide, but these problems have been minimized in our laboratory. Thus far, the presence of the mono- and dinitrato complexes have been detected in solutions of Lu(III)\(^37\) and Er(III),\(^38\) and these species plus two higher complexes in Ce(III)\(^39\) solutions. The present work describes the application of this technique to the Nd(III) system, an ion comparable in paramagnetic properties to Ce(III), and for which comparisons to the results of experiments by other methods could be made.