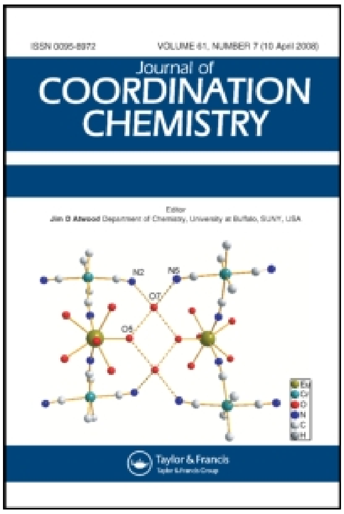

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pH-DEPENDENCE OF THE METAL ION HYDRATION STATE IN LANTHANIDE COMPLEXES OF POLYAMINOPOLYCARBOXYLATE LIGANDS

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pH-DEPENDENCE OF THE METAL ION HYDRATION STATE IN LANTHANIDE COMPLEXES OF POLYAMINOPOLYCARBOXYLATE LIGANDS

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A spectroscopic method has been used to determine the number of coordinated water molecules bound to the central lanthanide ion in a series of polyaminopolycarboxylate complexes. It was found that in complexes of simple polyaminotricarboxylates, almost 4 waters of hydration were bound at the inner coordination sphere of the metal ion. The lanthanide complexes of simple polyaminotetracarboxylate ligands were found to contain approximately 2.5 waters of hydration. Increasing the steric requirement of a polyaminotetracarboxylate ligand (either by increasing the number of groups in the ligand backbone or by increasing the number of groups in the carboxylate arms) did not appreciably change the lanthanide ion hydration state. The binding of ligands containing additional sites of coordination was found to reduce the hydration state to unity.

Keywords: Lanthanides, polyaminopolycarboxylates, hydration numbers, luminescence

INTRODUCTION

The solution chemistry associated with lanthanide complexes of polyaminopolycarboxylate ligands is rather well advanced in terms of stability constants and thermodynamics,[1–3] but there is still much to be learned about the structure and composition of the coordination spheres of these complexes. Since many of these ligands to not cause coordinative saturation for a lanthanide complex, it is of interest to evaluate the hydration state of the complexed metal ion.

To answer this question, the spectroscopic water counting method of Horrocks and Sudnick[4] was used to obtain the relation between pH and the number of water molecules coordinated in the inner sphere of the lanthanide ion in a series of polyaminopolycarboxylate complexes. Four categories of ligands were used in this study, chosen on the basis of their different chelation possibilities. The first class was polyaminotricarboxylates: *N*-methylethylenediaminetriacetic acid (MEDTA), *N*-benzylethylenediaminetriacetic acid (BEDTA), and *N*-hydroxyethylethylenediaminetriacetic acid (HEDTA). The second class was simple polyaminotetracarboxylate ligands: ethylenediaminetetraacetic acid (EDTA), 1,2-diaminopropanetetraacetic acid (PDTA), and *trans*-1,2-diaminocyclohexanetetraacetic acid (CDTA). The third class was polyaminotetracarboxylate ligands containing additional

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steric bulk: 1,3-diaminopropanetetraacetic acid (TMDTA) and ethylenediamine-*N*,*N*′-diacetic-*N*,*N*′- dipropionic acid (EDAP). The fourth class was two polyaminopolycarboxylate ligands containing additional functional groups: ethylenebisoxyethylenenitrilotetraacetic acid (EGTA) and diethylenetriaminepentaacetic acid (DTPA).

EXPERIMENTAL

Most of the ligands (EDTA, DTPA, BEDTA, EDAP, HEDTA, CDTA, PDTA, and EGTA) used in this study were used as received from commercial sources. MEDTA[5] and TMDTA[6] were synthesized by methods reported previously.

Tb(III) stock solutions were prepared from hydrated $TbCl_3$, while Eu(III) stock solutions were prepared by dissolving Eu_2O_3 in perchloric acid. Both such stock solutions were standardized using complexometric titrations with xylenol orange as the indicator.

The aminopolycarboxylate complex solutions were prepared by mixing stoichiometric amounts of the lanthanide ion and ligand stock solutions of known concentration. The pH of each solution was varied between 1.5 and 11 for luminescence measurements. Variation of the solution pH of each solution was effected by the addition of small amounts of standard NaOH or HCl directly to the cuvette.

The Tb(III) luminescence lifetimes were obtained by exciting the samples with the pulsed 337 nm output of a nitrogen laser (model LN-1000, Photochemical Research Associates), and capturing the decay curve on a boxcar averager (model SR-265, Stanford Research Associates). The luminescence decay times and rate constants were obtained by fitting the observed decay curves to an exponential function. The Eu(III) luminescence lifetimes were obtained by exciting the samples with a pulsed 395 nm laser beam. This excitation was obtained by using the pulsed (10 hz) 532 nm output of a Quanta Ray DCR 2A Nd-YaG laser to pump Rhodamine 640 (Exciton chemical, Dayton, Ohio; methanolic solution), in a Quanta Ray PDL2 dye laser head. The output from the dye laser was then converted to 395 nm by frequency doubling and mixing with the 1064 nm fundamental of a Quanta Ray WEX-1 Wavelength Extender. The luminescence decays was captured by a Lecroy TR 8828C Transient Recorder and, after being transferred to an IBM PC computer, were analyzed using a program written at the Florida State University.

RESULTS AND DISCUSSION

Lanthanide Ion Spectroscopy

UV excitation of Tb(III) results in reasonably efficient population of the luminescent $^5D_4$ excited state, and in subsequent emissive transitions to the $^7F_6$ (490 nm), $^7F_5$ (545 nm), $^7F_4$ (585 nm), and $^7F_3$ (625 nm) states of the ground manifold. Excitation of Eu(III) yields luminescence from the $^5D_0$ excited state, with emissive transitions to the $^7F_0$ (580 nm), $^7F_1$ (590 nm), and $^7F_2$ (615 nm) states of the ground manifold. The intensities and lifetimes of these various emission bands have been found to be reliable indicators of solution phase coordination chemistry.[7] The existence of a stable emission intensity or lifetime over a pH range usually indicates no change in the lanthanide speciation over that range. Generally, the trends associated with the pH dependence of the different emission bands are identical and, therefore, results obtained for any particular transition can be taken to be indicative of the overall trends.

The mechanisms which lead to changes in the luminescence lifetime of Eu(III) or Tb(III) species are similar to those which affect the intensities in the emission spectra. High-energy vibrations are efficient deactivators of the excited lanthanide ions, and are effective quenchers of the emission lifetime. The -OH stretching mode of coordinated water molecules is particularly effective in this regard.[4] Most ligands do not contain groups with vibrational frequencies required to effectively quench the excited state, and therefore do not reduce the luminescence lifetimes of Eu(III) and Tb(III). Since the binding of a ligand results in the expulsion of some of the coordinated water molecules, it affects the degree of excited state quenching. As a result, the emission lifetimes of Eu(III) and Tb(III) provide direct information of the state of residual hydration of the metal ion.

The existence of a deuterium isotope effect in luminescence lifetimes of lanthanides has been known for some time.[8] While the -OH stretching mode of coordinated water ($3500\,\mathrm{cm}^{-1}$) is effective at quenching the Eu(III) excited $^5D_0$ state and the Tb(III) excited $^5D_4$ state, the analogous -OD stretching mode of coordinated deuterium oxide ($2800\,\mathrm{cm}^{-1}$) is far less effective. Horrocks and Sudnick[4] have used this phenomenon to develop a spectroscopic method suitable for a determination of the number of water molecules bound at the inner coordination sphere of either Tb(III) or Eu(III). The luminescence lifetime of a given species is measured in both H_2O and D_2O, and the observed rate for luminescence decay obtained in each solvent system. The difference between the rate constants, Δk, obtained in H_2O and D_2O is directly proportional to the number of coordinated water molecules, q, and can be calculated using the relationship developed by Horrocks and Sudnick[4] as follows:

$$q = C\{k(H_2O) - k(D_2O)\} \qquad (1)$$

In equation (*1*), $C = 4.2$ for Tb(III) complexes and 1.05 for Eu(III) complexes. The uncertainty associated with the deduced q values is approximately ± 0.25 water molecules, and non-integral q values imply the co-existence of species of differing hydration states.[9]

Lanthanide Complexes of Polyaminotricarboxylates

The effect of pH on the metal ion hydration state is shown in Figure 1 for the Tb(III) and Eu(III) complexes of MEDTA, BEDTA, and HEDTA. The close identity of the Eu(III) and Tb(III) curves for each ligand system indicates the existence of equivalent hydration states for the analogous complexes. All curves appear to consist of an initial region (pH 1 to 3.5) where the number of coordinated water molecules decreases very rapidly, a region (pH 4 to 8) where the hydration state is quite stable, and a region (pH 9 to 11.5) where the number of coordinated water molecules decreases further.

The initial pH region is the interval where each ligand begins to bind a lanthanide ion. This process begins around pH 1.5, and full formation of the 1:1 complexes is complete by pH 3.5. The number of coordinated water molecules drops from eight or nine for the aquo-ion to between three and four for the complexes. The Ln(HEDTA) complexes are seen to be somewhat more stable with respect to acid hydrolysis than either Ln(MEDTA) or Ln(BEDTA), since they become fully formed by pH 3.

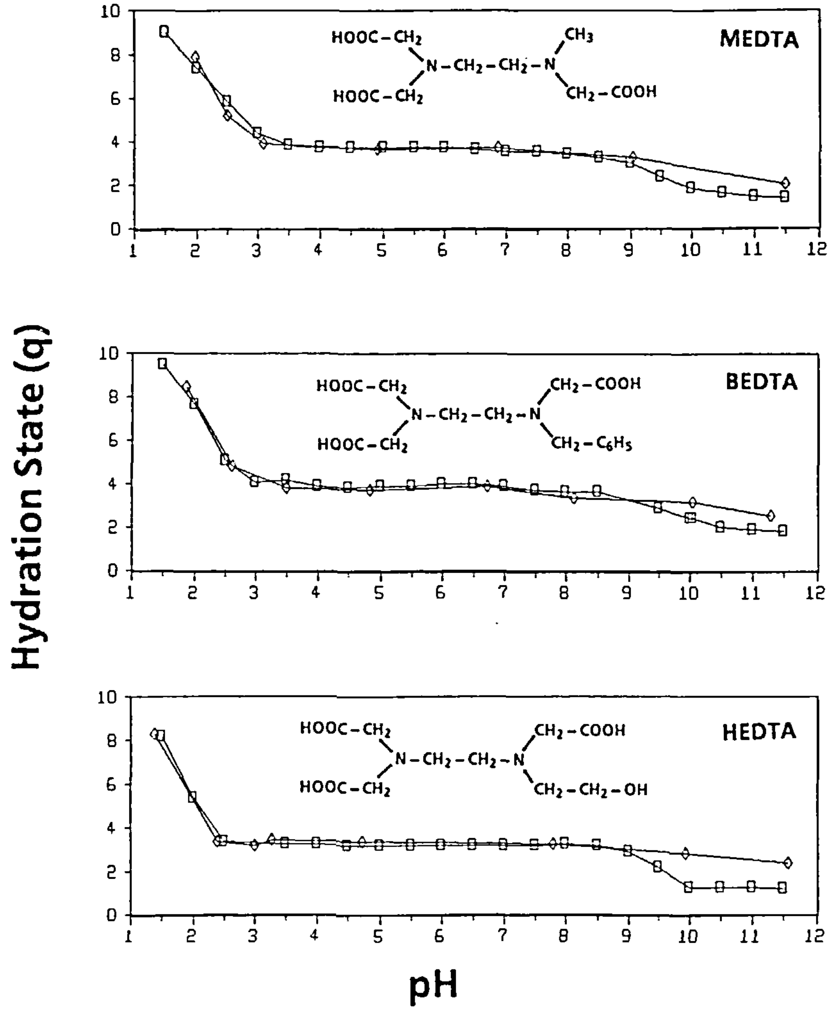

FIGURE 1 pH dependence of the lanthanide ion hydration state in the Tb(III) {points marked by open squares} and Eu(III) {points marked by open diamonds} complexes of polyaminotricarboxylate ligands. Data are shown for Ln(MEDTA) {upper curves}, Ln(BEDTA) {middle curves}, and Ln(HEDTA) {lower curves}.

These conclusions are in full accord with the known stability constants of the lanthanide polyaminotricarboxylate complexes. The log K values reported for Eu(MEDTA) and Tb(MEDTA) are 12.96 and 13.35, respectively,[10] while log K values for Eu(BEDTA) and Tb(BEDTA) have been reported to be 12.35 and 12.79, respectively.[11] Martell and Smith list values of 15.45 for Eu(HEDTA) and 15.42 for Tb(HEDTA).[12]

Within the stable pH region (pH 4 to 8), the average hydration state of the lanthanide ion was estimated from the lifetime data, and these values are listed in

TABLE I
Average number of coordinated water molecules for the Tb(III) and Eu(III) aminopolycarboxylate complexes.

Ligand	Hydration number
MEDTA	3.6
BEDTA	3.8
HEDTA	3.1
EDTA	2.6
PDTA	2.6
CDTA	2.3
TMDTA	2.4
EDAP	2.5
EGTA	1.0
DTPA	1.1

Table I. For the Ln(MEDTA) complexes an average of 3.6 water molecules was found, while an average hydration state of 3.8 coordinated water molecules was obtained for the Ln(BEDTA) complexes. On the other hand, an average hydration state of 3.1 was measured for the Ln(HEDTA) compleces, implying that the hydroxyethyl group of the HEDTA ligand participates in metal ion binding.

Above pH 8.5, the number of coordinated waters was found to decrease without reaching a second plateau. Within this third pH region, the hydration state of a given Tb(III) complex was invariably found to be less than the corresponding Eu(III) complex. It has been shown that the Ln(HEDTA) complexes exist as oligomers within this pH region,[12] implying that formation of these polynuclear species is the origin of the change in hydration state. No such data have been obtained for the Ln(MEDTA) or Ln(BEDTA) complexes, but it is reasonable to assume a similar coordination chemistry. The data of Figure 1 imply that the formation of the oligomeric species is less favourable for the Eu(III) complexes than for the corresponding Tb(III) complexes.

Lanthanide Complexes of Simple Polyaminotetracarboxylates

The pH dependence associated with the metal ion hydration state of the Tb(III) and Eu(III) complexes of EDTA, PDTA, and CDTA is shown in Figure 2. Again, the extremely close identity of Eu(III) and Tb(III) curves for each ligand system is further evidence that the hydration states of the central lanthanide ion are equivalent in the analogous complexes. The initial pH region of the hydration curves was found to be smaller than that observed for the polyaminotricarboxylate complexes (complete by pH 2.5), which is consistent with the stronger association constants of the polyaminotetracarboxylate complexes.[11]

The pH region of constant hydration exists over a greater range (pH 3 to 9). The average hydration numbers are found in Table I, from which it may be seen that the extra ligating group of the polyaminotetracarboxylate complexes results in the binding of less coordinated water than was observed for the polyaminotricarboxylate

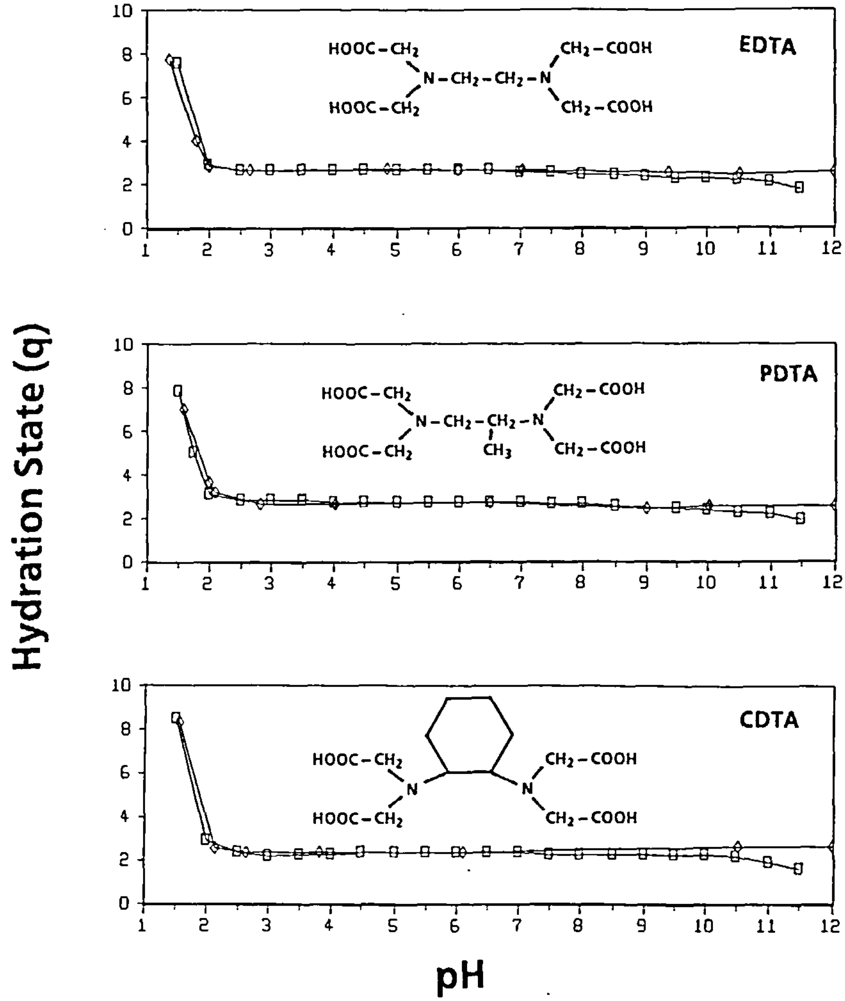

FIGURE 2 pH dependence of the lanthanide ion hydration state in the Tb(III) {points marked by open squares} and Eu(III) {points marked by open diamonds} complexes of simple polyaminotetracarboxylate ligands. Data are shown for Ln(EDTA) {upper curves}, Ln(PDTA) {middle curves}, and Ln(CDTA) {lower curves}.

complexes. The data also indicate that the additional steric bulk of the CDTA ligand (relative to either EDTA or PDTA) results in a slightly reduced hydration state, since only 2.3 coordinated waters are bound.

There is a final pH region (pH 10 to 11.5) in which the number of coordinated water molecules decreases further, although the decrease is smaller than that for the polyaminotricarboxylate complexes in this pH region. Formation of polynuclear species has also been detected at high pH values for these complexes,[12] although all data indicate that the extent of oligomer formation is less significant for the polyaminotricarboxylate complexes than for the polyaminotricarboxylate complexes.

Lanthanide Complexes of Polyaminotetracarboxylates with Additional Steric Bulk

The effect of additional steric bulk in the polyaminotetracarboxylate ligand system was investigated through characterization of the TMDTA and EDAP complexes. TMDTA contains an extra methylene group in the ligand backbone, which could occupy more of the metal ion coordination sphere. In EDAP, two of the acetate groups have been replaced by propionate groups, also possibly increasing the steric requirement of the ligand. The pH dependence of the coordinated water molecules is shown in Figure 3, and the average hydration numbers are given in Table I.

It is evident from Figure 3 that the complexation of lanthanide ions by either TMDTA or EDAP is less stable than by the simple polyaminotetracarboxylate ligand systems discussed in the previous sections. In the TMDTA solutions, the lanthanide aquo ion is present up to pH 3.5, after which complexation causes displacement of hydrate waters. The stable Ln(TMDTA) complexes are fully formed by pH 4.5, with an average value of 2.4 coordinated water molecules. This value is essentially identical

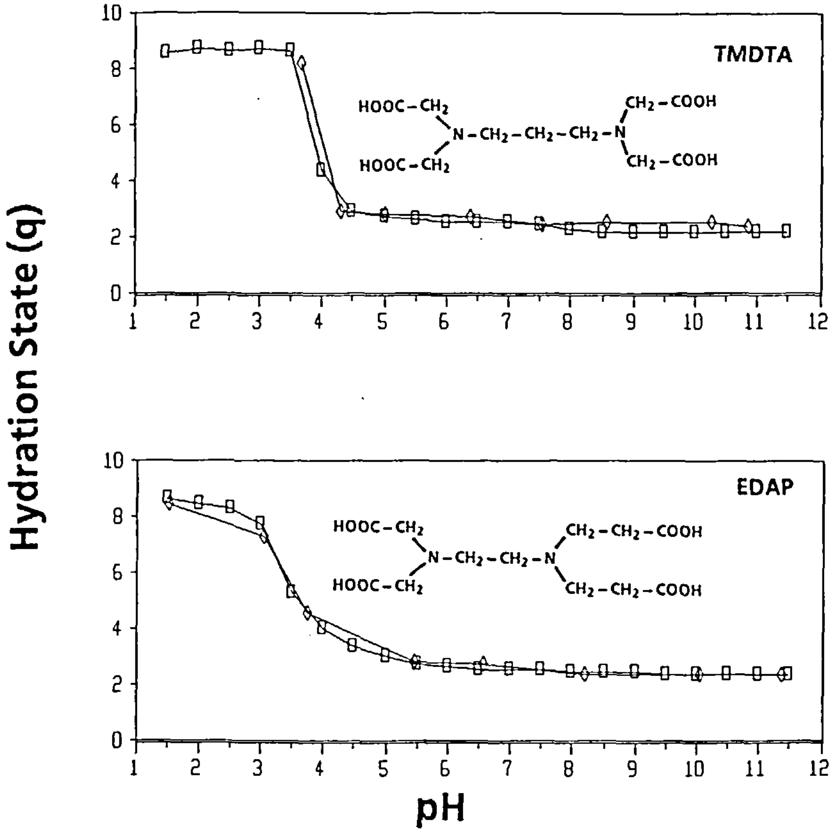

FIGURE 3 pH dependence of the lanthanide ion hydration state in the Tb(III) {points marked by open squares} and Eu(III) {points marked by open diamonds} complexes of polyaminotetracarboxylate ligands containing additional steric bulk. Data are shown for LN(TMDTA) {upper curves}, and Ln(EDAP) {lower curves}.

with the values noted for Ln(EDTA), Ln(PDTA), and Ln(CDTA), indicating that the extra methylene in the ligand backbone does not displace additional waters from the coordination sphere. However, the extra group appears to be effective in preventing the formation of oligomers at higher pH, since no additional decrease in hydration was noted up to pH 11.5.

For the Ln(EDAP) complexes, the lanthanide aquo ion is slightly perturbed by pH 3 and the complexation is not complete until pH 5.5. The gradual formation of the complex species suggests the existence of protonated species between pH 3.5 and 5.5. The Ln(EDAP) complex has an average of 2.5 coordinated water molecules. Since this value is the same as those for the simple polyaminotetracarboxylate ligand systems, it is concluded that the acetate and propionate groups have the same effect on the Ln(III) coordination sphere. However, the additional steric bulk of EDAP is also efficient in preventing the formation of oligomers at higher pH.

Lanthanide Complexes of Polyaminopolycarboxylates with Additional Functional Groups

Further insight into the relation between ligand steric requirement and the hydration state was obtained through the study of EGTA and DTPA complexes. EGTA comtains a significantly longer ligand backbone than the previously discussed ligands, imbedded in which are two ether oxygens capable of additional metal ion binding. DTPA also contains a large ligand backbone, as well as a fifth acetate group. The binding constants of Ln(DTPA) complexes are higher than those of any other polyaminopolycarboxylate ligand. The pH dependence of the Ln(EGTA) and Ln(DTPA) hydration states is shown in Figure 4, while the average number of coordinated water molecules is found in Table I.

EGTA begins to perturb the hydration state of the Ln(III) aquo ion by pH 1.5, and the complex is fully formed by pH 3 when only one water of hydration is bound in the inner coordination sphere. No further change in hydration state was noted up to pH 11.5, indicating that polynuclear species cannot be formed by the Ln(EGTA) complexes. These conclusions are in agreement with the energy transfer studies,[13] and can be attributed to the large backbone of the EGTA ligand, which is more effective at encapsulating the Ln(III) ion and preventing association with another Ln(EGTA) species.

The pH dependence of the Ln(DTPA) hydration state is very similar to that just described for the Ln(EGTA) complexes. DTPA binding to Ln(III) is essentially complete by pH 2, with the inclusion of a single water of hydration in the inner coordination sphere. No change in this hydration state is noted up to pH 11, indicating that no formation of polynuclear species takes place at elevated pH values which agrees with conclusions from energies transfer studies.[13]

Correlations of Hydration with Other Properties

In a recent paper, Chang *et al.*[14] found a linear correlation between the spin-lattice relaxivity of Gd(III) in 1:1 complexes with HEDTA, EDTA, DTPA, EGTA, and TTHA and the hydration of the complex (as measured by Tb(III) luminescence). Recently, Burcher and Kiraly[15] reported values of T_2 (the longitudinal relaxation time) for a series of Gd(III) complexes with aminopolycarboxylate ligands. As shown in Figure 5, a linear relation also exists between the $1/T_2$ values (after subtraction

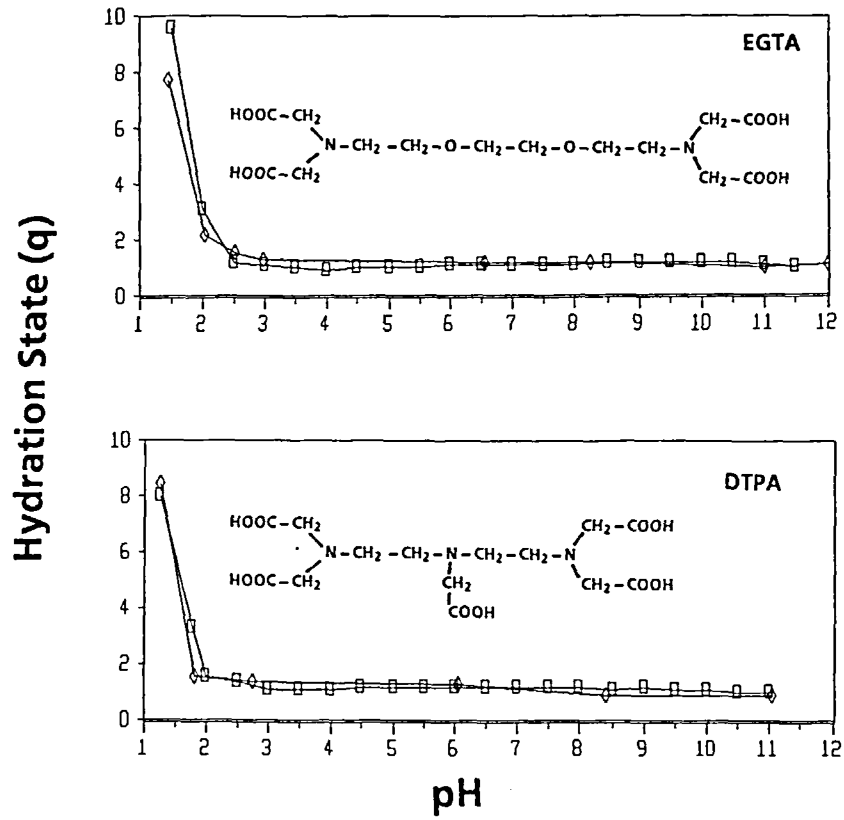

FIGURE 4 pH dependence of the lanthanide ion hydration state in the Tb(III) {points marked by open squares} and Eu(III) {points marked by open diamonds} complexes of polyaminotetracarboxylate ligands containing additional functional groups. Data are shown for Ln(EGTA) {upper curves}, and Ln(DTPA) {lower curves}.

of the diamagnetic effect) of reference 15 and the hydration of the complexes (assuming that the hydration state of a Gd(III) complex is the same as for the analogous Eu(III) and Tb(III) complexes. The slope has a value of 7.5 $\sec^{-1}$ per inner sphere water of hydration, and an intercept of 9 $\sec^{-1}$ due to the total outer sphere hydration.

Choppin has proposed that in the reactions of lanthanides with aminopolycarboxylate ligands, the entropy change is dominated by the dehydration of the cation.[16] This model has been very useful in interpreting thermodynamic parameters of complexation. In Figure 6, the entropy change in 1:1 complexation is plotted as a function of the number of water molecules displaced from the primary coordination sphere of the lanthanide ion by the ligand. A similar correlation was found[16] between the entropy of complexation and the number of carboxylate groups. This was interpreted as showing that the cation dehydration is due to the Ln(III) carboxylate interactions, with little or no Ln-N effects. However, the Ln-N bonding does play a significant role in the stability of these complexes through contribution to the enthalpy change.

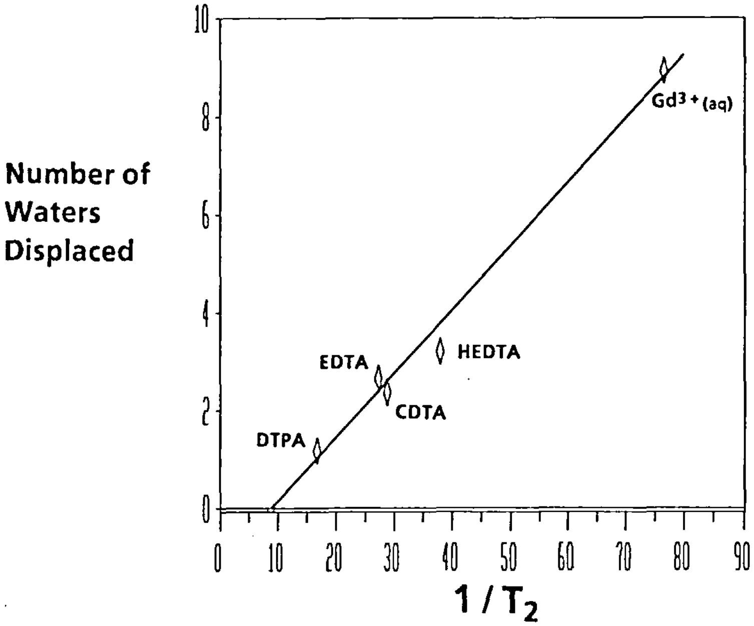

FIGURE 5 Correlation of the number of water molecules in the primary hydration sphere of Gd(III) complexes and the reciprocal of the longitudinal (spin-spin) relaxation time. The identity of the polyaminocarboxylate ligands is shown with the data points.

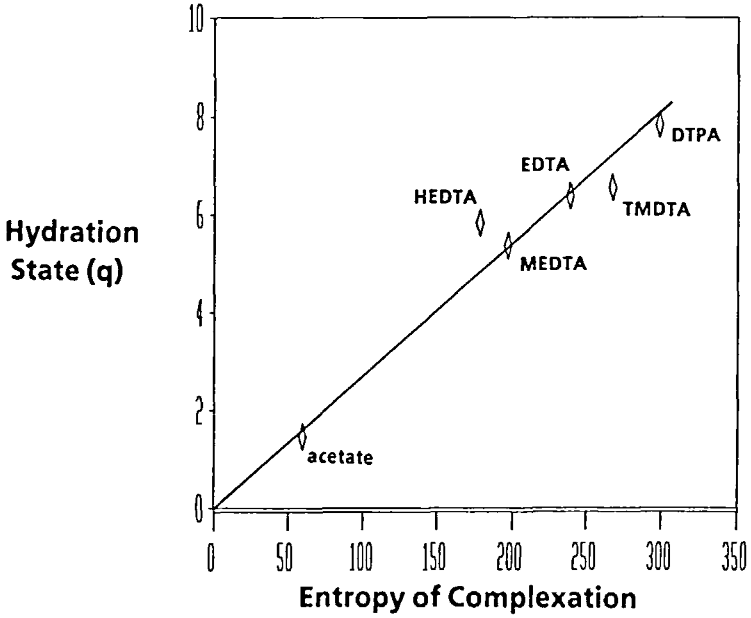

FIGURE 6 Correlation of the entropy change, ΔS_{101}, for formation of the Eu(III) polyaminocarboxylate complexes and the number of water molecules displaced by the ligand from the hydration sphere of the Eu(III) ion.

CONCLUSIONS

The pH dependence of lanthanide ion hydration has proven to be an effective probe of the solution phase coordination chemistry of polyaminopolycarboxylate complexes. In most cases, the number of coordinated water molecules was found to be non-integral in value, which implies that the solution phase species exist in a dynamic equilibrium among various hydration states, and that the spectroscopic method determines the average number of coordinated solvent molecules.

The hydration values provided the basis for evaluation of various bonding and structural effects of the aminopolycarboxylate ligands. They were shown, also, to correlate with $1/T_2$ from NMR data and ΔS_{101} data from complexation studies. These correlations provide support for models proposed previously regarding the nature of these complexes.

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