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Europium(III) Complexation Reactions in Water*

HERBERT B. SILBER

Chemistry Department, San Jose State University, San Jose, Calif. 95192, U.S.A.

Abstract

Ultrasonic absorption measurements on 0.200 M $Eu(ClO_4)_3$ in water demonstrated the absence of measurable inner sphere complexes. The addition of 3.382 M NaCl did not produce a significant change in the sound absorption. When 3.366 M $NaNO_3$ was added to the 0.200 M $Eu(ClO_4)_3$ solution, the sound absorption increased and varied with frequency, with two relaxations present within the experimental frequency range. Hence, inner sphere complexes are present between Eu(III) and NO_3^- in water. Assuming that only the one-to-one complex is present results in a calculated complexation rate constant of 5.4×10^8 s^{-1}, a value too large for the formation of the $EuNO_3^{2+}$ complex. Hence, the rate constant also includes contributions from $Eu(NO_3)_2^+$, which forms at a faster rate than the mono complex.

Introduction

For several decades lanthanide chemists have tried to describe the physical states of the lanthanides in solution. Thermodynamic measurements by Spedding and his associates more than twenty years ago were interpreted in terms of two series of lanthanide ions in water, each differing in coordination number, with a region in the middle of the series where both forms of lanthanide ions were in equilibrium [1–4]. Solution X-ray measurements have been carried out within the rare earth series for chloride salts by two groups. Spedding's group obtained nine-coordinate complexes for the light rare earths, eight-coordinate complexes for the heavy rare earths, and an intermediate region near the middle of the series [5]. Wertz's group obtained eight-coordinate rare earths throughout the series [6]. Even if the two groups agreed, the results at high concentration need not be the same as those obtained at lower concentrations. Hence, other techniques are necessary to describe the structures and bonding within the rare earth series. In addition to uncertainties in determining the coordination numbers within the lanthanide series, differences also exist about whether a particular lanthanide–ligand system exists as an outer sphere, solvent-separated complex or as an inner sphere, contact ion pair. Different techniques have been applied by different groups to deal with the questions.

^{139}La is NMR active and Reuben interpreted his data in terms of inner sphere nitrate and outer sphere chloride and perchlorate [7]. McCain has also used NMR on ^{139}La and found no inner sphere chlorides in water, but detected inner sphere chloride in aqueous methanol below a water mole fraction of 0.69 [8]. Other lanthanide NMR studies abound, but these are usually in mixed solvents and will not be described here.

Ultrasonic absorption measurements have been carried out on lanthanide nitrates [9–12], chlorides [13], sulfates [10, 14–16], perchlorates [17–18] and acetates [19] in water and aqueous organic solvents. In water, significant quantities of lanthanide inner sphere complexes are obtained with low concentrations of sulfate, mixtures of inner and outer sphere complexes for the nitrates and acetates, and both the chlorides and perchlorates form no inner sphere complexes in water for the lanthanides investigated. The addition of an organic solvent, like methanol, increases the concentrations of inner sphere complexes and even chlorides and perchlorates form complexes with Er(III), Nd(III) and Gd(III). Significant differences in the nature of the complexes was found as a function of which lanthanide was under investigation. For, example Nd(III) exhibited a significantly greater amount of outer sphere complexes in water than did the heavier lanthanides [12, 20]. Further information about differences for the nitrates within the rare earth series comes from Choppin's data summary on the nitrates, in which he concluded that the percentage of inner sphere complexes increases from the lighter to the heavier lanthanides [21].

Information about the nature of lanthanide complexes can also come from spectroscopic measurements. Some differences occur in the amount of inner sphere complexation detected by spectroscopic measurements if absorbance or lifetimes are used to detect complexation [22, 23], and some of the differences can exist because the techniques measure different interaction strengths. Visible spectroscopic

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measurements on Er(III) and Eu(III) in water and aqueous methanol have indicated that some differences occur within the rare earth series with nitrate [24, 25]. In water, Er(III) forms only a mono complex with nitrate [24], whereas Eu(III) forms both the mono and bis complexes [25, 26]. Horrocks has applied lifetime measurements to Eu(III) perchlorates in water and he measured no inner sphere complexation [22]. He measured inner sphere chloride complexes with Eu(III) in water and obtained a complexation constant of 0.13 ± 0.01 for inner sphere complexes [22].

Although Garnsey and Ebdon have carried out a preliminary ultrasonic absorption study of the complexation between Eu(III) and nitrate [9], little ultrasonic absorption data exist in the literature for Eu(III), a lanthanide ion which is increasingly utilized as a probe of calcium structures in biological systems because of its spectroscopic properties. Therefore, we have initiated this ultrasonic investigation of the complexation reactions between Eu(III) and perchlorate, nitrate and chloride in water. We also attempted to measure the kinetics of complexation.

Experimental

The ultrasonic equipment (Matec), the quartz piezoelectric crystals (Valpy Corp.) and the techniques have been described earlier [27]. The interferometer cell used in the experiments was thermostated at 25.0 °C with a Forma bath. The sound absorption, α, at each frequency, f, is reported as α/f^2. An examination of the sound absorption data as a function of frequency was used to calculate the relaxation amplitudes and frequencies for a system undergoing chemical relaxation in the frequency range of interest. In the absence of a chemical relaxation, the sound absorption gives a constant value which is approximately the same as that of the solvent background, B. In water B equals 21.7×10^{-17} nepers cm^{-1} s^2.

The test solutions were prepared from 99.99% Eu_2O_3 obtained from Molycorp. A stock solution was made by dissolving a weighed quantity of the oxide in a slight excess of perchloric acid and then diluting to volume to obtain a 2.00 M $Eu(ClO_4)_3$ stock solution. A 4.00 M $NaClO_4$ stock solution was made from a weighed quantity of $NaHCO_3$ which was neutralized with $HClO_4$ until no further CO_2 was released from the hot solution upon further addition of the acid. Weighed amounts of dried NaCl or $NaNO_3$ were added as needed to portions of the stock solutions to obtain the desired concentrations.

Results

A solution 0.200 M in $Eu(ClO_4)_3$ was investigated between 10 and 210 MHz. The results are shown in Fig. 1. The sound absorption was measured to be $(24.35 \pm 1.13) \times 10^{-17}$ nepers cm^{-1} s^2 and the absorption results showed no variation with frequency. Several interpretations of these results are possible. First, the absence of a variation in α/f^2 with frequency can be explained by assuming the absence of a measurable concentration of inner sphere complexes. Second, inner sphere complexes could exist, but both the enthalpy of reaction and the solution volume change are zero. A third possible reason is that the rate of inner sphere complexation is very slow and the resulting relaxation frequency occurs below 1 MHz, and hence no sound absorption would be evident above 10 MHz. Our equilibrium measurements on Eu(III) with perchlorate in water and in aqueous methanol up to 99 mole percent methanol indicate the absence of measurable complexes between Eu(III) and perchlorate [25, 26]. Ultrasonic relaxation studies on Er(III), Nd(III) and Gd(III) perchlorates indicate the absence of any inner sphere complexation in water, but as methanol is added sound absorption typical of rare earth inner sphere complexation occurs [17, 18]. When the complexation occurs, the relaxation frequency is within the range of our experimental measurements. Hence, the absence of a relaxation in water when Eu(III) is in the presence of a total perchlorate concentration equal to 0.600 M is interpreted in terms of the absence of any measurable inner sphere complexation.

Similar measurements were carried out on 0.200 M $Eu(ClO_4)_3$ in the presence of 3.382 M NaCl. Above 20 MHz, the sound absorption was frequency independent and had a value of $(22.03 \pm 0.95) \times 10^{-17}$ nepers cm^{-1} s^2, which is experimentally the same for water alone, as shown in Fig. 1. At both 12 and 10 MHz there was a small increase in α/f^2 to 25.11 and 26.69×10^{-17} nepers cm^{-1} s^2. Two possible explanations for this are: first, a small concentration

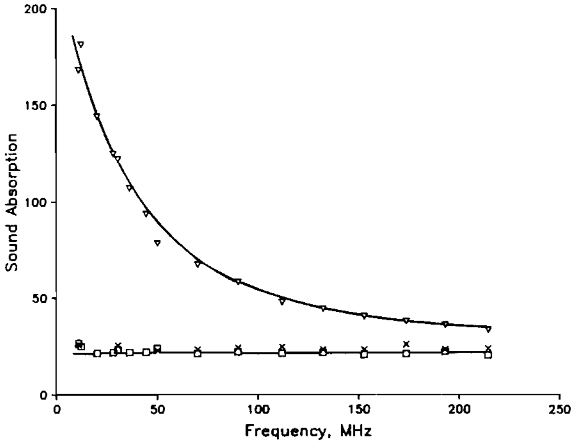

Fig. 1. The ultrasonic absorption for Eu(III) in water at 25 °C: (×), 0.200 M $Eu(ClO_4)_3$; (□), 0.200 M $Eu(ClO_4)_3$ + 3.382 M NaCl; (▽), 0.200 M $Eu(ClO_4)_3$ + 3.366 M $NaNO_3$.

of inner sphere chloride complex exists and second, no complexes are present and the increase in α/f^2 results from the scattering of the sound waves due to the low sound absorption in these solutions. In water, measurements below 20 MHz also have a great deal of scatter. Furthermore, an examination of the 10 MHz data point for the perchlorate solutions shows that the result, 25.94×10^{-17} nepers cm^{-1} s^2, is within experimental error of that for the chloride. Thus, this experiment cannot distinguish between the two possibilities. We will return to this experiment after the results in Eu(III) nitrate solutions are described.

The results for 0.200 M $Eu(ClO_4)_3$ in the presence of 3.366 M $NaNO_3$ are considerably different, as is also shown in Fig. 1. Even at high frequencies, the sound absorption is higher than that for either the chloride or perchlorate solutions. There is an increasing absorption of sound as the frequency decreases. This behavior is typical of the results in lanthanide systems where either inner sphere or mixtures of both outer and inner sphere complexes are detected. The data can be fitted to a single relaxation calculation, obtaining a relaxation frequency of 34.3 MHz, lower than the frequency of 60 ± 2 MHz obtained by Garnsey and Ebdon for 0.200 M $Eu(NO_3)_3$ solution [9]. However, the calculated value of the background, B, is 33.55×10^{-17} nepers cm^{-1} s^2, considerably greater than that for water alone. Hence, the data should be calculated also in terms of two relaxations being present. If this is done, we obtain relaxation frequencies of 30.10 and 159.0 MHz. Since we know that both $EuNO_3^+$ and $Eu(NO_3)_2^+$ coexist in this concentration range, identification of the two relaxations is complicated. For example, in the case of $Er(NO_3)_3$ in water where only one complex is stable, the high frequency relaxation is identified with outer sphere nitrate complexes and the low frequency result with inner sphere complexes [20]. However, in the temperature jump study between Dy(III) and acetate, the presence of bis complexes results in a higher relaxation time than would otherwise be obtained [28], and it is possible that the higher frequency represents the formation of the $Eu(NO_3)_2^+$ complex and that any outer sphere complexes that might be present would occur at frequencies higher than 210 MHz. In order to get further insight into these possibilities, we attempted to measure the complexation kinetics when essentially only the mono complex was present.

The measured successive complexation constants, K_i, for the formation of the $EuNO_3^+$ and $Eu(NO_3)_2^+$ ions at 25 °C and an ionic strength of 3.00 are 5.72 and 1.78 respectively [25]. In order to minimize the amount of $Eu(NO_3)_2^+$ formed, the ratio of [Eu(III)] to $[NO_3^-]$ should be large. However, if insufficient nitrate is present, the sound absorption due to the formation of low concentrations of complex at $I = 3.00$ would be too low to measure. Hence, a compromise in the concentrations of species was utilized. Two solutions were initially made up. The first consisted of [Eu(III)] = 0.20 M and $[NO_3^-] = 0.025$ M, giving $[EuNO_3^{2+}]$ and $[Eu(NO_3)_2^+]$ equal to 0.0128 and 2.61×10^{-4} M, respectively, for a $[EuNO_3^{2+}]/[Eu(NO_3)_2^+]$ ratio of 49:1. The second solution contained [Eu(III)] = 0.50 M and $[NO_3^-] = 0.025$ M, giving $[EuNO_3^{2+}]$ and $[Eu(NO_3)_2^+]$ equal to 0.0182 and 2.05×10^{-4} M, respectively, for a $[EuNO_3^{2+}]/[Eu(NO_3)_2^+]$ ratio of 89:1. The ultrasonic absorption was low for both solutions and the data are shown in Fig. 2. In both cases the sound absorption at most gave a maximum absorption of less than 50×10^{-17} nepers cm^{-1} s^2, an amplitude that is difficult to measure. The sound absorption results as a function of frequency were placed into the single relaxation program. The 0.20 M and 0.50 M Eu(III) solutions gave calculated solvent background values of 24.5 ± 0.9 and $28.9 \pm 0.5 \times 10^{-17}$ nepers cm^{-1} s^2, respectively. These values for B are higher than pure water and also increase with concentration, a result which suggests that a second relaxation is present at high frequencies. However, given the small differences between the calculated results for B and the water value, it would not be possible to get a reliable estimate of the high frequency relaxation. An examination of the calculated relaxation frequencies is in order. For the 0.200 M Eu(III) solution, the relaxation frequency, f_R, is 24.47 ± 5.49 MHz and the f_R value for 0.500 M Eu(III) solution was 23.60 ± 3.34 MHz. The difference between these two relaxation frequencies is much less than the experimental error caused by the low magnitude of the sound absorption, thereby suggesting that additional measurements would not yield a realistic kinetic evaluation of the results. However, an examination of the magnitudes of the relaxation frequencies is very interesting, when compared to the earlier study [9].

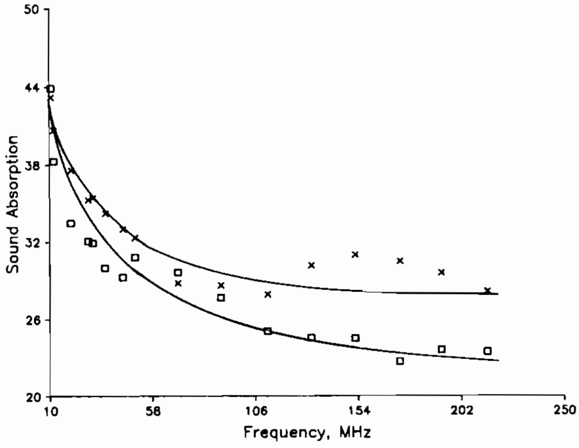

Fig. 2. The ultrasonic absorption for Eu(III) with $EuNO_3^{2+}$ as the predominant complex: (□), 0.200 M $Eu(ClO_4)_3$ + 0.025 M $NaNO_3$; (×), 0.500 M $Eu(ClO_4)_3$ + 0.025 M $NaNO_3$.

As mentioned earlier, the presence of higher complexes results in a faster relaxation time for the chemical system involving lanthanide–ligand complexation compared to the same system where only the mono complex forms [28]. We prepared solutions of $Eu(ClO_4)_3$ with excess nitate at an ionic strength of 3.0 ($NaClO_4$) from 0.1 to 0.6 M Eu(III). The double relaxation results are summarized in Table I. The experimental errors in the frequencies are high because the two relaxations are too close in frequency, except for the highest concentration solutions. This is the reason why the earlier study obtained a higher f_R value of about 60 MHz, which is the average of the high and low frequency results. We were unable to resolve the spectrum for the solution containing 0.1 M Eu(III) and 0.6 M NO_3^-. The fundamental question arises as to what these data mean? Is the system truly a single relaxation system or is it a double relaxation one? Earlier, we had demonstrated that the apparent fit of the data within a lanthanide nitrate system is a function of the frequency range and number of data points taken in the measurements [29], and by extending these, the single relaxation systems were double relaxation systems. Even though the data are calculated in terms of two relaxations, the identification of the processes for each relaxation is not easy. The high frequency relaxation can be identified either with the formation of outer sphere complexes, or it could represent the formation of the bis complex, which is more rapid than the formation of the mono complex. In order to determine which process it represents, we assumed that the low frequency relaxation is the formation of the inner sphere mono complex and the high frequency relaxation is the outer sphere complex. If the calculated complex formation rate constant is very much larger than other lanthanide–ligand systems, it would indicate that the low frequency relaxation represents a combined mono- and bis-complexation rate. The high frequency data are too scattered to calculate the kinetics for this relaxation. We will estimate the outer sphere nitrate association constant from the value of 2.9, obtained for Nd(III) [29]. Although this will introduce some error into the calculations, it will show up mostly in the complex dissociation rate constant, and we are only interested in determining if the formation of the bis complex modifies the apparent rate constants obtained, and the error introduced by making this assumption will not be great. If we assume that only the one to one complex forms, the complexation reaction will be:

$$Eu^{3+}(aq) + NO_3^-(aq) \underset{k_{21}}{\overset{k_{12}}{\rightleftharpoons}} Eu^{3+}(H_2O)_xNO_3^- \underset{k_{43}}{\overset{k_{34}}{\rightleftharpoons}} EuNO_3^{2+}(aq) \quad (1)$$

Here, $Eu^{3+}(H_2O)_xNO_3^-$ represents the solvent-separated outer sphere complex and $EuNO_3^{2+}(aq)$ is the contact inner sphere ion pair. The low frequency relaxation corresponding to inner sphere complex formation is given by:

$$\tau^{-1}_{III} = 2f_{III} = k_{34}\phi(C) + k_{43} \quad (2)$$

$$\theta(C) = [Eu(III)] + [NO_3^-] \quad (3)$$

$$\phi(C) = \theta(C)/\{K_{12}^{-1} + \theta(C)\} \quad (4)$$

The data are included in Table I and a graph of f_{III} as a function of $\phi(C)$ is shown in Fig. 3. The slope of the line is k_{34} and a value of 5.4×10^8 s^{-1} was calculated. This result is a factor of five to ten times greater than other lanthanide complex formation rate constants. Therefore, consistent with the Dy(III) acetate results [28], we believe that the calculated k_{34} value represents a combination of rate constants corresponding to inner sphere complexation for both the mono and bis complexes. Although it is possible to rewrite the reaction to include the additional reaction steps leading to the formation of inner sphere $Eu(NO_3)_2^+$, the scatter in the data is too great to determine inner sphere complexation rate constants for the mono and the bis complex.

One additional piece of information can be obtained from this study. The ultrasonic relaxation results for the solutions where only the mono com-

TABLE I. Kinetic Data for the Reaction between Eu(III) and Nitrate in Water at I = 3.00 ($NaClO_4$) and 25 °C

Total [Eu(III)] (M)	0.2500	0.5000	0.1000	0.2000	0.3000	0.4000	0.5000	0.6000
Total [NO_3^-] (M)	0.025	0.025	0.7001	0.6000	0.9000	1.200	1.500	1.200
[Eu^{3+}] (M)	0.2369	0.4816	0.0187	0.0436	0.0458	0.0468	0.0470	0.0879
[$EuNO_3^{2+}$] (M)	0.0128	0.0182	0.0554	0.1106	0.1695	0.2262	0.2815	0.3457
[$Eu(NO_3)_2^+$] (M)	0.0003	0.0002	0.0259	0.0458	0.0847	0.127	0.1715	0.1664
[NO_3^-] (M)	0.0117	0.0064	0.5929	0.3978	0.5611	0.7199	0.8756	0.5216
$\theta(C)$ (M)	0.2486	0.4880	0.6116	0.4414	0.6069	0.7667	0.9226	0.6095
$\phi(C)$	0.4190	0.5860	0.6395	0.5614	0.6377	0.6898	0.7279	0.6387
$10^{17} A_{III}$ (nepers cm^{-1} s^2)	18.39	15.92		65.91	16.13	141.9	223.7	280.6
f_{III} (MHz)	24.47	23.6		41.85	35.4	45.43	47.1	39.74
$10^{17} A_{12}$ (nepers cm^{-1} s^2)				28.79	114.3	67.76	55.91	33.67
f_{12} (MHz)				87.8	58.81	109.3	136.3	206
$10^{17} B$ (nepers cm^{-1} s^2)	24.51	28.9		21.7	21.7	21.7	21.7	21.7

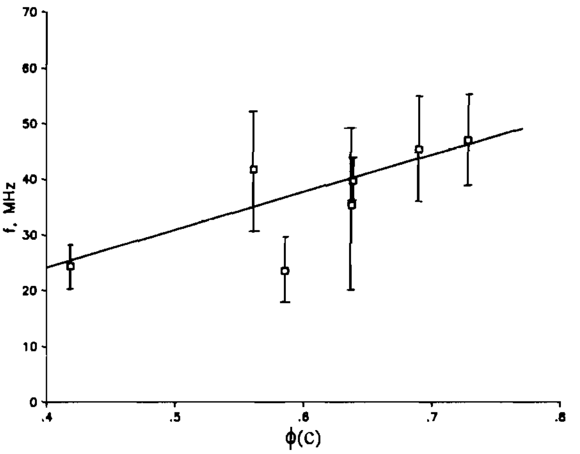

Fig. 3. The evaluation of the complexation rate constant assuming only $EuNO_3^{2+}$ is present.

plexes are present, provides information about the relative concentrations of inner sphere complexes that are necessary in 3:1 electrolyte systems involving the lanthanides in order to observe inner sphere complexation. A small, but observable, ultrasonic absorption was detected for Eu(III)–nitrate systems containing as little as 0.0128 M complex. If K for complexation between Eu(III) and Cl^- is 0.13 [22], then in our solution containing 0.200 M Eu(III) and 3.382 M Cl^-, the concentration of the $EuCl^{2+}$ complex is 0.069, about five times greater than that observed in our least concentrated nitrate solution. If we assume the volume change resulting from the reaction of Eu(III) with either nitrate or chloride is similar, then the amplitude of the sound absorption in the chloride solution should be significantly higher than 50×10^{-17} nepers cm^{-1} s^2, a feature not observed in our experiments. Therefore, three conclusions are possible. First, no inner sphere complexes exist between Eu(III) and Cl^- in water. Second, the measured value of K is significantly too high. Third, the volume change accompanying inner sphere Eu(III)–Cl^- complexes is at least an order of magnitude less than that which occurs between Eu(III) and nitrate. Of the three, we believe that our data most closely agree with the hypothesis that insignificant quantities of inner sphere complex are present in water.

Although the relaxation signals are too close together to accurately resolve the sound absorption spectrum to obtain accurate kinetic information, this study has defined some of the conditions necessary to detect inner sphere complexes in water between Eu(III) and a minus-one ligand. Experience with other lanthanide systems has shown that the addition of methanol lowers the f_{III} relaxation, which should allow a better separation of the relaxation frequencies, thereby improving the accuracy of the relaxation frequencies. Hence, future work should involve a kinetic study between Eu(III) and nitrate in aqueous methanol in order to determine the rate constants for the formation of both the mono and higher complexes. The results obtained in this study of Eu(III) differ from those for Er(III) only to the extent that the complexation kinetics are more complicated in the aqueous Eu(III) system due to the formation of multiple complexes.

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