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Europium Nitrate Complexation in Aqueous Methanol

HERBERT B. SILBER* and MAX S. STROZIER

*Chemistry Department, San Jose State University, San Jose, Calif. 95192, U.S.A.*** and Earth and Physical Sciences, University of Texas at San Antonio, San Antonio, Tex. 78285, U.S.A.*

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Abstract

In aqueous methanol in the presence of nitrate, Eu(III) forms $Eu(NO_3)^{2+}$, $Eu(NO_3)_2^+$ and $Eu(NO_3)_3$ complexes. At 25 °C and a water mole fraction of 0.01, $K_1 = 168.4 \pm 14.8$, $K_2 = 114.6 \pm 5.2$ and $K_3 = 41.1 \pm 3.6$. As the water mole fraction increases, the magnitude of each of the equilibrium constants decreases. In water, the tris complex is not present. No complexes are detected between Eu(III) and ClO_4^- between water mole fractions of 0.01 to 1.00. The behavior of Eu(III) in aqueous methanol appears to be somewhat different than that for Er(III) in aqueous methanol under similar conditions.

Introduction

The association reaction between Eu(III) and NO_3^- in water has been investigated by different workers using diverse techniques. Peppard used solvent extraction to determine $K = 2.0 \pm 0.3$ for $EuNO_3^{2+}$ formation at 22 °C, but the equations used assumed that only the one to one complex is present [1]. At an ionic strength of 1.0 and 25 °C, Choppin obtains $K_1 = 2.04 \pm 0.05$ for the same system [2]. Using visible spectroscopy and a multi-wavelength fitting program, Silber *et al.* found that both mono- and bis-complexes form with $K_1 = 5.72 \pm 1.10$ and $K_2 = 1.78$ [3]. Supporting evidence for the existence of a bis-nitrato complex in water comes from the luminescence excitation work of Horrocks, who measures an inner sphere association constant for the mono-complex of Eu(III) with nitrate equal to 1.41 ± 0.20 and who attributes a shoulder in the spectra to the bis-complex [4]. Since solvent extraction and spectroscopic measurements detect inner sphere and varying contributions of outer sphere complexation, these differences between the techniques are not unexpected. The existence of both outer and inner sphere complexes in lanthanide nitrate systems has been confirmed by ultrasonic experiments [5–7].

Choppin has proposed that for inner sphere complexes in water the enthalpy should be unfavorable and the entropy favorable, whereas the reverse should be true for outer sphere complexes [8]. Based upon this observation, both the mono- and bis-nitrato-europium(III) complexes are predominantly outer sphere in water [3].

Differences exist between Nd(III) and Er(III) compared to Eu(III) complexes in water [3, 9], where the experiments for both Nd(III) and Er(III) indicate that only the mono-complex is detectable at ionic strength of 3.0 ($NaClO_4$) in water. We believe that the chemical differences within the rare earth series may be partially responsible for the disagreements in the literature concerning coordination numbers and inner *versus* outer sphere complexes for different lanthanide ions using different techniques. We have decided to extend our studies of $Eu(NO_3)_3$ complexation to aqueous methanol to determine what differences can occur as the solvent changes from water to methanol. A secondary result of equilibrium studies would be to provide further evidence for or against the geometry changes we have postulated from ultrasonic measurements in aqueous methanol [5–7].

Experimental

The $Eu(ClO_4)_3$ and $Eu(NO_3)_3$ stock solutions were prepared from Eu_2O_3 (99.9%, Molycorp† and Cerac) using a slight excess of the acid to avoid hydrolysis. When aqueous stock solutions were used, the europium solutions were boiled and then the solution

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*Author to whom correspondence should be addressed.

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†A portion of the Eu_2O_3 from Molycorp was donated by Molycorp and the authors express their appreciation for the gift.

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was brought up to volume with distilled and/or deionized water. In order to remove the maximum amount of water for the methanol stocks, the solutions were placed in a Buchi rotorvapor and the solvent was removed at low pressure and 60 ℃ several times. The $NaClO_4$ to regulate the ionic strength was obtained from G. F. Smith and was used to make both aqueous and methanolic stock solutions. $NaNO_3$ and tetraethyl ammonium nitrate were used as the source of the excess nitrate, with the latter being used at low water mole fractions, X_w, because of its higher solubility in the organic solvent. The methanol, obtained from Spectrum was used without further purification. The ionic strength was adjusted to 3.0 using $NaClO_4$ for all solutions. All experimental solutions for the spectroscopic measurements were made by volume using burets to add reagents to 10 ml volumetric flasks.

All of the spectrophotometric measurements were carried out on a Gilford model 2600 microprocessor-controlled UV–Vis instrument interfaced to an Apple III computer. The computer stored both digital and graphical outputs on disks for later analysis. The system was maintained at 15, 20, 25 and 37 ℃ with a Gilford Thermoset coupled to a Forma bath. The Thermoset both maintains and reads the cell temperature to within ±0.1 ℃. As in the aqueous portion of this study, we used the wavelengths around the λ_{max} of 787.0 and 394.4 for a total of eight wavelengths, 790.2, 787.2, 787.0, 786.8, 396.2, 394.6, 394.4, and 394.2 nm*. The absorbance data were analyzed using the Gaizer multi-wavelength program [10–12].

The Gaizer program assumes the existence of one or more complexes of the type M_pL_q, with β defined as:

$$\beta = [M_pL_q]/[M]^p[L]^q \qquad (1)$$

At each wavelength it is assumed that Beer's Law is valid and that deviations from Beer's Law are attributed to the formation of at least one complex. The validity of this assumption is tested in $Eu(ClO_4)_3$ solutions, where Beer's Law is found to be valid. If we then assume that Beer's Law is valid for each free and complexed species, the absorbance, A, is equal to the sums of the absorbances of each species, given by:

$$A = A_M + A_L + \sum_1^{p,q} A_{M_pL_q} \qquad (2)$$

A matched set of quartz cells of one cm pathlength was used in the spectral measurements. The absorbance in the 1 cm cells becomes:

$$A = \epsilon_M[M] + \epsilon_L[L] + \sum_1^{p,q} \epsilon_{M_pL_q}[M_pL_q] \qquad (3)$$

At the wavelengths used in this study, neither the free ClO_4^- nor the free NO_3^- absorb so both species have $\epsilon_L = 0$. To utilize the program, the data that are required include the total metal ion concentration, the total ligand concentration, the number of wavelengths used, the absorbance of each solution at each wavelength and first estimates of each β and ϵ. Using the initial guess of the equilibrium constants, the program refines the best set of extinction coefficients at each wavelength independently and then when the set of 8 wavelengths are completed, the program applies the entire set of data at all of the wavelengths to refine the best equilibrium constants. The best values starting with the inputs are refined and printed along with the square of the residuals, which is a measure of the quality of the fit. The sequence is then repeated assuming a new set of equilibrium constants. This process is repeated until a minimum is found in the square of the residuals. If the wrong number and type of species is placed into the program, no satisfactory fit to the data occurs and new conditions must be assumed. Since Eu(III) is found not to complex with ClO_4^-, the extinction coefficient of free metal can be obtained from Beer's Law plots for $Eu(ClO_4)_3$. Although this allows us to place this value into the Gaizer program for each of the 8 wavelengths, we chose to allow this parameter to be refined and to use the difference between the measured and calculated free metal ion extinction coefficient as an internal check on the quality of the program fit.

Results

$Eu(ClO_4)_3$ obeys Beer's Law at all wavelengths, temperatures and solvent compositions in aqueous methanol. A plot of the absorbance as a function of the concentration ratio of $[ClO_4^-]/[Eu(III)]$ at constant [Eu(III)] is shown in Fig. 1 for the data at 394.4 nm at 25 ℃ and $X_w = 0.01$. The Figure demonstrates that there is no change in absorbance at constant [Eu(III)] with increasing $[ClO_4^-]$. Similar results were obtained at all of the other eight wavelengths used in this study at all water mole fractions and temperatures. This is identical to the aqueous results [3]. This observation can either be interpreted in terms of no complexation or that the peaks are insensitive to the complexation. Because a similar graph of the absorbance as a function of the $[NO_3^-]/[Eu(III)]$ ratio deviates from constant absorption, we believe that the perchlorate data are indicative of the absence of any measurable complexation.

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*The absorbance data and the calculated extinction coefficients are available upon request from the author.

TABLE I. Formation Constants of the Complexes between Eu(III) and Nitrate as a Function of Temperature and Solvent Composition

	Temperature			
	15 °C	20 °C	25 °C	37 °C
X_w = 1.00 [3]				
K_1	7.40 ± 2.51	6.50 ± 2.21	5.72 ± 1.94	4.50 ± 1.09
K_2	2.20 ± 0.60	1.97 ± 0.40	1.78 ± 0.73	1.38 ± 0.57
X_w = 0.87				
K_1	15.4 ± 2.6	14.1 ± 1.5	12.9 ± 1.9	10.7 ± 0.94
K_2	4.06 ± 0.76	3.57 ± 0.80	3.29 ± 0.91	2.65 ± 0.55
K_3	2.01 ± 0.55	1.89 ± 0.58	1.77 ± 0.60	1.65 ± 0.46
X_w = 0.69				
K_1	43.1 ± 2.9	40.4 ± 6.0	37.9 ± 4.1	32.8 ± 3.6
K_2	15.5 ± 2.6	15.0 ± 3.4	14.3 ± 3.7	13.0 ± 2.9
K_3	5.25 ± 1.62	5.09 ± 1.95	4.95 ± 1.68	4.58 ± 1.34
X_w = 0.43				
K_1	83.7 ± 10.8	80.8 ± 12.0	77.8 ± 3.5	72.0 ± 4.8
K_2	48.4 ± 11.9	45.6 ± 9.9	42.9 ± 3.8	37.5 ± 3.9
K_3	14.4 ± 4.9	14.2 ± 3.2	14.0 ± 1.5	13.6 ± 2.0
X_w = 0.20				
K_1	131.4 ± 11.6	127.1 ± 8.5	122.9 ± 5.6	114.9 ± 12.5
K_2	84.2 ± 3.8	81.1 ± 1.9	78.1 ± 6.9	72.0 ± 4.8
K_3	24.6 ± 1.6	24.2 ± 2.1	23.9 ± 1.6	23.3 ± 0.5
X_w = 0.01				
K_1	179.1 ± 19.5	173.7 ± 25.9	168.4 ± 14.8	157.7 ± 10.5
K_2	122.2 ± 8.2	118.4 ± 10.4	114.6 ± 5.2	107.0 ± 4.8
K_3	42.1 ± 3.7	41.6 ± 3.7	41.1 ± 3.6	40.1 ± 0.9

A different result is obtained for the nitrate system. Figure 1 shows the data at 394.4 nm for the nitrate system under the same conditions as in the perchlorate system, with a clear difference occurring. Figure 2 confirms this observation in the mole ratio plot of the absorbance as a function of the $[NO_3^-]/[Eu(III)]$ ratio at 787.0 nm and 790.2 nm. The higher wavelength peak represents the growth of a shoulder due to bis- and tris-complexes, consistent with the observation of Horrocks [4]. As seen in Figs. 1 and 2, the extrapolation of the nitrate data at all wavelength leads to the intersection of two straight lines at a 3:1 ligand to metal ion ratio, consistent with the suggestion that there are three ligands per Eu(III) in this system. The actual intersection was calculated from separate least squares determinations for the linear regions of the data points away from the region of curvature. Under similar conditions in water, the mole ratio plot indicated that up to 1:2 complexes were formed [3]. The existence of the tris-complex was confirmed by mole ratio plots in all of the aqueous methanol solutions at each of the eight wavelengths.

The absorption data were then placed into the multi-wavelength computer program. Although the mole ratio plots indicated that three complexes form in aqueous methanol, we initially checked the data by assuming first only one complex and then both the 1:1 and 1:2 complexes form. In either case, the program did not lead to a converging data fit. However, when 1:1, 1:2 and 1:3 complexes were assumed to be present, the data were fit by the program. The calculated best fits of the equilibrium constant data are shown in Table I and Fig. 3. The results are reported in terms of successive equilibrium constants, K_i. The Gaizer program calculates the results in terms of overall stability constants, β_i. However, $\beta_2 = K_1K_2$ and $\beta_3 = K_1K_2K_3$, thereby allowing a separation of the computer results into successive stability constants. The variations in each of the successive stability constants with solvent composition are shown in Fig. 3. Since each of the individual equilibrium constants was determined as a function of temperature, the complexation enthalpies and entropies were calculated for each complex from the variation of the equilibrium constants with temperature. These results are shown in Table II and Figs. 4 and 5, which show the variations in the thermodynamic properties as a function of solvent composition.

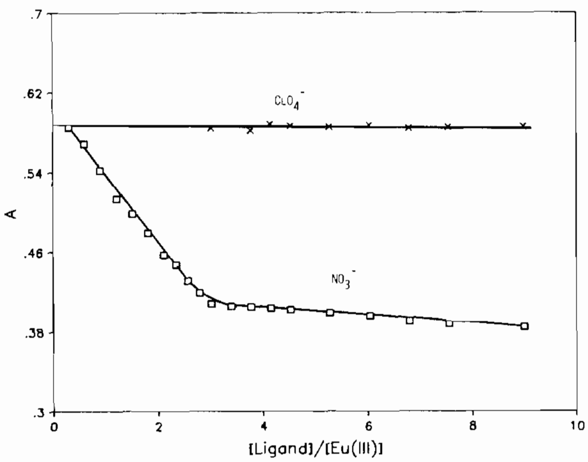

Fig. 1. The absorption data at 394.4 nm for 0.200 M Eu(III) solutions at 25 °C and X_w = 0.01.

TABLE II. The Thermodynamics of Successive Complexation Steps

	$EuNO_3^{2+}$	$Eu(NO_3)_2^+$	$Eu(NO_3)_3$
X_w = 1.00 [3]			
ΔH° (KJ/mol)	−16.7 ± 2.3	−15.8 ± 0.9	
ΔS° (J/mol K)	−41.4 ± 8.8	−48.5 ± 7.1	
X_w = 0.87			
ΔH° (KJ/mol)	−14.1 ± 0.5	−12.1 ± 0.8	−8.6 ± 0.9
ΔS° (J/mol K)	−19.6 ± 2.1	−37.6 ± 5.4	−23.8 ± 2.1
X_w = 0.69			
ΔH° (KJ/mol)	−13.2 ± 0.5	−9.2 ± 0.5	−4.6 ± 0.6
ΔS° (J/mol K)	−0.8 ± 0.4	−11.7 ± 1.3	−2.1 ± 0.8
X_w = 0.43			
ΔH° (KJ/mol)	−8.7 ± 1.5	−5.1 ± 0.2	−2.1 ± 0.4
ΔS° (J/mol K)	19.2 ± 1.3	2.1 ± 0.4	14.6 ± 1.7
X_w = 0.20			
ΔH° (KJ/mol)	−5.3 ± 0.3	−4.5 ± 0.2	−1.9 ± 0.1
ΔS° (J/mol K)	25.1 ± 2.5	18.4 ± 1.3	20.1 ± 0.8
X_w = 0.01			
ΔH° (KJ/mol)	−4.4 ± 0.5	−4.5 ± 0.2	−1.7 ± 0.2
ΔS° (J/mol K)	25.1 ± 2.9	24.7 ± 2.1	25.5 ± 1.3

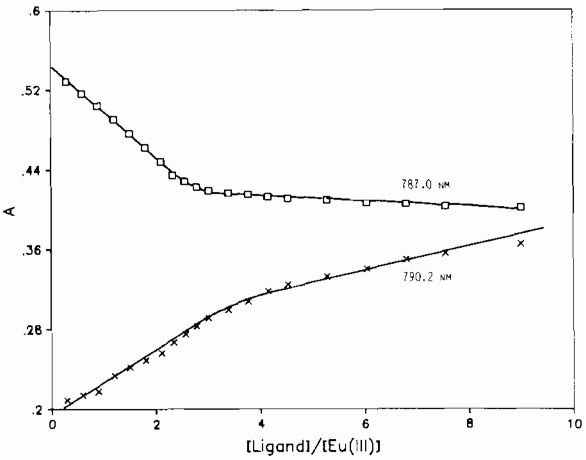

Fig. 2. The absorption data at 787.0 and 790.2 nm for 0.200 M Eu(III) as a function of added nitrate at 25 °C and X_w = 0.01.

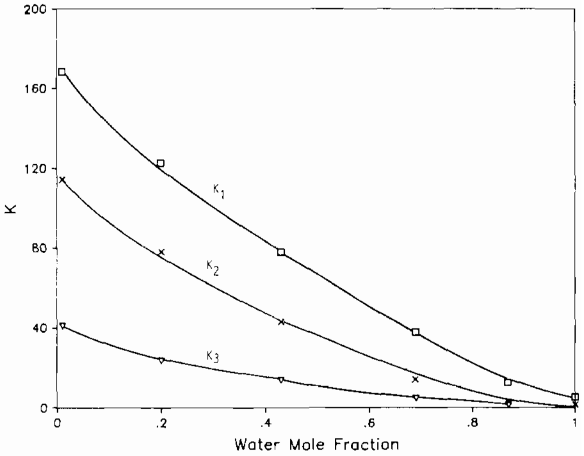

Fig. 3. The variation of successive equilibrium constants with X_w at 25 °C.

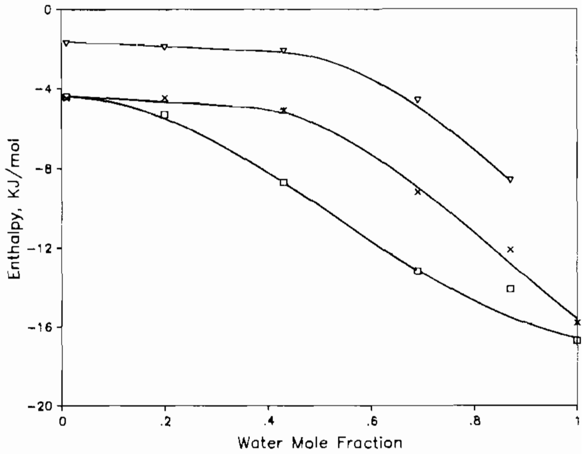

Fig. 4. The enthalpy of successive complexations as a function of solvent. Key: □, $Eu(NO_3)^{2+}$; ×, $Eu(NO_3)_2^+$; ▽, $Eu(NO_3)_3$.

Discussion

Figures 1 and 2 establish the absence of complexation with perchlorate and the presence of complexation with nitrate. The extinction coefficients of the complexes were lower than that of the free Eu(III) at all wavelengths except 790.2, the shoulder that is most sensitive to higher complexes due to an increasing extinction coefficient for the

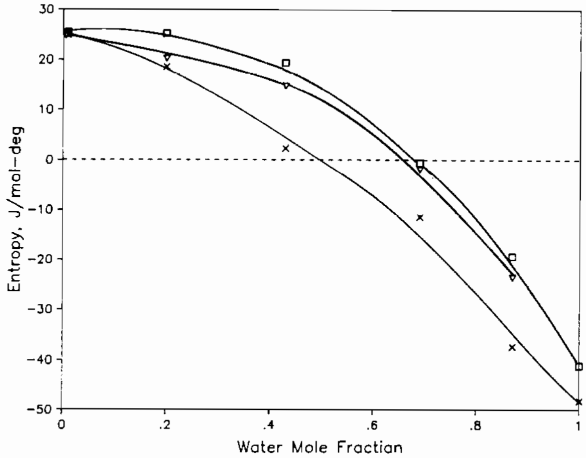

Fig. 5. The entropy of successive complexations as a function of solvent. Key: □, $Eu(NO_3)^{2+}$; ×, $Eu(NO_3)_2^+$; ▽, $Eu(NO_3)_3$.

complexes compared to the free metal. Although some of the wavelengths gave a sharper intersection of the two linear portions of the mole ratio plots, all of the intersections occurred at or near a ligand to metal ratio of 3:1.

As the solvent dielectric constant decreases caused by decreasing the water mole fraction, there is a regular increase in all three association constants (Fig. 3). No discontinuities are observed at any solvent composition, such as have been observed in the ultrasonic absorption data on selected lanthanide nitrate systems [7, 13]. Similar smooth variations are found for the complexation enthalpy (Fig. 4) and entropy (Fig. 5) for each successive complexation step. Unfortunately, no ultrasonic absorption data are available for the behavior of $Eu(NO_3)_3$ in aqueous methanol for comparisons. Although small differences in the complexation enthalpy and entropy are found for each of the three complexes, these differences are relatively small. There is a decreasing enthalpy at each solvent composition in going from mono- to bis- to tris-complexes, but the differences between complexes are not great enough to suggest fundamental structural differences between species, other than reduced charges for the higher complexes. Based upon entropy considerations, the bis-complex is the least favored of the three.

The enthalpies of each of the complexes is negative, but the enthalpy increases as the water composition decreases. In water and in aqueous methanol above $X_w = 0.69$, the entropy is also negative. Thus, these data indicate that $Eu(NO_3)_3$ forms predominantly outer sphere complexes. However, the data indicate that as the solvent composition decreases the dielectric constant, a greater amount of inner sphere complex occurs for each of the three types of complexes. At the lowest water composition, $X_w = 0.01$, the thermodynamic results are mixed and one cannot draw any conclusions concerning relative amounts of inner sphere or outer sphere complexes.

Preliminary data have been obtained on the $Er(NO_3)_3$ system at high water mole fractions [14]. First, in aqueous methanol there appears to be a weak, but measurable, mono-complex between Er(III) and ClO_4^- below $X_w = 0.87$ and no complex was found under the same conditions for Eu(III) in this study. At $X_w = 0.89$, the mono- and bis-nitrate complexes occur for Er(III), whereas the tris-complex is also stable for Eu(III). Hence, we can conclude that significant differences occur within the lanthanide nitrate series in aqueous methanol, as well as for water. This reinforces the caution that must be used before data on any lanthanide(III) salt in solution is applied to a different lanthanide under similar conditions, since the simple chemistry may indeed be different depending upon the choice of lanthanide.

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