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# Measurement and analysis of the temperature and pressure dependence of the ${}^7F_0 \rightarrow {}^5D_0$ excitation spectra of Eu(III) complexes with 4-phenylethynyl-2,6-pyridine-dicarboxylic acid

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## Abstract

The pressure and temperature dependence of the  ${}^5D_0 \rightarrow {}^7F_0$  transition of Eu(III) in complexes with 4-phenylethynyl-2,6-pyridinedicarboxylic acid has been measured at various metal to ligand ratios. The spectra have been fit to a sum of Lorentzian peaks, and the temperature dependence used to determine  $\Delta H$  for the equilibrium reaction for formation of the tris complex from the bis complex. The pressure dependence of the  ${}^5D_0 \rightarrow {}^7F_0$  transitions corresponding to the bis and tris species is analyzed in order to determine the associated difference in volume,  $\Delta V$ , between reactants and products. © 2000 Elsevier Science S.A. All rights reserved.

*Keywords:* Luminescence; Polarization; Complexation; Excitation spectrum; Europium

## 1. Introduction

Studies aimed at the determination of the complex solution equilibria involving lanthanide (III) ions continues to be an area of active interest [1,2]. This is primarily due to the fact that lanthanide (III) ions are often used as models for the speciation of radioactive actinide species found in nuclear waste sites [3], but this kind of information is also necessary to characterize the nature of lanthanide complexes used as luminescence or spin probes in biological samples.

Luminescence, absorption, and excitation measurements involving the non-degenerate  ${}^5D_0 \rightarrow {}^7F_0$  transition of Eu(III) have been shown to be particularly useful as a probe of the solution structure of these species, since it is often the case that a single resolvable peak is observed for each species present [4]. The use of these types of spectroscopic results for *quantitative* information concerning concentrations of species present, equilibrium constants, or related information is, however, quite limited. This is primarily due to the difficulties in relating relative luminescence intensities to concentration. In this laboratory we have used  ${}^5D_0 \rightarrow {}^7F_0$  excitation spectroscopy to determine the concentration of the mono- bis- and tris-complexes of Eu(III) with oxydiacetic acid (ODA) at pH 6 for a range of ligand concentrations through a curve-

fitting analysis [5]. These measurements are only possible if one can determine the factor relating peak area to concentration. This factor is linearly proportional to the individual oscillator strengths and is different for each species present in solution. In the Eu:ODA system this analysis is successful because at very high ligand:metal ratios it is possible to prepare solutions in which essentially all of the Eu(III) ions are bound in a tris-complex. Using simple mass balance relationships and curve deconvolution, the other proportionality factors and the concentrations of the individual complexes could be determined.

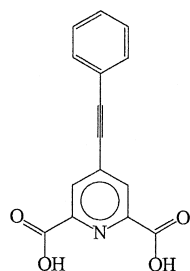
In this preliminary report we show how the use of  ${}^5D_0 \rightarrow {}^7F_0$  excitation spectroscopy may also be used to determine thermodynamic properties of these complex solution equilibria through measurement of the temperature and pressure dependence of the observed spectra. This report is concerned with Eu(III) complexes of 4-phenylethynyl-2,6-pyridinedicarboxylic acid. The advantages and limitations of this technique will be described, and the potential of this type of measurement to provide important information concerning other systems will be discussed.

## 2. Experimental

Stock solutions of Eu(III) were prepared by dissolving

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99.9%  $\text{EuCl}_3$  (Aldrich) into  $\text{H}_2\text{O}$ . The pH of these solutions were adjusted to between 3 and 3.5 with concentrated HCl. 4-phenylethynyl-2,6-pyridinedicarboxylic acid (PEDPA) was synthesized as described previously [6]. A stock solution containing this ligand was also prepared, and the pH adjusted to approximately 10 by addition of concentrated NaOH. Solutions of varying Eu(III): PEDPA ratios were prepared by combining aliquots of the two stock solutions. The pH of the final solutions were approximately 8.



**PEDPA**

Excitation of the  ${}^7\text{F}_0 \rightarrow {}^5\text{D}_0$  transition of Eu(III) (578–582 nm) was accomplished by using a Coherent-599 tunable dye laser (0.03 nm resolution) with a Coherent Innova-70 argon-ion laser as a pump source. The laser dye used in all measurements was Rhodamine 110 dissolved in ethylene glycol. Calibration of the emission monochromator (and subsequently the dye laser wavelength) was accomplished by passing scattered light from a low power He–Ne laser through the detection system. The error in the dye-laser wavelength is assumed to equal the resolution of the emission monochromator (0.1 nm). Before and after each excitation scan, the laser intensity was recorded in order to correct for any incident intensity

fluctuations. The optical detection system consisted of a focusing lens, long pass filter, and 0.22 m monochromator. The emission monochromator was set at 616 nm in order to detect the  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$  emission from Eu(III). The emitted light was detected by a cooled EMI-9558B photomultiplier tube. The temperature of the sample was controlled by placing the cuvet in an anodized aluminum cell jacket which was connected to a Lauda K-4/RD circulating temperature bath, and monitored by placing the temperature probe in the sample compartment before and after the measurement of the excitation. Measurements at greater than atmospheric pressure were accomplished in a custom-made stainless steel NOVA-SWISS high pressure liquid cell with three sapphire windows. The sample capsule consisted of a modified 10 mm cylindrical glass tube fitted with a Teflon piston with two o-rings. The solution sample is placed into the capsule, which is then placed inside the high pressure cell block already filled with water which acts as the hydraulic fluid. The high pressure cell is then pressurized to a fixed static pressure, and monitored using a Enerpac hydraulic hand pump and gauge.

### 3. Results

In Fig. 1 we plot the excitation spectrum for a solution of Eu(III) and  $\text{PEDPA}^{2-}$  with a metal to ligand ratio of 1:3.5. To obtain this spectrum the output of the dye laser was scanned from 551 to 592 nm while the emission at 616 nm from the strong  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$  transition was monitored. As can be seen from this spectrum, excitations arising from the ground ( ${}^7\text{F}_0$ ) and thermally populated excited ( ${}^7\text{F}_1$  and  ${}^7\text{F}_2$ ) states are observed. Additional peaks which may originate from even higher energy terms of the

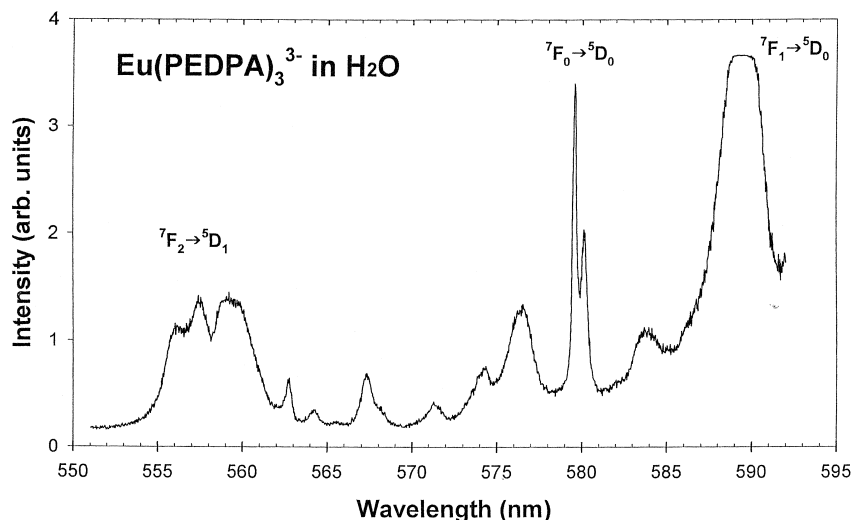


Fig. 1. Excitation spectrum of an aqueous solution of Eu(III) and  $\text{PEDPA}^{2-}$  at a ratio of 1:3.5. The luminescence was monitored at 616 nm.

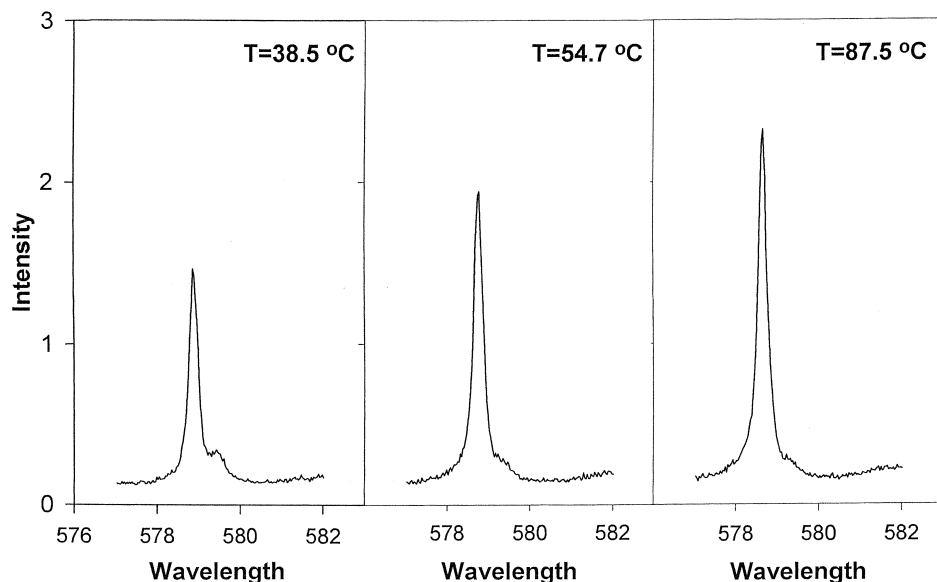


Fig. 2.  ${}^7F_0 \rightarrow {}^5D_0$  excitation spectra for an aqueous solution of Eu(III) and PEDPA $^{2-}$  at a metal to ligand ratio of 1:2.5 at three different temperatures. The luminescence was monitored at 616 nm.

ground state manifold are also evident in the spectral region between 565 and 578 nm. For the purposes of this study the doublet peak centered around 580 nm is of primary interest. The fact that two peaks are observed indicates that at least two different Eu(III) species are contributing to the broad emission at 616 nm. From a series of measurements covering a range of metal to ligand ratios, the two peaks in this spectrum can be associated with the bis [Eu(PEDPA) $_2^{1-}$ ] and tris [Eu(PEDPA) $_3^{3-}$ ] species with the  ${}^7F_0 \rightarrow {}^5D_0$  transition of Eu(III) for the tris complex occurring at higher wavelength.

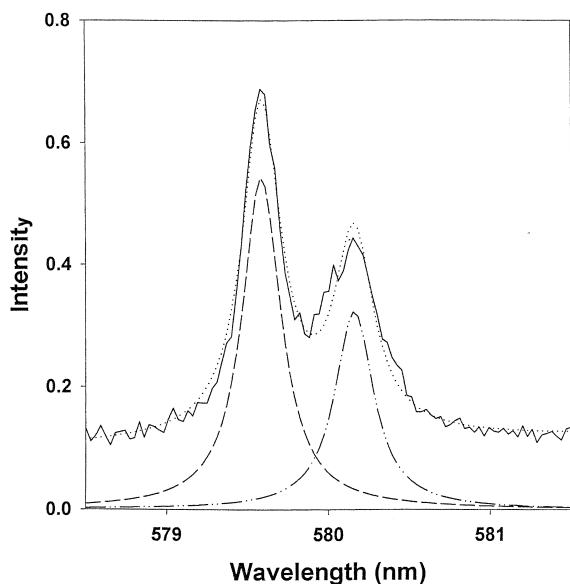


Fig. 3. Sample  ${}^7F_0 \rightarrow {}^5D_0$  excitation curve fitting results. The spectrum was fit to a sum of two Lorentzian peaks with a linear baseline using PeakFit (Jandel Scientific).

In Fig. 2 we show excitation spectra in the region of the  ${}^7F_0 \rightarrow {}^5D_0$  transition for an aqueous solution of Eu(III) and PEDPA $^{2-}$  at a metal to ligand ratio of 1:2.5 as a function of temperature. These results show that for this molar ratio essentially only one species, Eu(PEDPA) $_2^{1-}$ , is present at the highest temperature. These spectra may be fit to one, or the sum of two Lorentzian peaks (as demonstrated in Fig. 3). Using the assumption that at this high temperature all of the Eu(III) is complexed as the bis complex, the proportionality factor,  $k_{\text{bis}}$ , relating the concentration of the bis complex to the Lorentzian area,  $A_{\text{bis}}$ , may be determined.

$$[\text{Eu}(\text{PEDPA})_2^{1-}] = k_{\text{bis}} A_{\text{bis}} \quad (1)$$

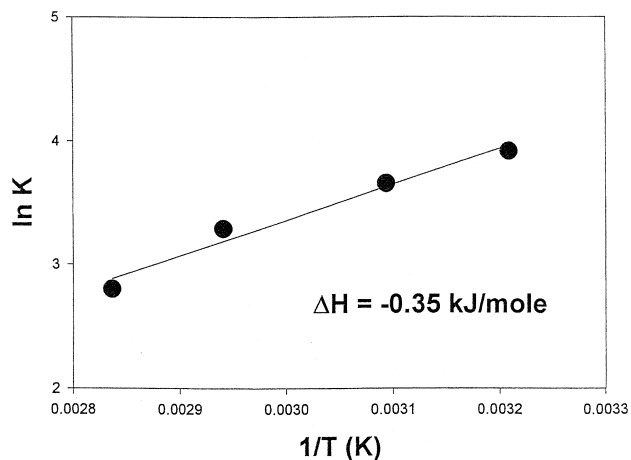


Fig. 4. Plot of the natural log of the equilibrium constant ( $K$ ) versus inverse temperature (see text). The solid line is a linear least squares fit to the data.

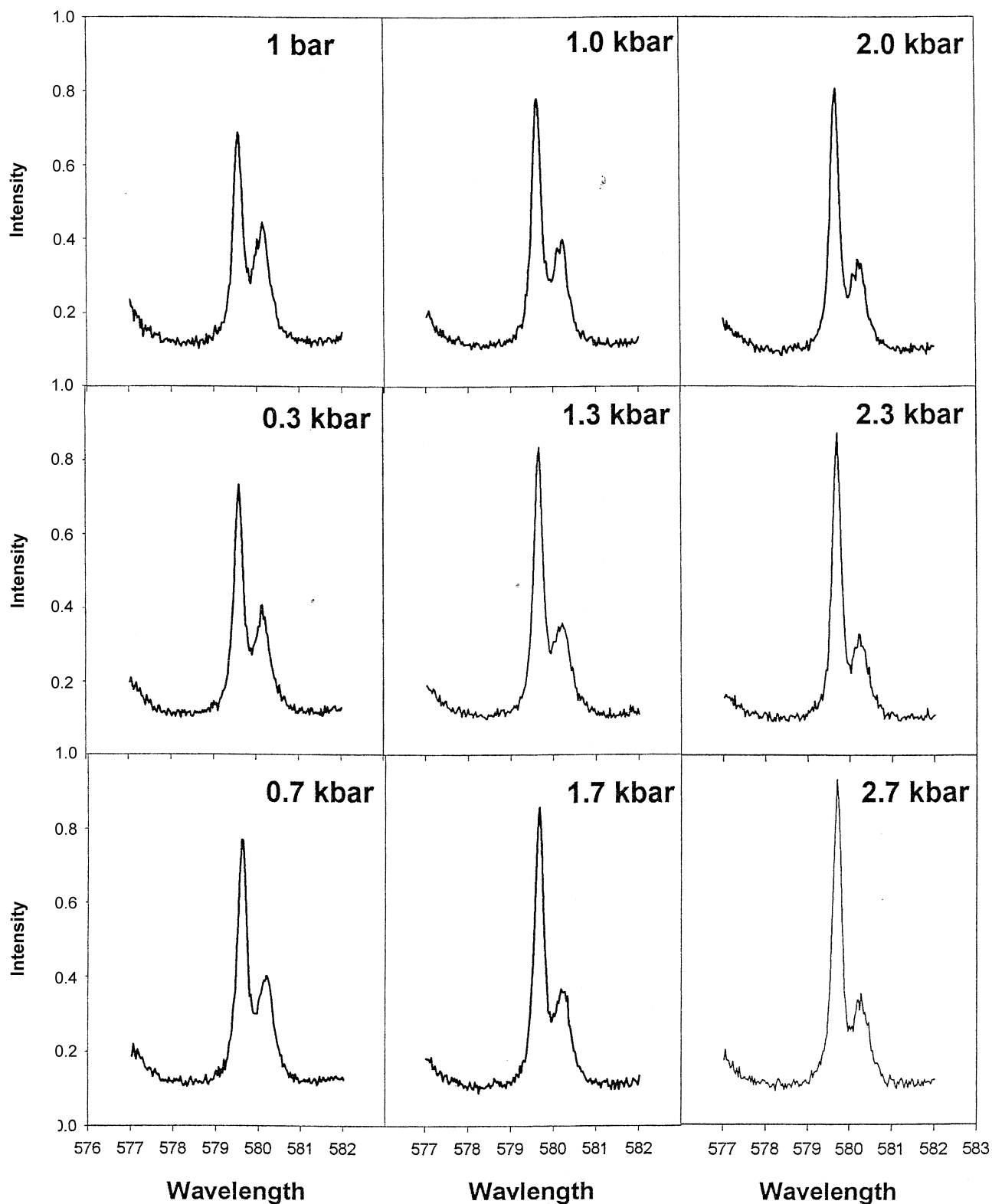


Fig. 5.  ${}^7F_0 \rightarrow {}^5D_0$  excitation spectra for an aqueous solution of Eu(III) and PEDPA $^{2-}$  at a metal to ligand ratio of 1:3.5 at different pressures. The luminescence was monitored at 616 nm.

At the lower temperatures the concentration of the tris complex may be obtained from mass balance on Eu(III)

$$[\text{Eu}(\text{PEDPA})_3^{3-}] = [\text{Eu}(\text{III})]_0 - [\text{Eu}(\text{PEDPA})_2^{1-}] \quad (2)$$

where  $[\text{Eu}(\text{III})]_0$  denotes the total Eu(III) concentration in the solution. Finally, the concentration of uncomplexed ligand may be obtained from the total ligand concentration (denoted  $[\text{PEDPA}]_0$ ) using the following equation

$$[\text{PEDPA}] = [\text{PEDPA}]_0 - 2[\text{Eu}(\text{PEDPA})_2^{1-}] - 3[\text{Eu}(\text{PEDPA})_3^{3-}] \quad (3)$$

These concentrations allow one to determine the equilibrium constant,  $K_{\text{eq}}$ , for formation of the tris complex from the bis complex

$$\text{Eu}(\text{PEDPA})_2^{1-} + \text{PEDPA}^{2-} \rightleftharpoons \text{Eu}(\text{PEDPA})_3^{3-}$$

$$K_{\text{eq}} = \frac{[\text{Eu}(\text{PEDPA})_3^{3-}]}{[\text{Eu}(\text{PEDPA})_2^{1-}][\text{PEDPA}]} \quad (4)$$

Since,

$$\left( \frac{\partial \ln K_{\text{eq}}}{\partial (1/T)} \right)_p = - \frac{\Delta H}{R} \quad (5)$$

a plot of  $\ln K_{\text{eq}}$  versus  $1/T$  yields  $\Delta H$  for this reaction. These results are plotted in Fig. 4. A slightly negative enthalpy ( $\Delta H = -0.35$  kJ/mole) is obtained for this equilibrium reaction.

Additional information concerning this equilibrium may be obtained by varying pressure. In Fig. 5 we plot a series of  ${}^7\text{F}_0 \rightarrow {}^5\text{D}_0$  excitation spectra for an aqueous solution prepared with a metal to ligand ratio of 1:3.5 measured at different liquid pressures. The qualitative effect of increased pressure is clearly seen in these spectra. As pressure is increased from atmospheric pressure, the intensity of the peak corresponding to the bis complex increases, and that of the peak corresponding to the tris complex decreases. As above, the concentration of the two complexes may be related to the areas of the individual Lorentzian peaks,  $A_{\text{bis}}$  and  $A_{\text{tris}}$ . The equilibrium constant may then be expressed as follows

$$K_{\text{eq}} = \frac{k_{\text{tris}} A_{\text{tris}}}{k_{\text{bis}} A_{\text{bis}} [\text{PEDPA}]} \quad (6)$$

It can be shown that the dependence of  $K_{\text{eq}}$  on pressure is given by the following equation

$$\left( \frac{\partial \ln K_{\text{eq}}}{\partial P} \right)_T = - \frac{\Delta V}{RT} \quad (7)$$

where  $\Delta V$  denotes the difference in volume of the products minus the reactants. Substituting Eq. (6) into the expression for the equilibrium constant and separating terms we obtain the following result

$$\ln K_{\text{eq}} = \ln \frac{k_{\text{tris}}}{k_{\text{bis}}} + \ln \frac{A_{\text{tris}}}{A_{\text{bis}}} + \ln \frac{1}{[\text{PEDPA}]} \quad (8)$$

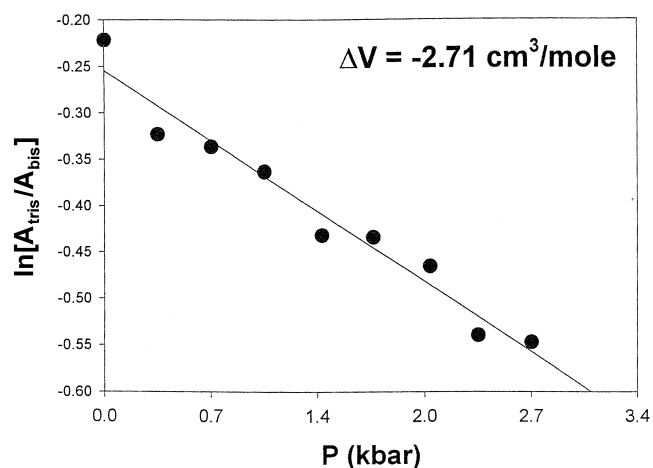


Fig. 6. Plot of the natural log of the ratio of Lorentzian peak areas ( $A_{\text{tris}}/A_{\text{bis}}$ ) versus pressure  $P$  (see text). The solid line is a linear least squares fit to the data.

The proportionality constants,  $k_{\text{bis}}$  and  $k_{\text{tris}}$  are independent of pressure, and under conditions of a large excess of ligand,  $[\text{PEDPA}]$  can also be assumed to be constant. Thus,  $\Delta V$  may be obtained from a plot of the natural log of the ratio of peak areas versus pressure. Results for a 1:3.5 metal:ligand ratio are given in Fig. 6. For this equilibrium we obtain a value of  $+2.71$  cm<sup>3</sup>/mole for  $\Delta V$ .

#### 4. Discussion

The spectroscopic results displayed in Figs. 2 and 5, and the subsequent analysis derived from Figs. 4 and 6 illustrate the usefulness of these kinds of measurements in studying the speciation and associated thermodynamics of lanthanide complexes. The small negative value ( $-0.35$  kJ/mole) for the enthalpy associated with formation of the tris complex from the bis complex is somewhat unexpected since the two species both have a negative charge. However, the overall reaction is a complicated one involving inner sphere and outer sphere coordinated water molecules, and it is not possible to make a reliable simple prediction of the sign of  $\Delta H$  in systems such as these. The positive value ( $+2.71$  cm<sup>3</sup>/mole) obtained for  $\Delta V$  for this reaction is consistent with arguments based upon the effect of electrostriction [7]. It is generally the case that in an equilibrium involving charged species, an increase in pressure favors the formation of the species with the lower net charge. This is due to the increased volume associated with the more organized solvent (water) structure for complexes that are more highly charged.

These preliminary results have formed the basis of continuing spectroscopic probes of the solution structure, thermodynamics, and kinetics of multidentate lanthanide complexes in solution. The particular measurements reported here are being applied to other lanthanide systems in which a small number of resolvable  ${}^7\text{F}_0 \rightarrow {}^5\text{D}_0$  peaks are observed in the excitation spectrum of Eu(III), and which

can also be identified with specific complexes. Additional structural and dynamic information is obtainable from measurements involving the linear [8] and circular [9,10] polarization in the luminescence from these types of complexes.

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