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Application of Laser Induced Photoacoustic Spectroscopy in the Investigation of Interaction of Neodymium(III) with Water Soluble Synthetic Polymer

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Laser-induced photoacoustic spectroscopy (LIPAS), which utilizes the photothermal effect that results from nonradiative relaxation of excited state molecules, was used in the speciation analysis of the complexes of neodymium(III) and water soluble synthetic polyelectrolyte, poly methacrylic acid (PMAA), in 0.1 M $NaClO_4$ at pH of 6.0. The minimum detection limit of Nd(III) by LIPAS was 5.0×10^{-6} M. Experiment was carried out at low concentration ratio of Nd(III) to PMAA to assure that 1:1 complexes predominate. The bound and free Nd(III) species were characterized by measuring nonradiative relaxation energy of the excited states ($^2G_{7/2}$ and $^4G_{5/2}$) to the metastable state ($^4F_{3/2}$). Two species were quantified by deconvolution of the mixed spectrum using their respective reference spectra. The conditional stability constant measured by LIPAS was 5.52 $L \cdot mol^{-1}$.

Introduction

The migrational behaviours of trivalent lanthanide or actinide ions in a natural environment are determined by their solubility, complex formation, and colloid generation. The complexation of these trivalent ions with naturally occurring organic polyelectrolyte ligands (*e.g.,* humic substances) has been investigated using a number of different methods. The separation methods used include equilibrium dialysis,[1] gel filtration,[2] and ultrafiltration technique.[3] There are many problems associated with the use of separation methods and they are: (1) the labile species can be lost by adsorption on membrane and other materials, (2) chemical equilibria may shift during the separation stage, and (3) low molecular weight complexes may pass through membranes. The nonse-

paration methods such as ISE (ion selective electrode) and conventional absorption spectroscopy are generally preferred, since fewer experimental difficulties are encountered. Even so, obtaining a reliable data is a difficult task, since the polyelectrolyte bound metal concentration is usually calculated as the difference between the total metal and free metal ion concentrations, and they may both be very large numbers. Furthermore, the ion selective electrode can be applied to only a few elements, and due to the low solubility of the trivalent ions (often less than 10^{-6} $mol \cdot L^{-1}$), the speciation analysis using the conventional absorption spectrophotometers poses many challenges, especially when the fingerprint characteristics of weak *f-f* transitions are exploited to identify metal complexes.

More recently, modern spectroscopic methods of high sen-

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sitivity have been applied to the complexation studies. The laser induced photoacoustic spectroscopy (LIPAS) is one such example that has been utilized in the praseodymium(III)[4] and americium(III)[5,6] chemical speciation studies. Photoacoustic spectroscopy measures nonradiative relaxation energy of excited state molecules. The solute molecules in a solution become excited by the absorption of modulated light source. The absorbed energy is subsequently released by a nonradiative relaxation process, causing a local heating in the volume illuminated by the pulse laser, which then expands. A periodic wave is generated with an amplitude proportional to the absorbance (εc in cm^{-1}) and laser pulse energy (E_λ). The electrical pulse amplitude (V) thus generated by the photoacoustic pressure on piezoelectric detector can be calculated using the relation in Eq. (1)

$$V = K \cdot \alpha_{t(tot)} \cdot P_{max} = \text{const} \cdot \varepsilon \cdot c \cdot E_\lambda \qquad (1)$$

where K is the sensitivity of the piezoelectric crystal, $\alpha_{t(tot)}$ is the total acoustic transmission coefficient of a detection assembly, and P_{max} is the maximum pressure caused by the absorption ($\varepsilon \cdot c$) and electrostriction in a given medium with the effective pulse energy of the laser radiation E_λ. The fundamental principles and some applications of this method have been discussed by Rosencwaig.[7] The application of this method for the speciation of transuranic elements in natural aquatic systems is reviewed by Kim *et al.*[6,8]

This work describes the laser induced photoacoustic spectroscopy setup to study the speciation of Nd(III)-PMAA complexes in a near neutral aquatic medium. The detailed description of LIPAS is given below. The trivalent neodymium was chosen for this investigation because of its relatively high absorption coefficient ($\varepsilon = 6.35$ cm^{-1} mol^{-1}·L) compared to other lanthanides. The use of Nd(III) as a reference to Am(III)[9] has been tested in the literature: The chemical analogy derives from common oxidation state and similar ionic radii of 111.5 pm (octahedrally coordinated Am(III)) and 112.3 pm (octahedral Nd(III)). The water soluble synthetic polymer, poly methacrylic acid (PMAA), comprising of aliphatic and carboxylic functionalities has been used as an analogue of naturally occurring polyelectrolyte ligands (humic substance). The investigation was carried out at a constant ionic strength (I=0.1) and at pH of 6.0 to avoid interference from metal ion hydrolysis.

Experimental

Instrumentation. A schematic diagram of the single beam double cell LIPAS system used in this investigation is shown in Figure 1. A XeCl excimer laser (308 nm, Lambda Physik, LPX 305icc)-pumped dye laser (Lambda Physik, LPD 3000) was used as the light source, yielding a dye pulse energy up to 16 mJ with 25 ns pulse width. For this investigation rhodamine 6G (Lambdachrom, LC 5900) with a spectral range of 569-608 nm was used as a dye medium. The spectral region was scanned repeatedly for 10 times and averaged for a better signal-to-noise ratio and hence improvement in the sensitivity was achieved. The laser pulse energy was measured by a pyroelectric detector (Coherent, ML-200), and the output signal was amplified 10 times and sent to an A/D converter (Stanford Research System, SR 245).

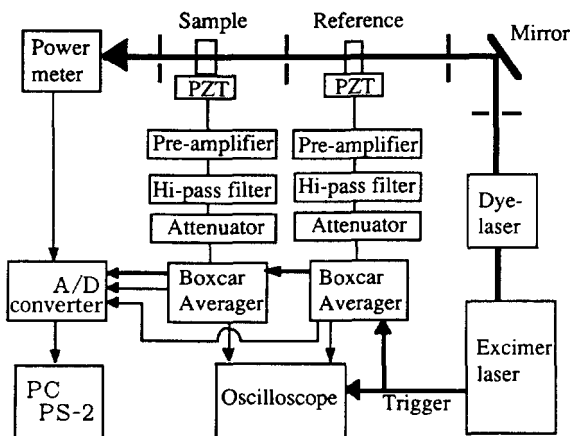For detecting low concentrations of Nd(III) species, it is

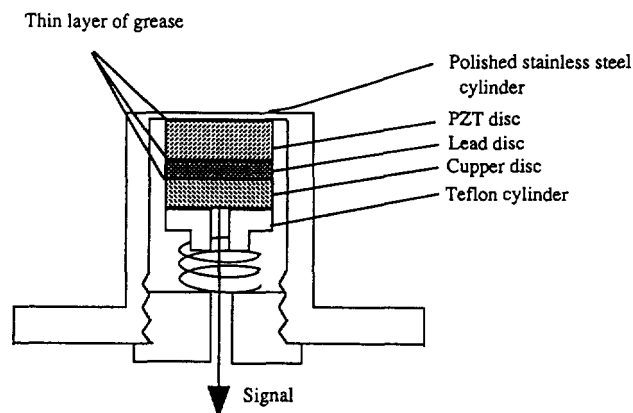**Figure 1.** Schematical diagram of the single beam double cell LIPAS system.

Figure 2. Cross sectional view of the piezoelectric transducer.

necessary to correct for background water absorption. For this purpose, a single beam double cell system was used. Briefly, a dye laser beam passed through the reference then the sample solutions contained in quartz spectrophotometer cells (1 cm×2 cm) that were mounted on two homemade polished stainless steel cylinders in which a pair of matched piezoelectric transducers (Venitron, 25 mm diameter disc of 6 mm thickness) were enclosed (see Figure 2). A better acoustic contact between the cell and the detector was maintained by glycerine. PA signal from the detector was amplified by a preamplifier (EG & G, ORTEC 142), and a home made high-pass filter was used to eliminate low-frequency noise. An attenuator was used to correct for differences in the laser energy between the cells, and slight differences in the characteristics of PZT and preamplifiers. Two separate boxcar averagers (Stanford Research System, SR 250) were used for gated integration (a 13.5 μs delayed gate with 0.8 μs width) of the reference and sample PA signals. The boxcar averaged signals were A/D converted, and were normalized with respect to the laser power intensity using a microcomputer (IBM, PS-2). The PA signal from the reference cell was subtracted from that of the sample cell.

Materials and Reagents. The Nd(III) stock solution was prepared by dissolving Nd$_2$O$_3$ (99.9%, Aldrich Chem. Co) in a minimum amount of conc. HClO$_4$ (69.0-72.0%, Aldrich Chem. Co) and further diluting it by 0.1 M NaClO$_4$ solution,
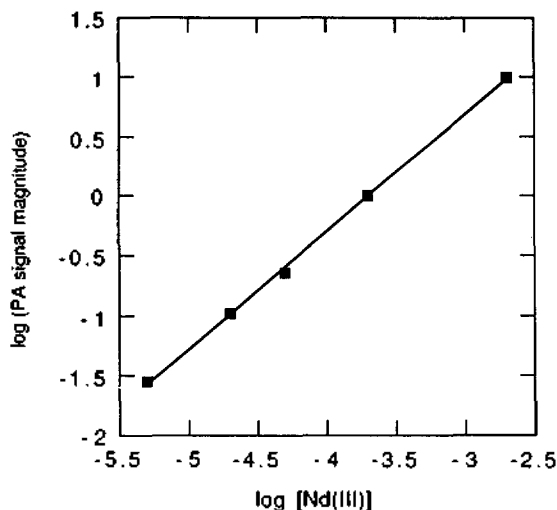
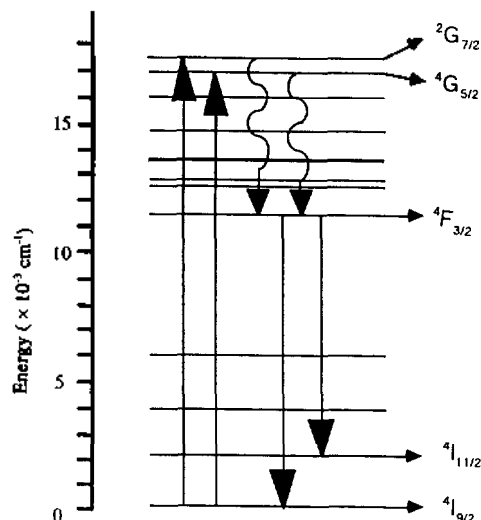**Figure 3.** A plot showing the relationship between the magnitude of photoacoustic signal at 575.2 nm and Nd(III) concentration.

Figure 4. Schematic diagram of Nd(III) energy level.

Figure 5. The photoacoustic spectra of (a) Nd(III) aquo ion (5.0 $\times10^{-5}$ M) and (b) Nd-PMAA complex ([Nd(III)]$_{total}$=5.0$\times10^{-5}$ M and [PMAA]=0.89 meq·L^{-1}) in 0.1 M NaClO$_4$ at pH=6.0.
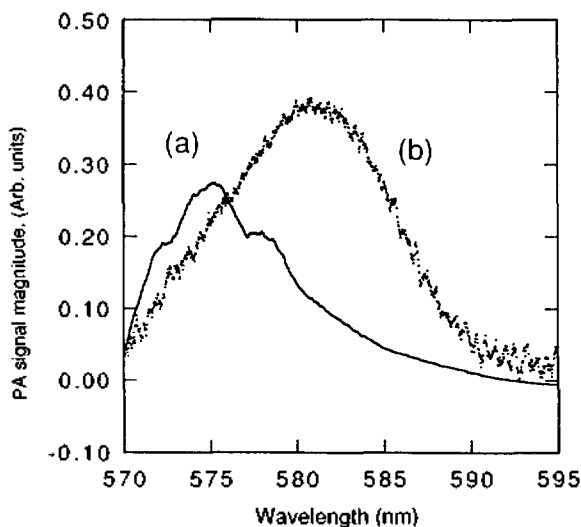
and pH adjusted to 6.0 using 0.1 M NaOH (Baker Co., carbonate free). PMAA used in this investigation was synthesized by a radical polymerization technique using ammonium persulfate initiator in ethanol-water medium and purified by precipitation procedure given in the literature[10]. The synthesized polymer was characterized by ^{1}H and ^{13}C-NMR (Bruker, AC 200) and proved to be a syndiotactic biased one[11]. The PMAA stock solution was prepared by slowly dissolving the accurately weighed solid material in 0.1 M NaClO$_4$ solution and pH was adjusted to 6.0. All reagents used were above reagent grade, and the solutions were prepared using double deionized water in an inert gas box free of interfering carbon dioxide. The sample solution was prepared by mixing an appropriate amount of Nd(III) and PMAA stock solutions, and allowed to stand for three days to equilibrate. All suspended particulates in solvents and Nd(III) solutions were removed by filtering them with YM 10 membrane filters (Amicon Co.) to reduce spurious LIPAS signal generated by light scattering.

Results and Discussion

Instrumental Performances. The performance of the system for sensitivity and reproducibility was tested using a series of Nd(III) reference solutions of differing concentration. The calibration curve was obtained by measuring the maximum peak intensities of the 575.2 nm of the Nd(III) aquo ion peak at concentration ranging from 2.0×10^{-3} M to 2.0×10^{-6} M, as shown in Figure 3. It showed that PA signal was linearly proportional to the aquo Nd(III) ion concentration. The sensitivity limit for Nd(III) aquo ion in 0.1 M NaClO$_4$ and pH of 6.0 was approximately 5.0×10^{-6} M. This detection sensitivity for Nd(III) aquo ion was limited by the finite absorption of the water medium rather than the absolute sensitivity of the PA detection. The compensation for water absorbance can be achieved in practice with an average accuracy of 2-3%.[5,6] The average accuracy obtained in this investigation corresponds to 3.9% of water absorption at 575.2 nm. A greater accuracy may be obtained stati-

stically by multiscanning to improve the signal-to-noise ratio, or by using Nd(III) solutions in acidic media (*e.g.* 0.1 M HClO$_4$) to reduce hydrolysis effects, and at higher temperature.[12] A similar single beam double cell LIPAS system has been applied to the Am(III) speciation probe (ε=400 L mol^{-1} at 503 nm) at much lower concentrations down to 2×10^{-8} M, corresponding to about 2.7% of background absorption.[13]

Spectroscopic Features of Nd(III) Aquo Ion and Nd-PMAA Complex. The energy scheme of the free Nd (III) ion is illustrated in Figure 4. The Nd(III) ion is excited to the $^2G_{7/2}$ and $^4G_{5/2}$ states from the $^4I_{9/2}$ ground state with radiations of 575.2 nm and 580.7 nm respectively. A subsequent deexcitation occurs through a non-radiative decay to the metastable $^4F_{3/2}$ state,[14] causing the PA signals. The photoacoustic spectrum of the Nd(III) aquo ion ([Nd]=5.0×10^{-5} mol·L^{-1} in 0.1 M NaClO$_4$ at pH of 6.0) is shown in the spectrum (a) in Figure 5. This PA spectrum shows fine structures that are not observed in a conventional absorption

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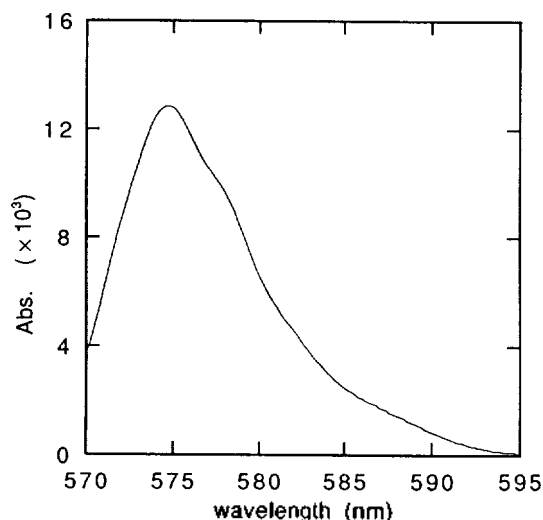
Figure 6. Conventional absorption spectrum of Nd(III) aquo ion $(2.0 \times 10^{-3}$ M) in 0.1 M $NaClO_4$ at pH=6.0.
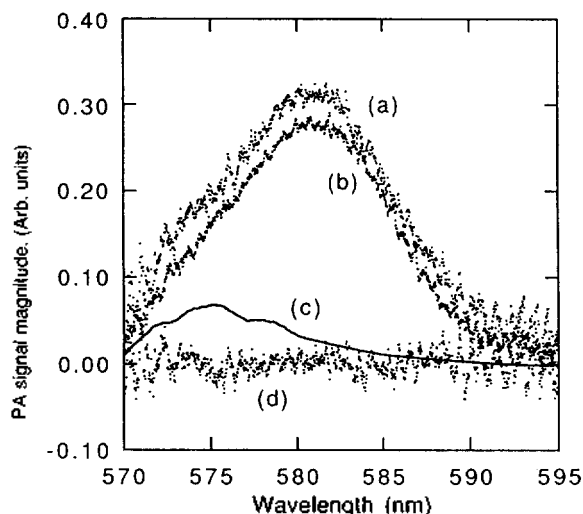
Figure 7. A mixed photoacoustic spectrum (a) of Nd(III) aquo ion and Nd-PMAA complex ([Nd(III)]$_{total}$=5.0×10^{-5} M and [PMAA]=0.103 meq·L^{-1}) in 0.1 M $NaClO_4$ at pH=6.0. The relative proportions of Nd-PMAA complex and Nd(III) ion are shown in spectrum (b) and spectrum (c). The difference between the spectrum (a) and the sum of the spectra (b) and (c) are shown as the spectrum (d).

spectrum (see Figure 6). The apparent splittings are due to the internal stark effect as a result of local electric field surrounding it.[14] When an excess of PMAA (0.89 Meq·L^{-1}) is added to the Nd(III) solution (5.0×10^{-5} mol·L^{-1}), the PA spectroscopic feature undergoes a change and this is shown in the spectrum (b) in Figure 5. The relatively sharp Nd(III) aquo ion peak (FWHM=8.8 nm) showing several shoulders is replaced by a very broad PA spectrum with the peak maximum at 580.7 nm (FWHM=10.5 nm). The changes in the spectral features shown in Figure 5 imply that Nd(III) ions became extensively bound to polyelectrolyte ligands in aquatic medium.

Determination of the Conditional Stability Constant of the Nd-PMAA Complex. LIPAS can be applied

to the direct speciation analysis of the free Nd(III) aquo ion and Nd(III) bound to PMAA. A mixed spectrum contains both the free and bound Nd(III) species. By using the reference spectra of Nd(III) aquo ion and Nd-PMAA complex (Figure 5), the mixed spectrum can be deconvoluted to yield relative quantities of free and bound Nd(III) as shown in Figure 7. The major advantage of this method is that both species in the system can be quantified directly, without concern for adsorption loss or chemical equilibria shift change. The sum of the spectrum (b) and spectrum (c) is almost identical to that of the spectrum (a). Subtracting the sum of the spectra (b) and (c) from the spectrum (a) yielded the spectrum (d) of virtually no signal intensity. The conditional stability constant of Nd-PMAA complex is calculated using Eq. (2), based on cooperative binding which assumes that Nd(III) ions bind at identical and indeperident sites of PMAA

$$K = [\text{Nd-PMAA}][\text{Nd(III)}]_f[\text{PMAA}]_f \qquad (2)$$

Where K represents the conditional stability constant, [Nd-PMAA] is the concentration of Nd(III) bound to PMAA, [Nd (III)]$_f$ is the free aquo ion concentration and [PMAA]$_f$ is the free and available binding site concentration. [Nd-PMAA] and [Nd(III)]$_f$ were obtained from the spectral data and the total Nd(III) concentration, [Nd]$_t$, in the solution. In the absence of known molecular weight, the ligand concentration of the polyelectrolyte, [PMAA]$_t$, is expressed in terms of binding site concentration obtained from the maximum binding ability (MBA) data as 0.103 meq·L^{-1}. [PMAA]$_f$ is obtained using Eq. (3) below.

$$[\text{PMAA}]_f = [\text{PMAA}]_t\text{-}[\text{Nd-PMAA}] \qquad (3)$$

The Nd(III) to PMAA concentration Ratio was kept low to ensure that 1 : 1 complexes (each binding site binds to a Nd(III) ion) predominate. The conditional stability constant of Nd-PMAA complex, obtained from Eq. (2), is 5.52 L·mol^{-1}, which is similar to 5.90 L·mol^{-1} obtained for the curium (III) complex of naturally occurring fulvic acid.[15]

Conclusion

The laser induced photoacoustic spectroscopy described in this work shows Nd(III) detection sensitivity much higher than the conventional absorption spectroscopy. It has also shown that LIPAS can be applied as a direct method of Nd (III) speciation analysis. Further improvements are being made to improve the detection sensitivity of the system and a temperature control unit is to be added to the cells, enabling Nd(III) speciation analysis to be carried in a submicromole range.

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Modified Analytic Solutions of F.C.C. Metal Clusters

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By including the overlap integrals between atomic orbitals, the modified cluster orbitals for a metal cluster of face centered cubic lattice are found. The modified analytic solutions of the cluster are obtained from them with the assumption that the cluster orbitals with different state indices do not mix together. The physical properties—the HOMO levels and the unit electronic energies—of Ni, Pd, and Pt clusters of various size, calculated by the modified cluster orbital method, agree better with the results obtained by the Extended Hückel calculation than those of the previous (unmodified) cluster orbital method do. As a result, it is verified that the physical properties, at least those related to the energy levels, obtained by the Extended Hückel method may be reproduced by use of the modified cluster orbital method instead.

Introduction

The molecular orbitals and their energies of a face-centered cubic (f.c.c.) metal cluster were found, in the previous work,[1] from the cluster orbitals[2] of nine types (one s-, three p-, and five d-types) instead of atomic orbitals. In order to obtain the analytic solutions which are not limited to the cluster size, it was assumed that the cluster orbitals with different state indices do not mix together. Several physical properties for the metal-hydrogen systems have been calculated in this way[3] and it has been shown that the results agreed well, at least qualitatively, with those obtained by the Extended Hückel (EH)[4] calculation. Though the assumption we have made seemed to be somewhat nonsensical, there was no other way than neglecting the off-diagonal submatrices (the Hamiltonian matrx elements denoting the interactions between the cluster orbitals with different state indices); they could not be treated easily. It was expected,[1] however, that better results might be obtained with some modification of the scheme.

If only one atomic orbital (of any type) is allowed per site (per each atom), the solutions (the molecular orbitals and their energies) may be obtained analytically without any assumption such that the off-diagonal mixings do not occur.[2,5-7] The density of states (DOS), the HOMO levels, and the total electronic energies of the hypothetical hydrogen clusters of f.c.c. lattice calculated by the analytic (cluster orbital) method, however, did not accord well with the results obtained by the EH calculation. The main difference between the two results was thought to arise from neglecting the overlap integrals between atomic orbitals in case of the cluster orbital method. It is reasonably expected, therefore, that the difference may disappear, or at least be reduced, by including the integrals.

In this work the modified cluster orbitals of an f.c.c. metal cluster, including the overlap integrals explicitly, are found and the analytic solutions of the cluster are obtained from them with the same assumption that the off-diagonal mixings do not occur. Since the same assumption as the earlier work[1] is made, the problem of the treatment of the off-diagonal submatrices is not still solved; nevertheless the scheme has been modified. The molecular orbitals, however, are not treated in this article and only the orbital energies are calculated, *i.e.*, the concern is limited only to the physical proper-