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Complexation of Lactate with Nd(III) and Eu(III) at Variable Temperatures: Studies by Potentiometry, Microcalorimetry, Optical Absorption and Luminescence Spectroscopy

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Abstract

Complexation of neodymium(III) and europium(III) with lactate was studied at variable temperatures by potentiometry, absorption spectrophotometry, luminescence spectroscopy and microcalorimetry. Stability constants of three successive lactate complexes (ML^{2+}, ML_2^{+} and ML_3(aq), where M stands for Nd and Eu, and L stands for lactate) at 10, 25, 40, 55 and 70ºC were determined. The enthalpies of complexation at 25ºC were determined by microcalorimetry. Thermodynamic data show that the complexation of trivalent lanthanides (Nd^{3+} and Eu^{3+}) with lactate is exothermic, and the complexation becomes weaker at higher temperatures. Results from optical absorption and luminescence spectroscopy suggest that the complexes are inner-sphere chelate complexes in which the protonated α-hydroxyl group of lactate participates in the complexation.

Key Words: Neodymium, Europium, Lactate, Complexation, Temperature effect

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1 Introduction

To reduce the long-term radioactive hazards and heat loading of used nuclear fuels, the advanced fuel cycles include a strategy of partitioning and transmutation (P-T). With this strategy, the long-lived trivalent actinides (An(III)) are separated from the short-lived trivalent lanthanides (Ln(III)) and transmuted to short-lived or stable isotopes in nuclear reactors or accelerator-driven systems. Some isotopes of lanthanides could interfere with the neutron balance in the transmutation process due to their high cross sections of neutron absorption. Therefore, they must be separated from the actinides before transmutation.

It is a very challenging task to separate An(III) from Ln(III) because of their chemical and physical similarities. A process, called TALSPEAK (Trivalent Actinide Lanthanide Separations by Phosphorus-reagent Extraction from Aqueous Komplexes),[1,2] has been shown to be a promising option for accomplishing this task in an advanced fuel cycle. The aqueous phase of the TALSPEAK contains lactic acid and diethylenetriaminepentaacetic acid (DTPA). Effective separations of An(III) from Ln(III) by TALSPEAK have been demonstrated in several pilot-scale operations.[3,4] However, the fundamental chemistry underlying the separations remains unclear. There are discrepancies between the experimentally measured distribution coefficients of An(III) and Ln(III) under TALSPEAK conditions and those predicted by thermodynamic models using the stability constants of An(III)/Ln(III) complexes in the literature. For example, in the regions of pC_H (i.e., -log[H^+]) above ~3.5, the measured distribution coefficients of

An(III) and Ln(III) decrease while the model predicted values increase as pC_H becomes higher.[5,6]

To achieve accurate prediction and precise control of the behavior of actinides and lanthanides in the TALSPEAK process, it is necessary to determine the thermodynamic parameters of the reactions in the TALSPEAK system, including the complexation of lanthanides and actinides with lactate and DTPA, and evaluate the effect of operating conditions (e.g. temperature) on these thermodynamic parameters. There have been a number of studies on the complexation of lanthanides with lactate, but only at or near 25°C.[7-12] Thermodynamic data for the complexation of An(III) and Ln(III) with lactate are still very scarce at temperatures above 25°C. Consequently, it is very difficult to predict the behavior of actinides and lanthanides in the TALSPEAK process if the "envelope" of operating conditions (e.g., the temperature) changes. To help with the development of advanced An(III)/Ln(III) separation processes, we have started systematic studies on the thermodynamics of major reactions involved in TALSPEAK, including the protonation of lactate and DTPA[13] and their complexation with actinides and lanthanides at different temperatures. This paper summarizes the results on the stability constants and enthalpy of complexation of lanthanide complexes with lactate at different temperatures.

2 Experimental

2.1 Chemicals. All chemicals were reagent grade or higher. Milli-Q water was used in preparations of all solutions. Stock solutions of Nd(III) perchlorate or Eu(III) perchlorate were prepared by dissolving Nd_2O_3 or Eu_2O_3 in perchloric acid (70%, Aldrich). The concentrations of lanthanides and perchloric acid in the stock solutions

were determined by EDTA complexometry,[14] and Gran's titration,[15] respectively. A stock solution of lactic acid (i.e., 2-hydroxypropanoic acid) was prepared by appropriate dilutions of the 85% DL-lactic acid solution (Aldrich). The concentration of lactic acid in the stock solution was determined by potentiometric titrations. The ionic strength of all working solutions was maintained at 1.0 M ($NaClO_4$) at 25°C. All the molar concentrations in this paper are referred to 25°C.

2.2 Potentiometry at variable temperatures. Potentiometric experiments were carried out at 10, 25, 40, 55 and 70°C for the complexation of Nd(III) and Eu(III) with lactate using a variable-temperature titration setup. Detailed description of the apparatus and the procedures are provided elsewhere.[16,17] Electromotive force (*EMF*, in millivolts) was measured with a Metrohm pH meter (Model 713) equipped with a Ross combination pH electrode (Orion Model 8102). The original electrode filling solution (3.0 M KCl) was replaced with 1.0 M NaCl to avoid clogging of the electrode frit septum due to the low solubility of $KClO_4$. The *EMF* of the glass electrode in the acidic region can be expressed by Eq. (1).

$$E = E^0 + RT/F \ln[H^+] + \gamma_H[H^+] \quad (1)$$

where R is the gas constant, F is the Faraday constant and T is the temperature in K. The last term is the electrode junction potential for the hydrogen ion ($\Delta E_{j,H+}$), assumed to be proportional to the concentration of the hydrogen ion. Prior to each titration, an acid/base titration with standard perchloric acid and sodium hydroxide was performed to obtain the electrode parameters of E^0 and γ_H. These parameters allowed the calculation of hydrogen ion concentrations from the *EMF*'s in the subsequent titration. Corrections for the electrode junction potential of the hydroxide ion were not necessary in these experiments.

In a typical titration, a solution (about 20 ml) containing appropriate amounts of lactate and lanthanides (Nd(III) or Eu(III)) was titrated with a solution of perchloric acid. The *EMF* data were collected at time intervals determined by the data collection criterion, i.e., the drift of *EMF* (ΔE) was less than 0.1 mV for 180 seconds. Fifty to seventy data points were collected in each titration. Multiple titrations were conducted at each temperature with solutions of different concentrations of C_M^0, C_L^0 and C_H^0. The stability constants of Nd(III)/lactate and Eu(III)/lactate complexes on the molarity scale were calculated with the Hyperquad program.[18] To allow comparison at different temperatures, the constants in molarity were converted to the constants in molality according to Eq.(2).[19]

$$\log_{10} K_m = \log_{10} K_M + \Sigma_r \nu_r \log_{10} \vartheta \qquad (2)$$

where K_m and K_M are the equilibrium constants of a reaction in molality and molarity, respectively. ϑ is the ratio of the values of molality to molarity for the specific ionic medium and equals 1.05 dm^3 of solution per kg of water for 1.0 M $NaClO_4$ at 25°C. $\Sigma_r \nu_r$ is the sum of the stoichiometric coefficients of the reaction (ν_r is positive for products and negative for reactants) and is equal to $-j$ for Nd(III)/lactate and Eu(III)/lactate complexation ($M^{3+} + jL^- = ML_j^{(3-j)+}$).

2.3 Spectrophotometric titrations at variable temperatures. Absorption spectra of Nd(III) (550 - 600 nm, 0.1 nm interval) were collected on a Varian Cary-6000i spectrophotometer equipped with sample holders that were maintained at constant temperatures. 10 mm quartz cells were used. Multiple titrations with different concentrations of Nd(III) were performed. The initial concentration of Nd(III) in the cell was around 0.10 M. In each titration, appropriate aliquots of the titrant (1.0 M sodium

lactate) were added into the cell and mixed thoroughly with an electromagnetic stirrer (for 1 - 2 minutes) before the spectrum was collected. The mixing time was found to be sufficient for the complexation to complete. Usually 15 - 20 additions were made, generating a set of 15 - 20 spectra in each titration. The stability constants of the Nd(III)/lactate complexes (on the molarity scale) were calculated by non-linear least-square regression using the Hyperquad program.[18]

2.4 Microcalorimetry at 25°C. Calorimetric titrations were conducted with an isothermal microcalorimeter (Model ITC 4200, Calorimetry Sciences Corp.) at 25°C. Procedures and results of the calibration of the calorimeter were provided elsewhere.[17,20]

Solutions of Nd(III)/lactate or Eu(III)/lactate (0.9 mL) were placed in the titration vessel and titrated with $HClO_4$. Multiple titrations with different concentrations of Nd(III) or Eu(III) (4 – 25 mM) were performed to reduce the uncertainty. In a typical titration, n additions of the titrant were made (usually n = 40 – 50), resulting in n experimental values of the total heat generated in the titration vessel ($Q_{ex,j}$, j = 1 to n). These values were corrected for the heats of dilution of the titrant ($Q_{dil,j}$) that were determined in separate runs. The net reaction heat at the j-th point ($Q_{r,j}$) was obtained from the difference: $Q_{r,j} = Q_{ex,j} - Q_{dil,j}$. The value of $Q_{r,j}$ is a function of the concentrations of the reactants (C_M, C_H and $C_{lactate}$), the equilibrium constants and the enthalpies of the reactions that occurred in the titration. A least-square minimization program, Letagrop,[21] was used to calculate the enthalpy of complexation of Nd(III) or Eu(III) with lactate.

2.5 Luminescence spectroscopy. Luminescence emission spectra and lifetime of Eu(III) in aqueous solutions ([Eu(III)] = 2 mM, [lactate] = 0 – 72 mM) were acquired on a HORIBA Jobin Yvon IBH FluoroLog-3 fluorometer adapted for time-resolved

measurements. 10 mm quartz cells were used. A sub-microsecond Xenon flash lamp (Jobin Yvon, 5000XeF) was the light source and coupled to a double grating excitation monochromator for spectral selection. The input pulse energy (100 nF discharge capacitance) was about 50 mJ and the optical pulse duration was less than 300 ns at fwhm. A thermoelectrically cooled single photon detection module (HORIBA Jobin Yvon IBH, TBX-04-D) that incorporates a fast risetime PMT, a wide bandwidth preamplifier, and a picosecond constant fraction discriminator was used as the detector. Signals were acquired using an IBH Data Station Hub and data were analyzed using the commercially available DAS 6 decay analysis software package from HORIBA Jobin Yvon IBH. The goodness of fit was assessed by minimizing the reduced function, χ^2, and visually inspecting the weighted residuals. Each trace contained at least 10,000 points, and the reported lifetime values resulted from at least three independent measurements.

3 Results

3.1 Stability constants of Nd(III)/lactate and Eu(III)/lactate complexes at variable temperatures. The stability constants of Nd(III)/lactate complexes were determined with potentiometry and spectrophotometry, while those of Eu(III)/lactate complexes were determined with potentiometry and luminescence spectroscopy.

Nd(III)/lactate and Eu(III)/lactate complexes – potentiometry. Representative potentiometric titrations (at 25 and 70^{o}C, respectively) for Nd(III)/lactate and Eu(III) lactate are shown in Figure 1. The best fit of the data by the Hyperquad program indicates that three successive monomeric Nd(III)/lactate or Eu(III)/lactate complexes form during the titration. The overall complexation reactions are represented by equilibrium (3),

$$M^{3+} + j\ L^{-} \leftrightarrows ML_j^{(3-j)+} \qquad j = 1, 2, 3 \qquad (3)$$

$$\beta_j = [ML_j^{(3-j)+}]/([M^{3+}][L^-]^j) \quad (4)$$

where M stands for Nd or Eu. The stability constants (β_j) on the molarity scale at different temperatures were calculated by Hyperquad and are listed Table 1.

Nd(III)/lactate complexes – Spectrophotometry. Figure 2 shows the absorption spectra of two representative titrations for Nd(III)/lactate complexation at 25 and 70°C. The absorption band around 575 nm corresponds to the hypersensitive $^4I_{9/2} \rightarrow {}^4G_{5/2}, {}^2G_{7/2}$ transition of Nd(III) that is sensitive to the coordination environment.[23-26] At each temperature, the $^4I_{9/2} \rightarrow {}^4G_{5/2}, {}^2G_{7/2}$ transition was intensified and red-shifted as the concentration of lactate was increased. Analysis by the Hyperquad program indicated that there are four absorbing species of Nd(III) and the spectra were best-fitted with the formation of successive complexes described by Eq.(3). The molar absorptivities of free Nd^{3+} and three Nd(III)/lactate complexes at 25 and 70°C calculated by Hyperquad are shown in the lower part of Figure 2. The spectra and absorptivities at other temperatures are not shown, but the trends in the spectra features are similar at each temperature. The stability constants of Nd(III)/lactate complexes determined by spectrophotometry are also listed in Table 1 and compared with the constants obtained by potentiometry. Except for the value of log β_3 at 55°C, the stability constants obtained by the two methods are in fair agreement within the 3σ uncertainties.

Eu(III)/lactate complexes – Luminescence spectroscopy. The luminescence emission spectra of Eu(III)/lactate solutions at variable temperatures (10, 25, 40, 55 and 70°C) were collected and analyzed with Hyperquad, in the same way as in the processing of the absorption spectra for Nd(III)/lactate, to obtain the stability constants of the Eu(III)/lactate complexes at different temperatures. As compared in Table 1, the stability

constants of EuL^{2+} and $EuL_3(aq)$ obtained by luminescence are in fairly good agreement with those by potentiometry, but the stability constants of EuL_2^+ by the two methods differ significantly. It is believed that the results by potentiometry are more reliable, because the emission spectra are analyzed based on the assumption that the emission intensities of all Eu(III) species are proportional to their concentrations. Such an assumption may not be true for all systems. Therefore, the stability constants obtained from luminescence are listed in Table 1 for comparison, but are not used for calculating the enthalpy and entropy of complexation for the Eu(III)/lactate complexes.

3.2 Direct determination of enthalpy of complexation for Nd(III)/lactate and Eu(III)/lactate complexes at 25°C by calorimetry. Figure 3 shows the data from calorimetric titrations, in the form of the accumulated reaction heat as a function of the volume of the titrant. Titrations with different concentrations of C_M^0 (M = Nd or Eu), C_L^0 and C_H^0 are shown. Using these data in conjunction with the stability constants obtained by potentiometry and spectrophotometry, the enthalpies of complexation at 25°C were calculated. The enthalpies, as well as the entropies of complexation accordingly calculated, are summarized in Table 1.

3.3 Luminescence emission spectra and lifetime of Eu(III)/lactate solutions. Figure 4 shows the luminescence emission spectra (upper figure) of Eu(III)/lactate solutions at 25°C. The spectra contains features originating from electronic transitions from the lowest excited state, $^5D_0$, to the ground state manifold, ^7F_J (J = 0, 1, 2, 3……). As the concentration of lactate was increased from 0 to 0.072 M, the intensity of the hypersensitive $^5D_0 \rightarrow {}^7F_2$ transition (around 615 - 620 nm) increased significantly. On the contrary, the intensity of the $^5D_0 \rightarrow {}^7F_1$ transition (around 590 - 600 nm) is little affected

because it is a magnetic dipole transition and insensitive to the coordination environment of the luminescent ion.[27] In fact, this band is often used as the internal standard for intensity comparison.

Previous studies have shown that the lifetime of Eu(III) luminescence in aqueous solutions is linearly correlated with the number of water molecules in the inner coordination sphere, due to the efficient energy transfer from the excited state ($^5D_0$) of Eu(III) to the O-H vibration of the coordinated water molecules.[28] The luminescence decay patterns of Eu(III)/lactate solutions from this work are shown in Figure 4 (lower part). Single exponential functions are used to fit the data to obtain the luminescence lifetimes (τ). It is evident that τ becomes longer as $C_{lactate}$ is increased, suggesting the number of water molecules (or, the number of O-H oscillators) in the inner coordination sphere of Eu^{3+} is reduced due to the complexation with lactate. Using the previously established linear correlation between the luminescence lifetime and the number of water molecules ($n_{H2O} = 1.05 \times \tau^{-1} - 0.7$, where τ is in milliseconds[29]) and based on the observation that one water molecule corresponds to two O-H oscillators in terms of luminescence quenching,[30] the average number of O-H oscillators per Eu(III) in the solutions, $n_{OH,exp}$, could be calculated (Table 2). These data provide insight into the coordination mode of lactate in the Eu(III) complexes, and are discussed in details below.

4 Discussion

4.1 Coordination modes in the lanthanide/lactate complexes. Three coordination modes could exist in the monomeric lanthanide/lactate complexes as shown in Figure 5. The thermodynamic parameters and luminescence data from this work help to identify the most probable coordination mode.

Does the α-hydroxyl group participate in the complexation? As a typical hard acid cation, the interaction of Nd^{3+} or Eu^{3+} with carboxylate ligands in aqueous solution is expected to be ionic and strongly electrostatic in nature.[31] This implies that the strength of carboxylate complexation with Nd^{3+} or Eu^{3+} may parallel that of electrostatic interaction of protons with the same carboxylates. As a result, a relationship can be expected between the complex formation constants and the pK_a of the ligands.[32] Such a relationship for a series of carboxylic acids is shown in Figure 6. The data for most alkylcarboxylic acids fall on a straight line. However, the data for lactate and a few other α-hydroxycarboxylates are significantly above the line, indicating these complexes have "enhanced" stability with respect to the log β - pK_a correlation. Such enhancement suggests that the α-hydroxyl group in lactate probably participates in the complexation with lanthanides. Therefore, mode (a) in Figure 5 is unlikely to occur in the lanthanide/lactate complexes.

Is the α-hydroxyl group in the complex protonated or deprotonated? With both coordination modes (b) and (c), one lactate molecule would replace two water molecules, thus reducing the number of O-H oscillators around Eu(III) (n_{OH}) by four, However, the protonated complex in mode (c) would contribute to the luminescence quenching with one additional O-H oscillator. As a result, coordination of one lactate molecule with mode (c) would result in a net loss of one and half water molecules (equivalent to three O-H oscillators).

Using the stability constants from this work, the concentrations of all Eu(III) species (Eu^{3+}, EuL^{2+}, EuL_2^{+} and EuL_3(aq)) in the solutions for the luminescence lifetime measurements were calculated. Then the average number of O-H oscillators in the inner

coordination sphere of Eu(III) corresponding to coordination modes (b) or (c), $n_{OH,cal}$, could be calculated.

The calculated $n_{OH,cal}$ with coordination mode (b) or (c) are compared with the experimentally observed $n_{OH,exp}$ in Table 2 and Figure 7. It is evident that the experimental data supports that mode (c), where the protonated α-hydroxyl group participates in the coordination, is the most probable coordination mode.

4.2 Effect of temperature. Figure 8 shows that the stability constants of Nd(III)/lactate and Eu(III)/lactate complexes generally decrease as the temperature is increased. Such trends are consistent with the negative enthalpies of complexation obtained by calorimetry. On the contrary, the complexation of simple carboxylates (acetate, propionate, etc.) with lanthanides usually becomes stronger at higher temperatures and the enthalpy of complexation is slightly endothermic (ΔH = 5 - 15 kJ/M for lanthanide complexes with acetate or propionate[22]). The difference in the enthalpy of complexation between the Ln(III)/lactate and Ln(III)/acetate systems probably results from the difference in the energetics of two processes: (1) the dehydration of the two ligands, and (2) the Ln^{3+}-ligand interaction. Process 1 requires energy and results in positive enthalpy (endothermic), while process 2 releases energy and results in negative enthalpy (exothermic). The complexation of Ln(III) with lactate, and α-hydroxycarboxylates in general, is more favored by the enthalpy probably because (1) the α-hydroxyl group is less hydrated than the carboxylate group so that less dehydration energy is required to form the coordination bond, and (2) the Ln^{3+}-lactate interaction is stronger than the Ln^{3+}-acetate interaction so that more energy is gained in the former.

It should be noted that, as the data in Table 1 and Figure 8 indicate, Eu(III)/lactate complexation is generally stronger than Nd(III)/lactate complexation (by about 0.2 units for logβ) at all temperatures. This trend is consistent with the expected behavior for the lanthanide series where the ionic radii of lanthanides decrease as the atomic number increases.

The changes in the optical absorption oscillator strength of the hypersensitive $^4I_{9/2} \rightarrow {}^4G_{5/2}$, $^2G_{7/2}$ transition have been used to probe the coordination environment of the Nd^{3+} ion in aqueous solutions[33,34] and could be related to the change in the temperature. Jϕrgensen and Judd have concluded that the hypersensitive transitions in lanthanides are probably "pseudoquadrupole" in nature and the hypersensitivity is believed to be due to coulombic correlation of dipoles induced in the ligands by the transition quadrupole moment of the metal ion.[23-26] Previous studies have found that the oscillator strength of the $^4I_{9/2} \rightarrow {}^4G_{5/2}$, $^2G_{7/2}$ transition was greatly intensified as Nd(III) formed complexes with acetate[34] and nitrate.[35] In the present work, the oscillator strengths for the Nd(III)/lactate complexes were calculated from the integrated band areas of the deconvoluted spectra (Figure 2) in 1.0 M $NaClO_4$ at 25°C and 70°C. As summarized in Table 3, the oscillator strength becomes larger from free Nd^{3+} to successively higher complexes at both temperatures, which seems to support the "pseudoquadrupole" mechanism of the intensity enhancement, because the higher complexes are bulkier and probably more asymmetric than the free Nd^{3+} species and the pseudoquadrupole transitions should be more intense in the higher complexes.

5 Summary

Thermodynamic data show that, in the temperature range from 10°C to 70°C, the complexation of trivalent lanthanides (Nd^{3+} and Eu^{3+}) with lactate becomes weaker as the temperature is increased. The complexation is both enthalpy- and entropy-driven. Compared with lanthanide complexes with simple monocarboxylates, the complexes with lactate are stronger due to the participation of the α-hydroxyl group. Data from luminescence spectroscopy suggest that the complexes are inner-sphere and lactate coordinates to Eu(III) in a bidentate mode with one oxygen from the carboxylate group and the other oxygen from the protonated α-hydroxyl group.

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References

1. Weaver, B.; Kappelman, F.A. "TALSPEAK, A new method of separating americium and curium from the lanthanides by extraction from an aqueous solution of an aminopolyacetic acid complex with a monoacidic organophosphate or phosphonate." *ORNL-3559,* August, 1964.
2. Weaver, B.; Kappelmann, F. A. *J. Inorg. Nucl. Chem*. **1968**, 30, 263.
3. Liljenzin, J. O.; Persson, G.; Svantesson, I.; Wingefors, S. *Radiochim. Acta* **1984**, 35, 155.

4. Persson, G.; Wingefors, S.; Liljenzin, J.O.; Svantesson, I. *Radiochim. Acta* **1984**, 35, 163.
5. Nilsson, M.; Nash, K. L. *Solvent Extraction & Ion Exchange* **2009**, 27, 354.
6. Nilsson, M.; Nash, K. L. *Solvent Extraction & Ion Exchange* **2007**, 25(6), 665.
7. Dickins, R. S.; Aime, S.; Batsanov, A. S.; Beeby, A.; Botta, M.; Bruce, J. I.; Howard, J. A. K.; Love, C. S.; Parker, D.; Peacock, R. D.; Puschmann H. *J. Am. Chem. Soc*. **2002**, 124, 12697.
8. De Marco, D. *Thermochimica Acta* **1991**, 189, 213.
9. Bukietynska, K.; Mondry, A.; Osmeda, E. *J. Inorg. Nucl. Chem*. **1981**, 43, 1311.
10. Choppin, G. R.; Friedman, Jr. H. G. Inorg. Chem. **1966**, 5, 1599.
11. Gouveia, M. A.; de Carvalho, R. G. *J. Inorg. Nucl. Chem*. **1966**, 28, 1683.
12. Zalupski, P. R.; Nash, K. L.; Martin, L. R. *J. Soln. Chem*. **2010**, DOI 10.1007/s10953-010-9573-2**.**
13. Tian, G.; Rao, L. *Separation Science and Technology,* **2010**, 45, 1718.
14. Dean, J. A. *Analytical Chemistry Handbook*, McGraw-Hill, Inc., New York, 1995, p.3-108.
15. Gran. G. *Analyst* **1952**, 77, 661.
16. Di Bernardo, P.; Zanonato, P.; Tian, G.; Tolazzi, M.; Rao, L. *J. Chem. Soc. Dalton Trans*. **2009**, 23, 4450.
17. Zanonato, P.; Di Bernardo, P.; Bismondo, A.; Liu, G.; Chen, X.; Rao, L. *J. Am. Chem, Soc.* **2004**, 126, 5515.
18. Gans, P.; Sabatini, A.; Vacca, A. *Talanta* **1996**, 43, 1739.
19. Hummel, W.; Anderegg, G.; Puigdomènech, I.; Rao, L.; Tochiyama, O. "*Chemical Thermodynamics of Compounds and Complexes of: U, Np, Pu, Am, Tc, Zr, Ni and Se*

with Selected Organic Ligands", (Mompean, F. J.; Illemassene, M.; Perrone, J. eds.), Amsterdam: Elsevier B.V. 2005.

20. Rao, L.; Srinivasan, T. G.; Garnov, A. Yu.; Zanonato, P.; Di Bernardo, P.; Bismondo, A. *Geochim. Cosmochim. Acta* **2004**, 68, 4821.
21. Arnek, R. *Arkiv Kemi* **1970**, 32, 81.
22. NIST Standard Reference Database 46: *NIST Critically Selected Stability Constants of Metal Complexes Database,* Version 8.0, U.S. Department of Commerce, 2004.
23. Jϕrgensen, C. K. *Absorption Spectra and Chemical Bonding in Complexes*, Pergamon Press, London, 1962.
24. Jϕrgensen, C. K.; Judd, B. R. *Mol. Phys*. **1964**, 8, 281.
25. Judd, B. R. *Atomic theory and optical spectroscopy*, in: Handbook on the Physics and Chemistry of Rare Earths, Vol.11, Eds. K. A. Gschneidner Jr. and L. Eyring, North-Holland, Amsterdam, Ch.74, 1988.
26. Mason, S. F.; Peacock, R. D.; Stewart, B. *Chem. Phys. Lett*. **1974**, 29, 149.
27. Bünzli, J-C. G.; Wessner, D. *Coord. Chem. Rev.* **1984**, 60, 191.
28. Horrocks Jr., W. DeW.; Sudnick, D. R. *J. Am. Chem. Soc*. **1979**, 101, 334.
29. Barthelemy, P. P.; Choppin, G. R. *Inorg. Chem*. **1989**, 28, 3354.
30. Kimura, T.; Nagaishi, R.; Kato, Y.; Yoshida, Z. *Radiochim. Acta* **2001**, 89, 125.
31. Rizkalla, E. N., Choppin, G. R.: in "*Handbook on the Physics and Chemistry of Rare Earths, Vol. 18 – Lanthanides/Actinides: Chemistry*" (Gschneider, K. A. Jr., Eyring, L., Choppin, G. R., Lander, G. H., ed.) Elsevier Science B.V., New York 1994.

32. Bertrand, P. A., Choppin, G. R.: in Gmelin Handbook of Inorganic Chemistry, U, Suppl. Vol. D1, Haase V. and Keim R., ed., Springer-Verlag, Berlin-Heidelberg, 1983, pp. 195-279.
33. Henrie, D. E.; Fellows, R. L.; Choppin, G. R. *Coord. Chem. Rev*. **1976**, 18, 199.
34. Choppin, G. R.; Henrie, D. E.; Buijs, K. *Inorg. Chem*. **1966**, 5, 1743.
35. Rao, L.; Tian, G. *Inorg. Chem*. **2009**, 48, 964.

Table 1 Thermodynamic data on Nd(III)/lactate and Eu(III)/lactate complexation at different temperatures (I = 1.05 mol·kg^{-1} $NaClO_4$). The values of logβ_m for Nd(III)/lactate complexes were calculated with Eq. (2) from the average of the two values obtained by potentiometry and spectrophotometry. [a]Values of logβ_M obtained by spectrophotometry. [b]Data for D-lactate at I = 2.0 M from the literature. [c]Values of logβ_M obtained by luminescence spectroscopy. [d]Values of logβ_M obtained by potentiometry at I = 1.0 M NaTf (sodium triflate). All other values of logβ_M were determined by potentiometry in the present work (p.w.).

Reaction	t °C	logβ_M	logβ_m	ΔH kJ·mol^{-1}	ΔS J·K^{-1}·mol^{-1}	Ref.
$H^+ + L^- = HL(aq)$	10	3.46 ± 0.04	3.44 ± 0.04			5
	25	3.67 ± 0.03	3.65 ± 0.03	-0.55 ± 0.22	68 ± 1	
		3.65 ± 0.02		-1.48 ± 0.04	65 ± 1	12[d]
	40	3.68 ± 0.04	3.66 ± 0.04			
	55	3.70 ± 0.04	3.68 ± 0.04			
	70	3.72 ± 0.04	3.70 ± 0.04			
$Nd^{3+} + L^- = NdL^{2+}$	10	2.71 ± 0.14 2.42 ± 0.02[a]	2.54 ± 0.14			p.w.
	25	2.67 ± 0.06 2.58 ± 0.05[a]	2.60 ± 0.06	-2.02 ± 0.22	43 ± 1	
		2.45 ± 0.03		-13	2	22[b]
		2.60 ± 0.01		-3.96 ± 0.07	36 ± 1	12[d]
	40	2.70 ± 0.22 2.47 ± 0.20[a]	2.56 ± 0.22			
	55	2.74 ± 0.11 2.60 ± 0.02[a]	2.65 ± 0.11			
	70	2.59 ± 0.11 2.49 ± 0.01[a]	2.52 ± 0.11			
$Nd^{3+} + 2L^- = NdL_2^+$	10	4.57 ± 0.13 4.42 ± 0.05[a]	4.46 ± 0.13			p.w.
	25	4.52 ± 0.05 4.60 ± 0.06[a]	4.52 ± 0.05	-7.87 ± 0.20	60 ± 1	
		4.38 ± 0.02		-4	62	22[b]
		4.66 ± 0.02		-8.4 ± 0.1	61 ± 2	12[d]
	40	4.30 ± 0.20 4.45 ± 0.05[a]	4.34 ± 0.20			
	55	4.53 ± 0.31 4.46 ± 0.08[a]	4.45 ± 0.31			
	70	4.13 ± 0.11 4.44 ± 0.06[a]	4.25 ± 0.11			
$Nd^{3+} + 3L^- = NdL_3$	10	6.20 ± 0.15 6.28 ± 0.15[a]	6.18 ± 0.15			p.w.
	25	6.01 ± 0.06 6.15 ± 0.24[a]	6.02 ± 0.06	-11.90 ± 0.32	75 ± 2	
		5.60 ± 0.04				22[b]

		5.6 ± 0.1		-24.4 ± 0.5	25 ± 2	12[d]
	40	5.96 ± 0.21	6.02 ± 0.21			
		6.20 ± 0.15[a]				
	55	5.98 ± 0.11	6.14 ± 0.11			
		6.41 ± 0.17[a]				
	70	5.89 ± 0.10	5.79 ± 0.10			
		5.81 ± 0.22[a]				
$Eu^{3+} + L^{-} = EuL^{2+}$	10	2.90 ± 0.36	2.88 ± 0.36			p.w.
		2.91 ± 0.24[c]				
	25	2.80 ± 0.02	2.78 ± 0.02	-2.14 ± 0.77	46 ± 3	
		2.99 ± 0.17[c]				
		2.51 ± 0.02		-6.2	27	22[b]
	40	2.78 ± 0.15	2.76 ± 0.15			
		2.91 ± 0.17[c]				
	55	2.70 ± 0.11	2.68 ± 0.11			
		3.04 ± 0.24[c]				
	70	2.81 ± 0.19	2.79 ± 0.19			
		2.99 ± 0.23[c]				
$Eu^{3+} + 2L^{-} = EuL_2^{+}$	10	4.90 ± 0.37	4.86 ± 0.37			p.w.
		5.02 ± 0.22[c]				
	25	4.76 ± 0.02	4.72 ± 0.02			
		5.09 ± 0.23[c]				
		4.62 ± 0.02		-4.31± 0.42	76 ± 2	22[b]
	40	4.57 ± 0.11	4.53 ± 0.11			
		5.04 ± 0.27[c]				
	55	4.43 ± 0.15	4.39 ± 0.15			
		5.00 ± 0.27[c]				
	70	4.49 ± 0.21	4.45 ± 0.21			
		4.88 ± 0.25[c]				
$Eu^{3+} + 3L^{-} = EuL_3^{+}$	10	6.24 ± 0.30	6.18 ± 0.30			p.w.
		6.03 ± 0.28[c]				
	25	6.33 ± 0.02	6.27 ± 0.02	-12.37 ± 0.67	78 ± 29	
		6.09 ± 0.27[c]				
		5.85 ± 0.04		-20	41	22[b]
	40	6.25 ± 0.21	6.19 ± 0.21			
		6.17 ± 0.25[c]				
	55	6.28 ± 0.11	6.22 ± 0.11			
		5.95 ± 0.26[c]				
	70	6.33 ± 0.20	6.27 ± 0.20			
		5.98 ± 0.26[c]				

Table 2 Luminescence lifetime and the average number of O-H oscillators per Eu(III) in Eu(III)/lactate solutions (C_{Eu} = 0.017 – 0.020 M, I = 1.0 M $NaClO_4$, λ_{ex} = 394 nm, λ_{em} = 615 – 620 nm). *In the calculations of $n_{OH,cal}$, a hydration number of nine was used for the free Eu^{3+} cation.

$C_{Lactate}$	τ_{exp} (± 4)	$n_{OH,\,exp}$	$n_{OH,\,cal}$*	
mM	μs	(± 1.0)	Coordination mode (b)	Coordination mode (c)
0	109.1	18.1	18.0	18.0
5.0	110.4	17.8	17.8	17.9
9.8	111.2	17.7	17.5	17.7
14.6	112.7	17.5	17.0	17.2
19.2	117.3	16.8	15.7	16.3
23.8	125.7	15.6	13.9	14.9
28.3	139.9	14.0	12.4	13.8
32.7	150.4	13.0	11.3	13.0
37.0	156.9	12.4	10.5	12.4
41.3	163.3	11.9	9.9	11.9
45.5	169.6	11.5	9.4	11.6
49.6	175.2	11.1	9.0	11.3
53.6	179.3	10.8	8.7	11.0
57.5	183.8	10.5	8.5	10.9
61.4	187.5	10.3	8.3	10.7
65.2	190.9	10.1	8.1	10.6
69.0	193.5	10.0	8.0	10.5
72.7	196.9	9.8	7.9	10.4

Table 3 Optical absorption oscillator strength of the hypersensitive transition ($^4I_{9/2} \rightarrow {}^4G_{5/2}, {}^2G_{7/2}$) of Nd(III) in aqueous solutions (lac – lactate, ac – acetate, p.w. – present work).

Species	Medium	$f = \int \varepsilon(\nu) d\nu$		Ref.
		25°C	70°C	
Nd^{3+}	1 M $NaClO_4$	9.59×10^{-6}	9.12×10^{-6}	p.w.
$Nd(lac)^{2+}$		1.27×10^{-5}	1.25×10^{-5}	
$Nd(lac)_2^{+}$		1.64×10^{-5}	1.60×10^{-5}	
$Nd(lac)_3(aq)$		1.96×10^{-5}	1.99×10^{-5}	
Nd^{3+}	1 M $NaClO_4$	9.53×10^{-6}	9.05×10^{-6}	35
$NdNO_3^{2+}$		1.46×10^{-5}	1.48×10^{-5}	
Nd^{3+}	2 M $NaClO_4$	7.9×10^{-6}		34
$Nd(ac)^{2+}$		9.5×10^{-6}		
$Nd(ac)_2^{+}$		4.6×10^{-5}		

Figure Captions

Fig. 1 Potentiometric titrations of Nd(III)/lactate (left) and Eu(III)/lactate (right) complexation at 25°C (upper) and 70°C (lower). I = 1.05 mol·kg^{-1} $NaClO_4$, V^0 = 20.0 ml, titrant 0.9994 M $HClO_4$. Symbols: ◇ - experimental data (pC_H); dashed curve – fit (pC_H); solid lines - percentage of Nd(III) or Eu(III) species (right y-axis). Initial concentrations ($C_H^0/C_M^0/C_L^0$ in mM): Upper left - 7.93/11.18/150.0; lower left - 7.93/11.18/110.0; upper right - 4.905/12.08/150.0; lower right - 3.27/8.05/100.0.

Fig. 2 Representative spectrophotometric titrations of Nd(III)/lactate complexation. I = 1.05 mol·kg^{-1} $NaClO_4$. Upper figures – absorption spectra of the titrations at 25 and 70°C. Initial solution in cuvette: 2.50 mL, 0.1118 M $Nd(ClO_4)_3$/0.0793 M $HClO_4$; titrant: 1.00 M sodium lactate. Lower figures – calculated molar absorptivity of Nd^{3+} and Nd(III)/lactate complexes.

Fig. 3 Calorimetric titrations of Nd(III)/lactate (left) and Eu(III)/lactate (right) complexation, t = 25°C, I = 1.00 M $NaClO_4$. V^0 = 0.900 mL, titrant 0.300 M $HClO_4$. Initial concentrations ($C_H^0/C_M^0/C_L^0$ in mM): Lower left - (1) 17.60/24.80/66.70; (2) 13.20/18.60/66.70; (3) 8.80/12.40/66.70; (4) 4.40/6.20/66.70. Lower right - (1) 5.45/13.40/66.70; (2) 3.63/8.94/66.70 mM; (3) 1.82/4.47/66.70. The upper figures are the thermograms of the first titration for Nd(III) and Eu(III) systems.

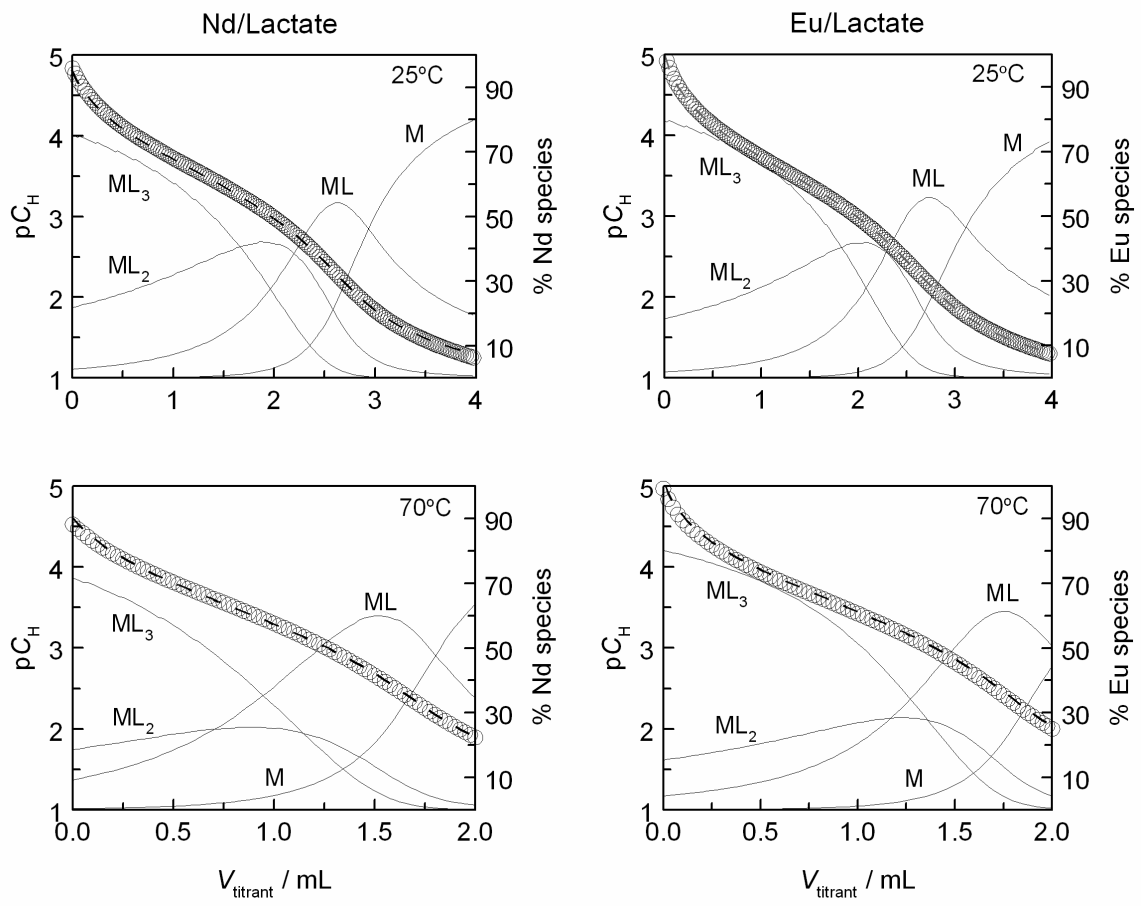
Fig. 4 Luminescence emission spectra (upper) and luminescence decay (lower) of Eu(III)/lactate systems, t = 25°C, I = 1.00 M $NaClO_4$. V^0 = 2.50 mL, C_H^0 = 20.0 mM, C_{Eu}^0 = 2.00 mM; titrant: 0.500 M sodium lactate; $[lactate]_{total}$ increased from 0 to 0.072 M during the titration. Excitation wavelength: 394 nm.

Fig. 5 Coordination modes in Eu(III)/lactate complexes. (a) bidentate with the carboxylate group; (b) bidentate (carboxylate + deprotonated α-hydroxyl group); (c) bidentate (carboxylate + protonated α-hydroxyl group).

Fig. 6 Correlation between the pK_a of monocarboxylic acids and the formation constants of Ln(III)/carboxylate complexes. (●) Nd(III)/lactate from this work (I = 1 M, t = 25°C). Other values are from ref. 22 (I = 1 - 2 M, t = 20 - 25°C): (1) Eu(III)/chloroacetate, (2) Sm(III)/formate, (3) Eu(III)/3-chloropropanoate, (4) Nd(III)/acetate, (5) Nd(III)/propanoate, (6) Nd(III)/glycolate, (7) Nd(III)/lactate, (8) Nd(III)/2-hydroxy-2-methylpropanoate.

Fig. 7 Comparison between the experimental values of $n_{OH,exp}$ (●) from luminescence lifetime measurements and the calculated values of $n_{OH,cal}$ based on coordination modes (b, □) and (c, ▽). C_{Eu} = 0.017 – 0.020 M, I = 1.0 M, t = 25°C. n_{OH} denotes the number of O-H oscillators in the inner coordination sphere of Eu(III).

Fig. 8 Effect of temperature on Nd(III)/lactate and Eu(III)/lactate complexation. I = 1.05 mol·kg^{-1} $NaClO_4$. (●○) ML, (▲△) ML_2, (▼▽) ML_3. Solid symbols – data obtained by potentiometry; open symbols – data obtained by absorption spectroscopy (for Nd) or luminescence spectroscopy (for Eu).



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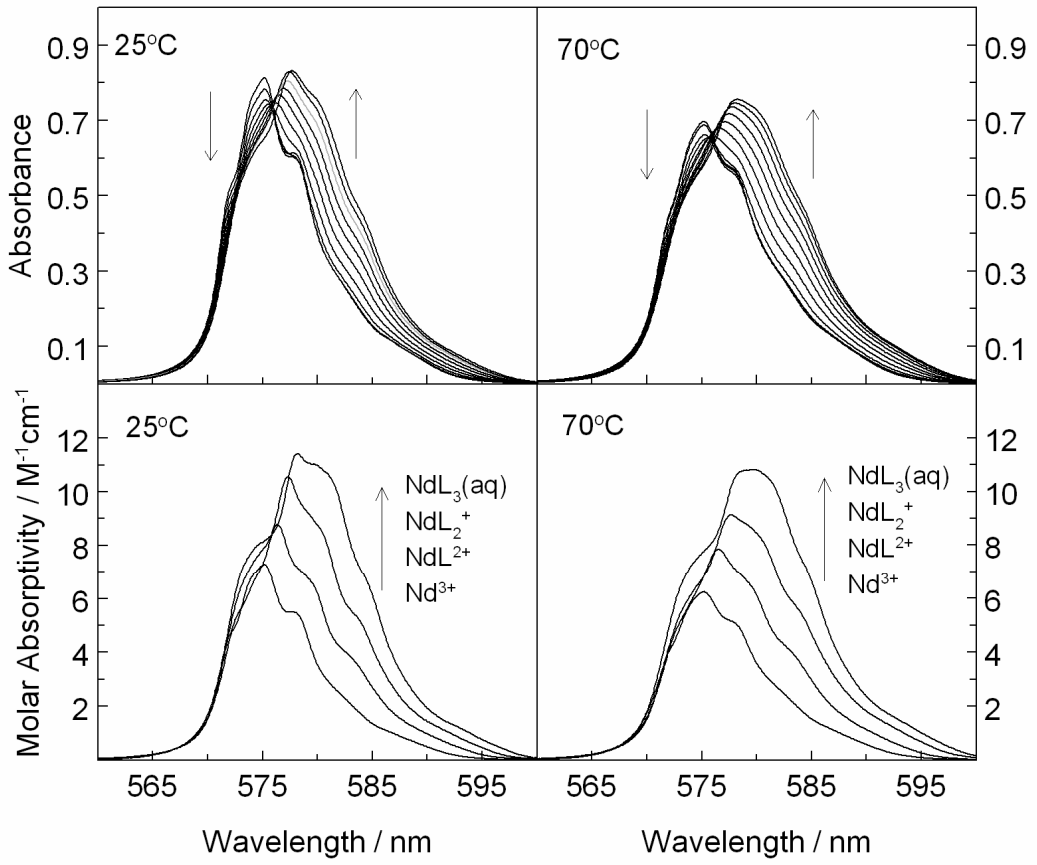

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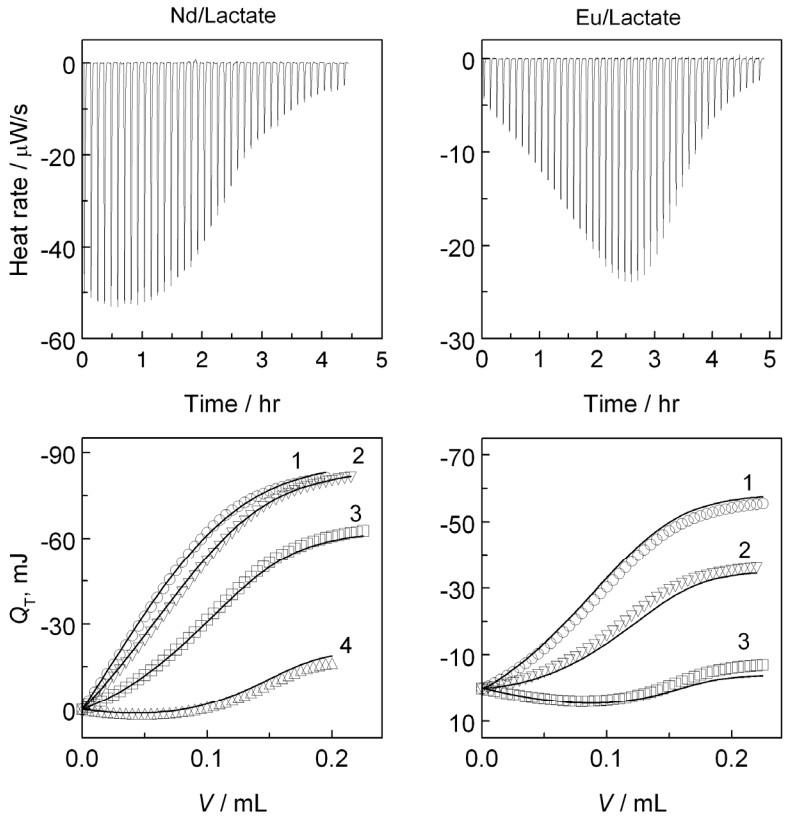

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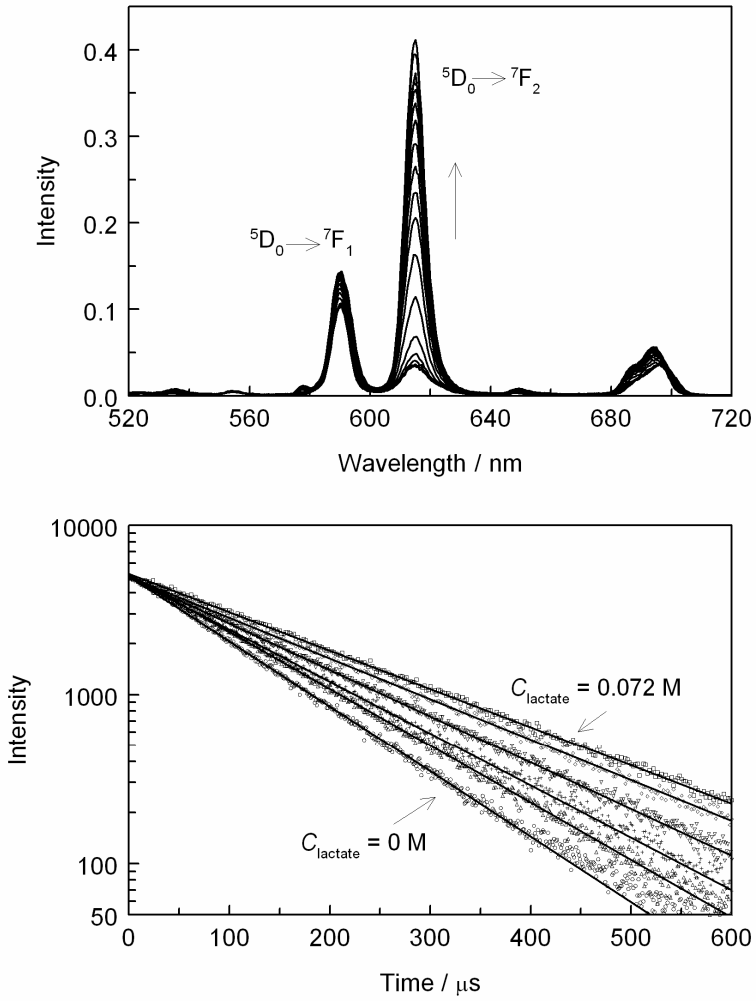

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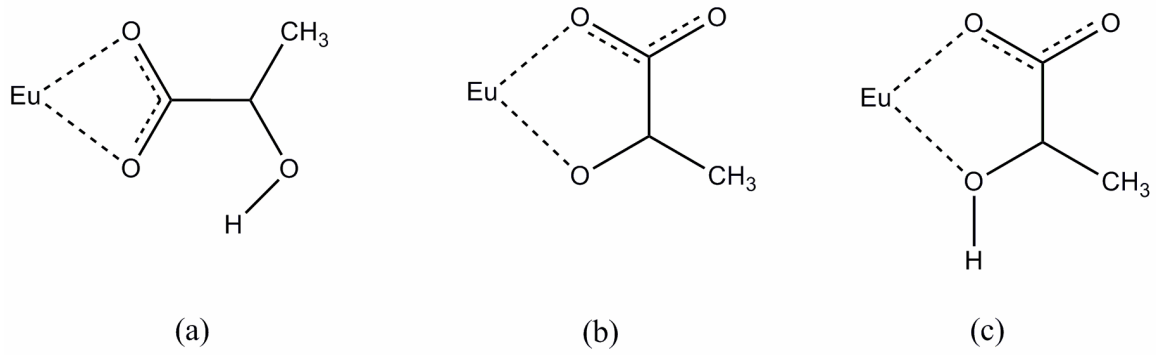

(a) (b) (c)

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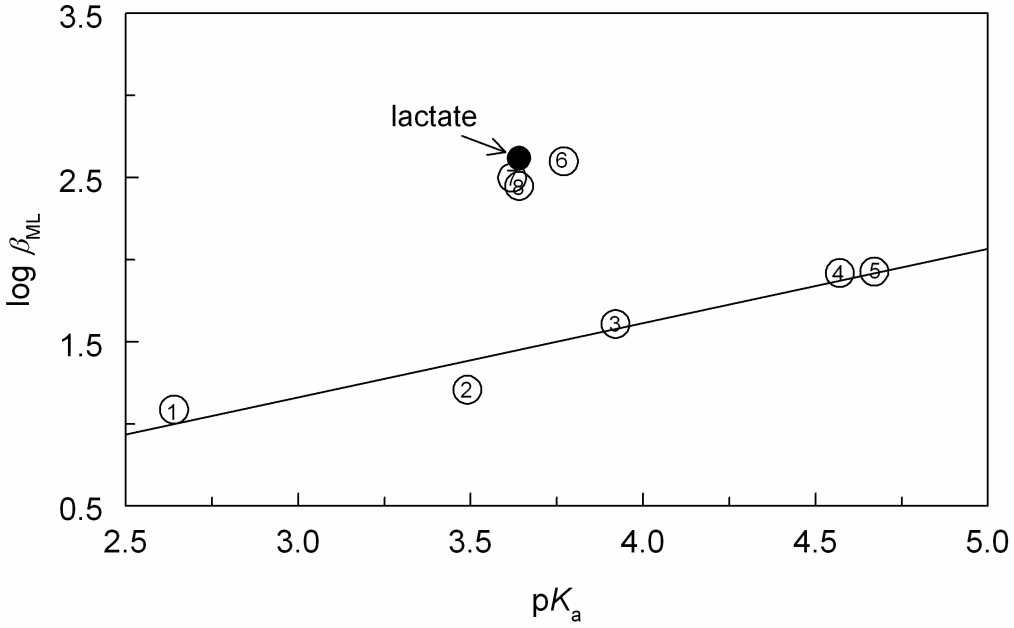

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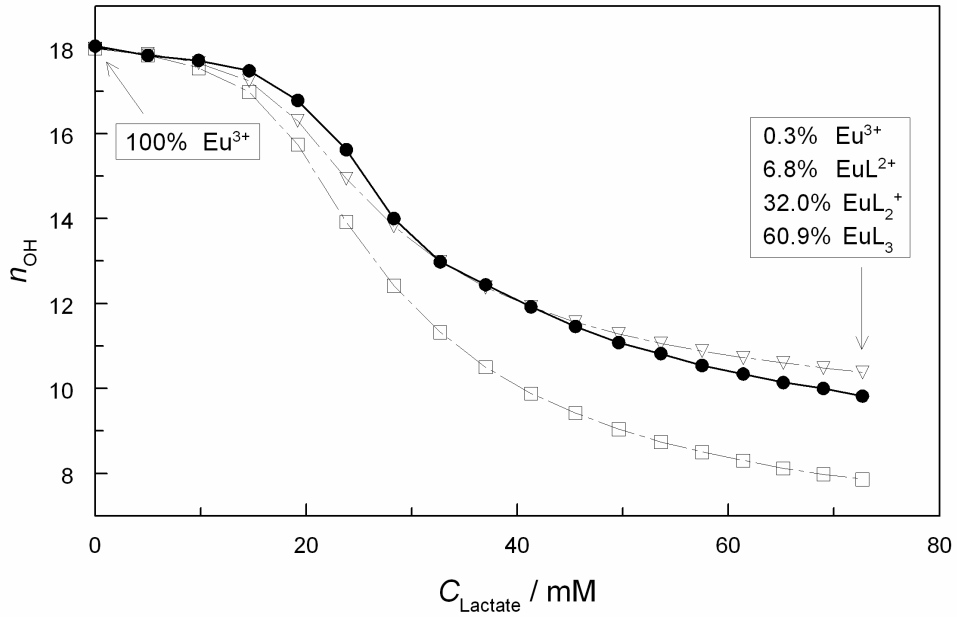

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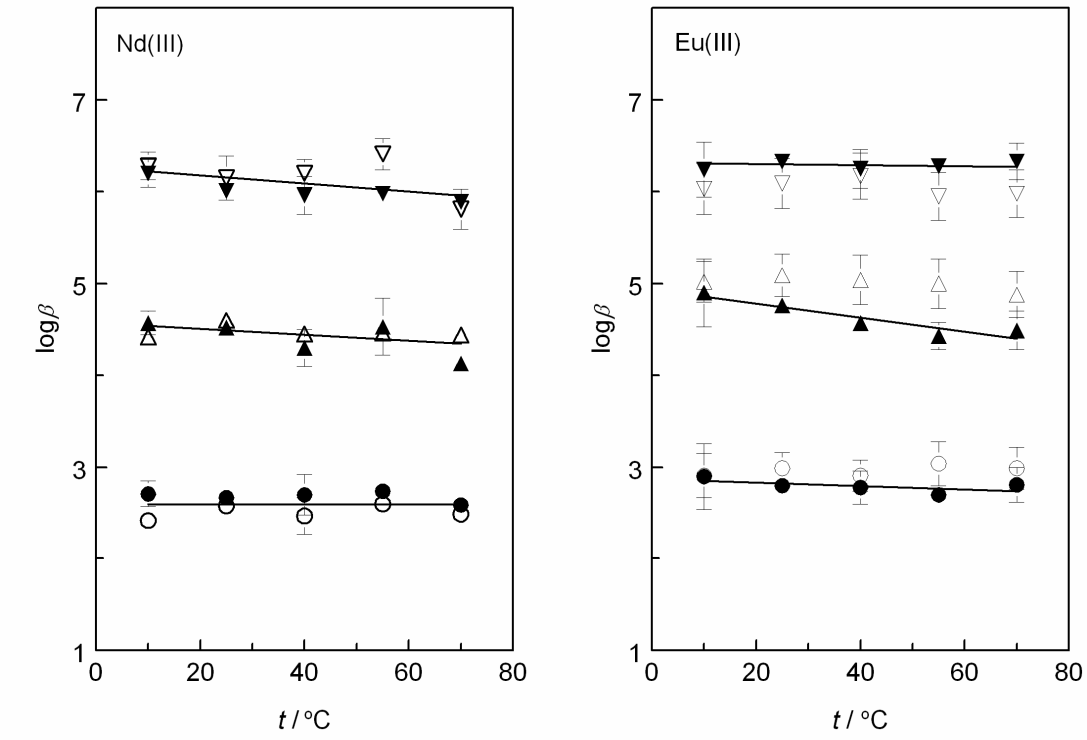

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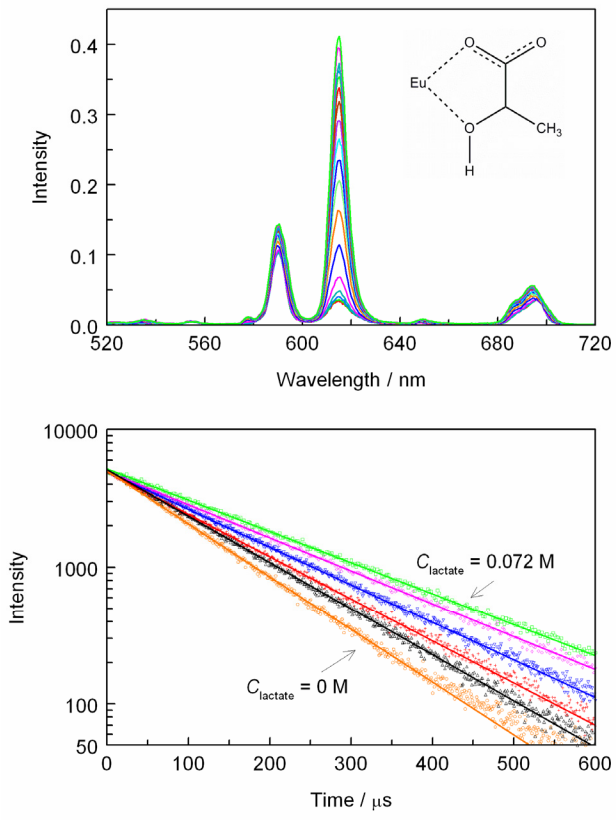
TOC graphic



Thermodynamic and spectroscopic data indicate that lactate forms bidentate chelate inner-sphere complex with trivalent lanthanides in aqueous solutions. The protonated α-hydroxyl group of lactate participates in the complexation. The complexes become weaker at higher temperatures due to the exothermic contribution of the hydroxyl group coordination to the overall enthalpy of complexation.