

A potentiometric and microcalorimetric study of the complexation of trivalent europium with lactate: The ionic strength dependency of $\log \beta'_n$, $\Delta_r H_{m,n}$ and $\Delta_r S_{m,n}$

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ABSTRACT

The complexation of Eu(III) by lactate and the ligand protonation were studied at 25 °C as a function of the ionic strength ($I_m = 0.10 - 5.61 \text{ mol kg}^{-1} \text{ H}_2\text{O, NaCl}$). The experimental formation constants of the three $[\text{Eu}(\text{Lac})_n]^{3-n}$ ($n = 1, 2, 3$) mononuclear complexes ($\log \beta'_n$) and the protonation constant of lactate ($\log \beta'_{\text{HLac}}$) were determined by potentiometric titrations. The experimental values were extrapolated to zero ionic strength by means of the SIT approach, yielding the thermodynamic constants ($\log \beta_n^0$) and the specific ion interaction coefficients of the ionic species ($\epsilon(i,k)$). The reaction enthalpies ($\Delta_r H_{m,n}$), determined independently by isothermal calorimetry, and entropies ($\Delta_r S_{m,n}$) are also reported. The ionic strength dependence of $\Delta_r H_{m,n}$ was fitted by means of the enthalpy SIT approach, giving the standard reaction enthalpies ($\Delta_r H_{m,n}^0$), entropies ($\Delta_r S_{m,n}^0$) and the partial molar enthalpy specific ion interaction coefficients ($\Delta \epsilon_l(i,k)$). The results show negative conditional reaction enthalpies for all complexes, which become more exothermic with increasing ionic strength. Simultaneously, the $\Delta_r S_{m,n}$ decrease steadily with I_m , resulting in a gradual change of the driving force of the reactions: at low ionic strength the reaction is driven almost exclusively by entropy. As I_m increases the contribution of the enthalpy term becomes relevant and the reactions are driven almost equally by $\Delta_r H_{m,n}$ and $\Delta_r S_{m,n}$ at the highest value of I_m studied.

1. Introduction

The storage of high-level nuclear waste in deep geological formations is considered as the best option for its final disposal. Actinide elements form in the reactor due to neutron capture reactions and subsequent β^- -decay reactions and are thus present in the nuclear waste. These elements will determine the radiotoxicity of the waste over very long time scales. A comprehensive knowledge of the geochemical reactions of the actinides is therefore of major importance for the safety case of a nuclear waste repository. Organic molecules are present in almost all natural systems as well as used in different technical applications (e.g. compounds in cement admixtures). They range from larger macromolecular organic matter (e.g. humic and formic acids, superplasticizers) to small molecules like acetate or lactate. These organic compounds are potential ligands towards the actinides and

capable of forming stable metal-ligand complexes, which may have a strong impact on their chemical behavior. In the case of trivalent actinides, lanthanides can serve as non-radioactive analogues in these complexation studies, due to their similar chemical behavior.

Lactate is for several reasons of particular interest as a ligand for actinides and REE. Lactate is present in the pore water of natural clay formations and may interact with actinides in natural systems [1,2]. The formation of An-lactate complexes may alter the sorption behavior of the metal ions and would therefore influence the mobility of the respective radionuclides. Furthermore, lactate may serve as a representative for a broad variety of small carboxylic acids with hydroxyl groups in α -position as well as natural occurring macromolecular ligands (e.g. humic and fulvic acids). Furthermore, lactate was used as buffer of the aqueous phase within TALSPEAK process, which is a possible recycling process of spent nuclear fuel, which is an alternative

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to its direct disposal [3–8].

A large number of studies on the thermodynamics of the complexation of trivalent lanthanides and actinides with lactate are available in the literature, giving stability constants ($\log \beta'_n$), reaction enthalpies ($\Delta_r H_{m,n}$) and entropies ($\Delta_r S'_{m,n}$) [9–20]. However, the majority of these studies were performed at defined experimental conditions (e.g. fixed ionic strength), reporting only conditional data. The majority of the available conditional thermodynamic data is valid only for NaClO_4 media. Only few data are available for NaCl solutions, despite NaCl being the main constituent of the ionic matrix in pore waters of clay formations and brines in salt rock formations. For example, pore waters of certain clay rock formations in northern Germany show high electrolyte concentrations leading to aqueous solutions of high ionic strengths ($I_m \leq 4 \text{ mol L}^{-1}$). Unfortunately, no systematic studies on the ionic strength dependence of the thermodynamics of the An and Ln complexes with lactate are available in the literature. Besides the change of the conditional stability constants, it is known that the ionic strength significantly affects the reaction enthalpy and entropy. The complexation reaction may even change from exothermic to endothermic or vice versa with increasing concentration of a background electrolyte. Therefore, a detailed knowledge on the ionic strength dependency of thermodynamic data of the actinides is mandatory.

The present paper gives a detailed potentiometric and microcalorimetric study of the protonation reaction of lactate and the formation of the $[\text{Eu}(\text{Lac})_n]^{3-n}$ complexes ($n = 1, 2, 3$) in diluted to concentrated NaCl media, yielding the conditional thermodynamic data as a function of the ionic strength. These data are extrapolated to the IUPAC reference state ($I_m = 0 \text{ mol kg}^{-1} \text{ H}_2\text{O}$, $\gamma_i = 1.0$) with the specific ion interaction theory (SIT), yielding the thermodynamic standard state data ($\log \beta_{m,n}^0$, $\Delta_r H_{m,n}^0$, $\Delta_r S_{m,n}^0$). Furthermore, the SIT specific ion interaction coefficients of the ionic species ($\epsilon_{i,k}$) and of the reaction enthalpy ($\Delta \epsilon_{L,i}$) are determined. These data are required for the extrapolation of standard state data to real conditions. $\text{Eu}(\text{III})$ is used as a non-radioactive analogue for trivalent actinides like $\text{Am}(\text{III})$ or $\text{Cm}(\text{III})$.

2. Experimental section

All samples were prepared on the molal concentration scale ($\text{mol kg}^{-1} \text{ H}_2\text{O}$, “m”) to avoid changes of the concentration due to density variations at different ionic strengths. MilliQ© water was used in the preparation of all samples. All used chemicals were reagent grade or higher in purity and used as purchased without further purification. The experiments were performed under atmospheric pressure and at room temperature. The ionic strength of all samples was adjusted by adding solid NaCl (Merck, Suprapure) and set to values of $I_m = 0.10$ to $5.61 \text{ mol kg}^{-1} \text{ H}_2\text{O}$, respectively. The proton concentration was adjusted by addition of aliquots of HCl and NaOH (both Merck Titrisol) in appropriate dilutions. The pH of the solutions varied in the range of $\text{pH} = 3.0$ – 5.1 , depending on the total concentrations of $\text{Eu}(\text{III})$, lactate and H^+ during the titration experiments. The initial concentration of $\text{Eu}(\text{III})$ in the samples was set to $[\text{Eu}(\text{III})]_{\text{ini}} = 10^{-2}$ or $1.4 \cdot 10^{-2} \text{ mol kg}^{-1} \text{ H}_2\text{O}$ by addition of anhydrous $\text{Eu}(\text{Cl}_3)_6$. Stock solutions with different concentrations of lactate ($[\text{Lac}]_{\text{tot}} = (10^{-2}, 2 \cdot 10^{-2}, 10^{-1}) \text{ mol kg}^{-1} \text{ H}_2\text{O}$, $[\text{H}^+]_{\text{tot}} = (10^{-1}, 2 \cdot 10^{-1}, 5 \cdot 10^{-3}) \text{ mol kg}^{-1} \text{ H}_2\text{O}$) were prepared. For this, two commercial lactic acid solutions (DL and L, 85% (w/w), Sigma-Aldrich) as well as solid Na-L-Lactate (Applichem) was used. The chemical compounds that were used in the present work are summarized in Table 1.

2.1. Potentiometric titrations

A total of 41 potentiometric titrations were performed; all data were collected at 25°C in sodium chloride ionic media. The electromotive force (*emf*) was measured using an Amel Model 338 pH-meter equipped with a double junction Metrohm combination glass electrode (Model 6.0259.100). The outer jacket of the electrode was filled with a 3.0 mol

Table 1

Chemical compounds used in the present work for sample preparation.

Chemical Name	Source	Initial Mole Fraction Purity
Lactic acid (D/L) ^a	Sigma-Aldrich	0.99
Lactic acid (L) ^b	Sigma-Aldrich	0.99
Na-L-Lactate	Applichem	0.99
HCl (Titrisol)	Merck Millipore	0.99
NaOH (Titrisol)	Merck Millipore	0.99
NaCl (Suprapure)	Merck Millipore	0.9999
$\text{Eu}(\text{Cl}_3)_6$ (anhydrous)	Merck Millipore	0.9999

^a used with Thermometric 2277 Thermal Activity Monitor.

^b used with ITC 200 (GE Healthcare).

$\text{L}^{-1} \text{ NaCl}$ solution. The experimental data were collected using a home-built PC-controlled automatic data acquisition system. Equilibrium was assumed when the *emf* change was less than 0.1 mV during 120 s , typically after about 4 – 5 min . Prior to each potentiometric titration, the electrode was standardized to measure the hydrogen ion concentration. Eq. (1) was used to obtain E^0 and the electrode junction potentials for the hydrogen ion, $E_{j,H}$.

$$E = E^0 + \frac{RT}{nF} \cdot \ln[\text{H}^+] + E_{j,H}[\text{H}^+] \quad (1)$$

Junction potentials for the hydroxide ion were negligible in our experiments. Experimental equilibrium constants for the lactate protonation and complexation of europium in Table 2 were obtained by Hyperquad 2006. [21]

3. Calorimetric titrations

The calorimetric titrations were performed by two isothermal titration calorimeters, with different sample volumes. The first isothermal calorimeter, Thermometric 2277 Thermal Activity Monitor (University of Padova), is equipped with a 2.5 mL cell and is very well suited for measurements on stable elements (e.g. lanthanides) and radionuclides with long half-lives, e.g. U , Th which can be handled in larger amounts. The measurements were performed by addition of aliquots of titrant (50 adds, $10 \mu\text{L}$ of ligand solution) to the reaction vessel containing the $\text{Eu}(\text{III})$ sample solution. A time interval of 480 – 840 s between two additions was applied. The second isothermal titration calorimeter ITC 200 (GE Healthcare, Technische Universität Dresden) has a distinctively smaller sample volume of $200 \mu\text{L}$. This enables the investigation of solutions of radionuclides with higher activities (e.g. Am or Pu). The results on the $\text{Eu}(\text{III})$ -lactate system obtained with both calorimeter types were compared and used to validate the micro titration calorimeter ITC2000 with regard to thermodynamic investigations with trivalent actinides. The measurements with ITC200 were performed by addition of 0.5 – $2 \mu\text{L}$ aliquots of the titrant (at least 19 additions, $V_{\text{max}} = 40 \mu\text{L}$) to the $200 \mu\text{L}$ $\text{Eu}(\text{III})$ -solution in the cell. A

Table 2

Conditional and thermodynamic (first row) $\log \beta_{m,n}$ for the protonation of lactate and for the formation of the $[\text{Eu}(\text{Lac})_n]^{3-n}$ ($n = 1, 2, 3$) complexes. I_m = molal ionic strength ($\text{mol kg}^{-1} \text{ H}_2\text{O}$), σ = confidence interval.

I_m (NaCl) mol kg^{-1}	$\log \beta_{m,\text{Hlac}} \pm 3\sigma$	$\log \beta_{m,1} \pm 3\sigma$	$\log \beta_{m,2} \pm 3\sigma$	$\log \beta_{m,3} \pm 3\sigma$
0.00	3.88 ± 0.20	3.48 ± 0.15	6.16 ± 0.18	7.76 ± 0.48
0.10	3.67 ± 0.20	2.75 ± 0.06	5.02 ± 0.06	6.17 ± 0.18
0.51	3.59 ± 0.20	2.50 ± 0.06	4.54 ± 0.06	5.72 ± 0.18
1.02	3.62 ± 0.20	2.48 ± 0.09	4.31 ± 0.09	5.84 ± 0.18
2.09	3.66 ± 0.20	2.41 ± 0.09	4.26 ± 0.12	5.59 ± 0.18
5.61	4.06 ± 0.20	2.62 ± 0.05	4.54 ± 0.05	5.78 ± 0.06

$p = 10^5 \text{ Pa}$ (atm); $T = 293 \text{ K}$ (r.t.).

Standard uncertainties for temperature, pressure and molality are $u(T) = \pm 1 \text{ K}$, $u(p) = 0.5 \text{ kPa}$ and $u(m) = \pm 10^{-5} \text{ mol kg}^{-1} \text{ H}_2\text{O}$.

time interval of 120–180 s between two ligand additions was applied. The performance of the ITC-200 titration calorimeter was validated by measuring the enthalpy of the reaction of CaCl_2 with EDTA in MES buffer at 25 °C. The obtained value ($-16.96 \pm 0.05 \text{ kJ mol}^{-1}$) is in good agreement with the literature data ($-17.97 \pm 1.80 \text{ kJ mol}^{-1}$) (Test Kit of GE Healthcare).

The enthalpies of the protonation of lactate and of the complexation of Eu(III) with lactate were determined by multiple titrations experiments with different proton to lactate or metal to lactate ratios, respectively. For all measurements the temperature was kept constant at 25 °C. Reaction heats ($Q_{\text{exp,step}}$) were corrected for the heat of dilution of the titrant ($Q_{\text{dil,step}}$), which was determined in separate runs. The net reaction heat ($Q_{\text{r,step}}$) for each addition was obtained from the difference $Q_{\text{r,step}} = Q_{\text{exp,step}} - Q_{\text{dil,step}}$. Successively, the experimental enthalpies of protonation and complexation were determined by least-squares minimization of $Q_{\text{r,step}}$ with the program *LETACALPD* (a home modified version of the *LETAGROP* program [22]). The stability constant of the ionic product of water and the heat of formation of water were taken from the NIST database [23].

4. Results and discussion

4.1. Stability constants of the protonation of lactate and the $[\text{Eu}(\text{Lac})_n]^{3-n}$ complexes at $I_m = 0\text{--}5.61 \text{ mol kg}^{-1} \text{ H}_2\text{O}$ (NaCl)

The stability constants of the protonation of lactate ($\log \beta_{\text{m,HLac}}$; eq 2) and of the formation of the $[\text{Eu}(\text{Lac})_n]^{3-n}$ complexes ($\log \beta_{\text{m,n}}$, $n = 1, 2, 3$; Eq. (3)–(5)) were determined at different ionic strengths from the potentiometric titration data. The results are summarized in Table 2.



The stability constants decrease from low to medium ionic strength and increases slightly at higher ionic strength. This behavior results from the typical change of the activity coefficients (γ_i) of the ionic species, which initially decrease to a minimum at intermediate ionic strength and thereafter increase at higher I_m . The experimental $\log \beta_{\text{m,n}}$ are extrapolated to zero ionic strength ($I_m = 0 \text{ mol kg}^{-1} \text{ H}_2\text{O}$) using the specific ion interaction theory (SIT, eq 6), yielding the thermodynamic equilibrium constants ($\log \beta_{\text{m,n}}^0$).

$$\log \beta'_{\text{m,n}} - \Delta z^2 \cdot D = \log \beta_{\text{m,n}}^0 - \Delta \varepsilon \cdot I_m \quad (6)$$

With $\Delta z^2 = \sum z_{\text{Products}}^2 - \sum z_{\text{Reactants}}^2$, $\Delta \varepsilon = \sum \varepsilon_{\text{Products}} - \sum \varepsilon_{\text{Reactants}}$ and $D = (0.509 \cdot (I_m)^{0.5}) \cdot (1 + 1.5 \cdot (I_m)^{0.5})^{-1}$. The thermodynamic values are reported in the first row of Table 2. The value of $\log \beta_{\text{m,HLac}}^0 = 3.88 \pm 0.20$ for the protonation of lactate is in excellent agreement with the literature. [23,24]

Literature data of stability constants of the Eu(III) lactate complexes in NaCl media which allow a direct comparison are scarce. Therefore, the comparison is restricted to results of Danesi et al. [14] on the complexation of Eu(III) with lactate in $1.0 \text{ mol L}^{-1} \text{ H}_2\text{O}$ NaCl solution studied by means of solvent extraction. The given $\log \beta_{\text{m,1}}([\text{Eu}(\text{Lac})]^{2+}) = 2.95$ and $\log \beta_{\text{m,2}}([\text{Eu}(\text{Lac})]_2^+) = 4.40$ are slightly higher compared to the results of the present work, while the $\log \beta_{\text{m,3}}([\text{Eu}(\text{Lac})]_3) = 5.47$ is slightly lower. However, the two data sets agree within the error range. Barkleit et al. studied the complexation of Eu(III) with lactate in aqueous NaClO_4 solution ($I_m = 0.1 \text{ mol kg}^{-1} \text{ H}_2\text{O}$) using TRLFS and calculated the $\log \beta_{\text{m,n}}^0$ values with the SIT approach.²⁰ Their $\log \beta_{\text{m,n}}^0$ values of 3.14 ± 0.28 , 5.49 ± 0.28 and 7.07 ± 0.28 for $n = 1, 2$ and 3 , are approximately 0.5 logarithmic units lower compared to those of the present work. These differences may rise, at least

Table 3

Sum of the binary interaction coefficients $\Delta \varepsilon_{\text{on}}$ for the protonation of lactate and the formation of the $[\text{Eu}(\text{Lac})_n]^{3-n}$ ($n = 1, 2, 3$) complexes. σ = confidence interval.

Reaction	$\Delta \varepsilon_{\text{on}} \pm 3\sigma / \text{kg} \cdot \text{mol}^{-1}$
$\text{H}^+ + \text{Lac}^- \rightleftharpoons \text{HLac}$	-0.13 ± 0.05
$\text{Eu}^{3+} + \text{Lac}^- \rightleftharpoons \text{Eu}(\text{Lac})^{2+}$	-0.13 ± 0.06
$\text{Eu}^{3+} + 2 \text{Lac}^- \rightleftharpoons \text{Eu}(\text{Lac})_2^+$	-0.19 ± 0.12
$\text{Eu}^{3+} + 3 \text{Lac}^- \rightleftharpoons \text{Eu}(\text{Lac})_3$	-0.23 ± 0.18

$p = 1 \text{ bar (atm)}$; $T = 293 \text{ K (r.t.)}$.

Standard uncertainties for temperature, pressure and molality are $u(T) = \pm 1 \text{ K}$, $u(p) = 0.5 \text{ kPa}$ and $u(m) = \pm 10^{-5} \text{ mol kg}^{-1} \text{ H}_2\text{O}$.

in part, from the fact that the calculations were performed assuming $\varepsilon(\text{Lac}, \text{Na}^+) \approx \varepsilon(\text{Ac}, \text{Na}^+)$ and using estimated ε -values for the Eu(III) lactate species. In our case the $\log \beta_{\text{m,n}}^0$ are extrapolated directly from the experimental $\log \beta_{\text{m,n}}$ data.

Furthermore, a comparison with the structurally analogous ligand glycolate (gly) is made. Grenthe determined the conditional stability constants of the $\text{Eu}(\text{gly})_n^{3-n}$ ($n = 1, 2, 3, 4$) complexes in $0.5 \text{ mol L}^{-1} \text{ NaClO}_4$ solution, using potentiometry [25]. The given $\log \beta_{\text{m,n}}$ values are in good agreement with the conditional stability constants at $I_m = 0.5 \text{ mol kg}^{-1} \text{ H}_2\text{O}$ (NaCl) given in the present work. Choppin et al report the conditional $\log \beta_{\text{m,n}}$ values of the $\text{Eu}(\text{gly})_n^{3-n}$ ($n = 1, 2$) complexes in $2.0 \text{ mol L}^{-1} \text{ NaClO}_4$, determined by solvent extraction.²⁶ The given values are by 0.1 to 0.3 logarithmic units higher compared to the analogous values of the present work. This difference is attributed to the different ionic matrices, which affects the activity coefficients of the ions in solution even though the ionic strength is the same.

The $\Delta \varepsilon_{\text{on}}$ values (see Eq. (6)) for the protonation reaction of lactate as well as for the formation of the different Eu(III) lactate complexes are determined using the SIT regression analysis. The results are given in Table 3.

In order to calculate the binary ion-ion interaction coefficients ($\varepsilon(i,k)$) of lactate with Na^+ , the value of $\varepsilon(\text{H}^+, \text{Cl}^-) = 0.12 \pm 0.01 \text{ kg mol}^{-1}$ was used, as given by the NEA-TDB [27]. The calculation of the $\varepsilon(i,k)$ for the Eu(III) lactate complexes requires the value $\varepsilon(\text{Eu}^{3+}, \text{Cl}^-)$ which is not available in the literature. Thus, following the recommendation of the NEA-TDB, a value of $\varepsilon(\text{Nd}^{3+}, \text{Cl}^-) = 0.23 \pm 0.02 \text{ kg mol}^{-1}$ was chosen as a reasonable estimate of $\varepsilon(\text{Eu}^{3+}, \text{Cl}^-)$. The so calculated binary ion interactions coefficients are:

$$\varepsilon(\text{Na}^+, \text{Lac}^-) = 0.01 \pm 0.05 \text{ kg} \cdot \text{mol}^{-1}$$

$$\varepsilon(\text{Eu}(\text{Lac})^{2+}, \text{Cl}^-) = 0.11 \pm 0.12 \text{ kg} \cdot \text{mol}^{-1}$$

$$\varepsilon(\text{Eu}(\text{Lac})_2^+, \text{Lac}^-) = 0.06 \pm 0.18 \text{ kg} \cdot \text{mol}^{-1}$$

The errors represent 3σ intervals. No binary interaction coefficient is given for the uncharged $[\text{Eu}(\text{Lac})_3]$ species, since the $\varepsilon(i,k)$ of neutral species are considered to be zero according to the SIT. The $\varepsilon_{i,k}$ values of the different Eu(III) lactate complexes decrease successively with increasing number of lactate ligands. This is in good agreement with the analogue $\varepsilon(i,k)$ values of Cm(III) oxalate species [28]. Furthermore, the results show a smaller $\varepsilon(\text{Na}^+, \text{Lac}^-)$ compared to $\varepsilon(\text{Na}^+, \text{Ac}^-) = 0.08 \pm 0.01 \text{ kg mol}^{-1}$. Thus the impact of the additional α -hydroxy group of lactate on the binary ion-interaction coefficient play a significant role and the assumption $(\text{Lac}^-, \text{Na}^+) = \varepsilon(\text{Ac}^-, \text{Na}^+)$, which is usually made in the literature, is not accurate.

4.2. Reaction enthalpies and entropies at $I_m = 0\text{--}5.61 \text{ (NaCl)}$

4.2.1. Protonation reaction of lactate

The protonation enthalpies of lactate were determined by calorimetric titrations. The stepwise enthalpy changes per mole of titrant

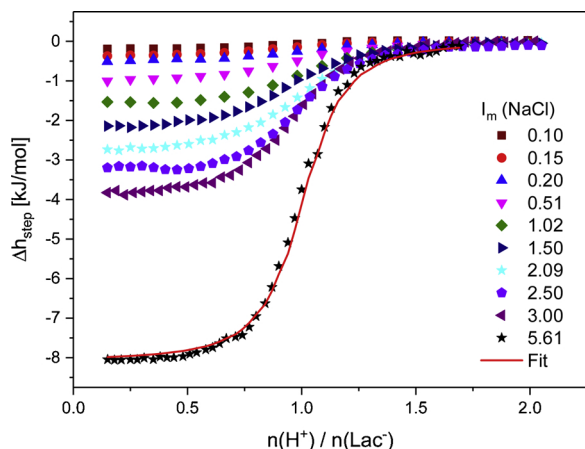


Fig. 1. Calorimetric titrations for the protonation of lactate: Stepwise enthalpy changes (and fit for $I_m = 5.61 \text{ mol kg}^{-1} \text{ H}_2\text{O}$) per mole of titrant (HCl) vs the proton/ligand ratio. $I_m = 0.10\text{--}5.61 \text{ mol kg}^{-1}$ (NaCl). Data acquired by the Thermometric 2277 Thermal Activity Monitor ($I_m = 0.10, 0.51, 2.09, 5.61 \text{ mol kg}^{-1} \text{ H}_2\text{O}$) and the ITC 200 ($I_m = 0.15, 0.20, 1.02, 1.50, 2.50, 3.00 \text{ mol kg}^{-1} \text{ H}_2\text{O}$).

(HCl) at different ionic strengths (NaCl) are displayed in Fig. 1.

At low ionic strength, the heat curves show values near zero with no pronounced sigmoidal shape. As the ionic strength increases, the reaction heat increases and the sigmoidal shape of the curves becomes more distinct. This indicates that the reaction is getting more exothermic with increasing ionic strength. The conditional protonation enthalpies ($\Delta_r H'_{m,\text{HLac}}$) were determined by fitting the stepwise heat of reaction, using the correspondent $\log \beta'_{m,\text{HLac}}$ values reported in Table 2. If the stability constant was not available for a specific ionic strength its value was calculated according to the SIT model using the $\varepsilon_{i,k}$ values reported in Section 3.1 or given in the NEA-TDB.²⁷ As an example, the fit for $I_m = 5.61 \text{ mol kg}^{-1} \text{ H}_2\text{O}$ is given in Fig. 1, showing the excellent consistency of the here determined $\Delta_r H'_{m,\text{HLac}}$ and $\log \beta'_{m,\text{HLac}}$ values. The $\Delta_r S'_{m,\text{HLac}}$ values were calculated according to the Gibbs-Helmholtz equation. The results are summarized in Table 4.

They show that at low ionic strength the reaction enthalpy is almost zero and becomes successively more exothermic with increasing

Table 4

Enthalpies ($\Delta_r H_{m,\text{HLac}}$), entropies ($\Delta_r S_{m,\text{HLac}}$) and free energies ($\Delta_r G_{m,\text{HLac}}$) of the lactate protonation at different ionic strength (NaCl). Thermodynamic values for $I_m = 0 \text{ mol kg}^{-1} \text{ H}_2\text{O}$ are reported in the first row of the table. $I_m = \text{molal ionic strength (mol kg}^{-1} \text{ H}_2\text{O)}$, $\sigma = \text{confidence interval}$.

I_m (NaCl) mol $\text{kg}^{-1} \text{ H}_2\text{O}$	$\Delta_r H_{m,\text{HLac}} \pm 3\sigma$ $\text{kJ}\cdot\text{mol}^{-1}$	$\Delta_r S_{m,\text{HLac}} \pm 3\sigma$ $\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$	$\Delta_r G_{m,\text{HLac}} \pm 3\sigma$ $\text{kJ}\cdot\text{mol}^{-1}$
0.00	0.55 ± 0.80	76.1 ± 5.7	-22.13 ± 2.50
0.10*	-0.20 ± 0.50	69.7 ± 2.4	-20.96 ± 1.20
0.15 [†]	-0.34 ± 0.03	68.7 ± 3.9	-20.82 ± 1.20
0.20 [†]	-0.43 ± 0.02	68.1 ± 4.0	-20.72 ± 1.20
0.25 [†]	-0.56 ± 0.04	67.4 ± 3.9	-20.65 ± 1.20
0.30 [†]	-0.62 ± 0.03	67.1 ± 3.9	-20.60 ± 1.20
0.51*	-0.96 ± 0.50	65.6 ± 2.4	-20.50 ± 1.20
0.75 [†]	-1.22 ± 0.03	64.6 ± 3.9	-20.48 ± 1.20
1.00 [†]	-1.56 ± 0.50	63.6 ± 2.4	-20.52 ± 1.20
1.25 [†]	-1.81 ± 0.04	63.1 ± 3.9	-20.60 ± 1.20
1.50 [†]	-2.11 ± 0.10	62.4 ± 3.7	-20.70 ± 1.20
2.09*	-2.93 ± 0.50	60.4 ± 2.4	-20.93 ± 1.20
2.50 [†]	-3.28 ± 0.09	60.1 ± 3.7	-21.19 ± 1.20
3.00 [†]	-3.74 ± 0.17	59.5 ± 3.7	-21.48 ± 1.20
5.61*	-8.06 ± 0.60	50.5 ± 2.0	-23.11 ± 1.20

$p = 1 \text{ bar (atm)}$; $T = 293 \text{ K (r.t.)}$, *Thermometric 2277 Thermal Activity Monitor, [†]ITC 200; $\Delta_r G_{m,\text{HLac}}$ data calculated from values given in Table 2. Standard uncertainties for temperature, pressure and molality are $u(T) = \pm 1 \text{ K}$, $u(p) = 0.5 \text{ kPa}$ and $u(m) = \pm 10^{-5} \text{ mol kg}^{-1} \text{ H}_2\text{O}$.

concentration of the background electrolyte. The reaction entropy is largely positive at low I_m values and decreases steadily with increasing I_m .

No enthalpy $\Delta_r H'_{m,\text{HLac}}$ and $\Delta_r S'_{m,\text{HLac}}$ data for the protonation of lactate in NaCl media are available in the literature. Thus, our results can only be compared with thermodynamic data obtained in NaClO_4 and NaTf. Tian et al report $\Delta_r H'_{m,\text{HLac}} = (-0.55 \pm 0.22) \text{ kJ}\cdot\text{mol}^{-1}$ and $\Delta_r S'_{m,\text{HLac}} = (68 \pm 1) \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ for the protonation of lactate in $1.05 \text{ mol kg}^{-1} \text{ NaClO}_4$.¹⁸ Their reaction enthalpy and entropy are $1 \text{ kJ}\cdot\text{mol}^{-1}$ ($\Delta_r H'_{m,\text{HLac}}$) and $4\text{--}5 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ ($\Delta_r S'_{m,\text{HLac}}$) higher than the present results. These differences can be attributed to the different ionic matrices, resulting in different interactions of the reagents with the background electrolytes. On the other hand, Zalupski et al determined $\Delta_r H'_{\text{HLac}} = (-1.48 \pm 0.04) \text{ kJ}\cdot\text{mol}^{-1}$ and $\Delta_r S'_{\text{HLac}} = (65 \pm 1) \text{ kJ}\cdot\text{mol}^{-1}$ in $1.0 \text{ mol L}^{-1} \text{ NaTf}$ solution, which are in excellent agreement with the present results [29].

The $\Delta_r H'_{m,\text{HLac}}$ values were extrapolated to $I_m = 0 \text{ mol kg}^{-1} \text{ H}_2\text{O}$ according to the enthalpy specific SIT model (Eq. (7))

$$\Delta_r H'_m - \Delta z^2 D_L = \Delta_r H_m^0 - RT^2 \Delta \varepsilon_L \cdot I_m \quad (7)$$

with $D_L = 0.75 \cdot (A_L \cdot (I_m)^{0.5}) \cdot (1 + 1.5 \cdot (I_m)^{0.5})^{-1}$, A_L being the Debye-Hückel constant ($A_L = 1.989 \text{ kJ}\cdot\text{kg}^{0.5}\cdot\text{mol}^{-1.5}$ at 298 K) and $\Delta \varepsilon_L = \sum_i \nu_i \cdot \varepsilon_L(i, k)$. The stoichiometric coefficients ν_i are positive for products and negative for reactants. The $\varepsilon_L(i, k)$ values are the relative partial molar enthalpy specific ion interaction coefficients. These are related to the binary ion-interaction parameters $\varepsilon_{i,k}$ by Eq. (8).

$$\varepsilon_L(i, k) = \left(\frac{\delta \varepsilon_{i,k}}{\delta T} \right)_p \quad (8)$$

A plot of $\Delta_r H'_m - \Delta z^2 D_L$ versus I_m together with the linear SIT-regression analysis is given in Fig. 2a for the protonation of lactate.

The data shows a linear correlation with the concentration of NaCl, with the exception of the value at $I_m = 5.61 \text{ mol kg}^{-1} \text{ H}_2\text{O}$. The deviation of this single data point is due to the high ionic strength, which is out of the validity range of the SIT [27]. This data point is therefore not considered in the fit. The standard state protonation enthalpy $\Delta_r H_m^0$ is determined from the y-axis intercept at $I_m = 0 \text{ mol kg}^{-1} \text{ H}_2\text{O}$ and $\Delta \varepsilon_{L,\text{HLac}}$ is determined from the slope of the linear fit. The $\Delta_r H_m^0$ and $\Delta_r S_m^0$ values are summarized in the first row of Table 4. The results are in excellent agreement with literature data given in the NIST thermodynamic database ($\Delta_r H_{\text{HLac}}^0 = 0.33 \text{ kJ mol}^{-1}$; $\Delta_r S_{\text{HLac}}^0 = 75 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$) [23]. It is noteworthy that the individual $\Delta_r H_m^0$ values determined with the two calorimeters used in the present work are in excellent agreement to each other ($\Delta_r H_m^0(\text{Thermometric 2277}) = 0.55 \pm 0.09 \text{ kJ}\cdot\text{mol}^{-1}$, $\Delta_r H_m^0(\text{ITC-200}) = 0.55 \pm 0.06 \text{ kJ}\cdot\text{mol}^{-1}$).

The value of $\Delta \varepsilon_{L,\text{HLac}} = (1.31 \pm 0.03) \cdot 10^{-3} \text{ kg}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ determined by this study cannot be compared with literature data due to the lack of corresponding data. Thus, individual ε_L values of the different reactive species can not be calculated.

An interesting result is the change of the driving force of the protonation reaction with increasing ionic strength. The fractions of $\Delta_r H'_{m,\text{HLac}}$ and $-T \Delta_r S'_{m,\text{HLac}}$ relative to $\Delta_r G_{m,\text{HLac}}$ are displayed in Fig. 2b as function of I_m . The plot shows that at $I_m = 0 \text{ mol kg}^{-1} \text{ H}_2\text{O}$ the protonation reaction is solely driven by the reaction entropy with a positive $\Delta_r H_m^0$. As the ionic strength increases the driving force of the complexation changes gradually towards an enthalpy-driven reaction. This proves the changes of the reaction enthalpy and entropy with I_m and is explained by the decreasing energy required for the partial dehydration of the reacting species during the complexation reaction at higher ionic strength. These findings are in good agreement to literature data.^{20,30,31} More details are given in the following section.

4.2.2. Formation of the $[\text{Eu}(\text{Lac})_n]^{3-n}$ ($n = 1, 2, 3$) species

The formation enthalpies and entropies of the $[\text{Eu}(\text{Lac})_n]^{3-n}$ complexes ($n = 1, 2, 3$) at different ionic strengths were determined by

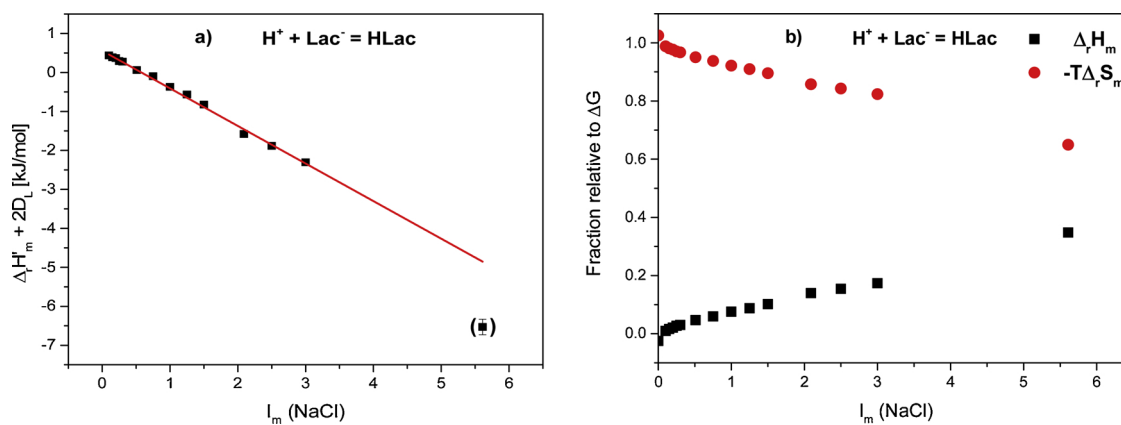


Fig. 2. Thermodynamic results for the protonation reaction of lactate. **a)** Enthalpy specific SIT regression analysis of $\Delta_r H'_m, \text{HLac} - D_L$ versus I_m . **b)** Fractions of $\Delta_r H_{m, \text{HLac}}$ and $-T\Delta_r S_{m, \text{HLac}}$ relative to $\Delta_r G_{m, \text{HLac}}$ as function of the molal ionic strength I_m (mol kg^{-1} H_2O).

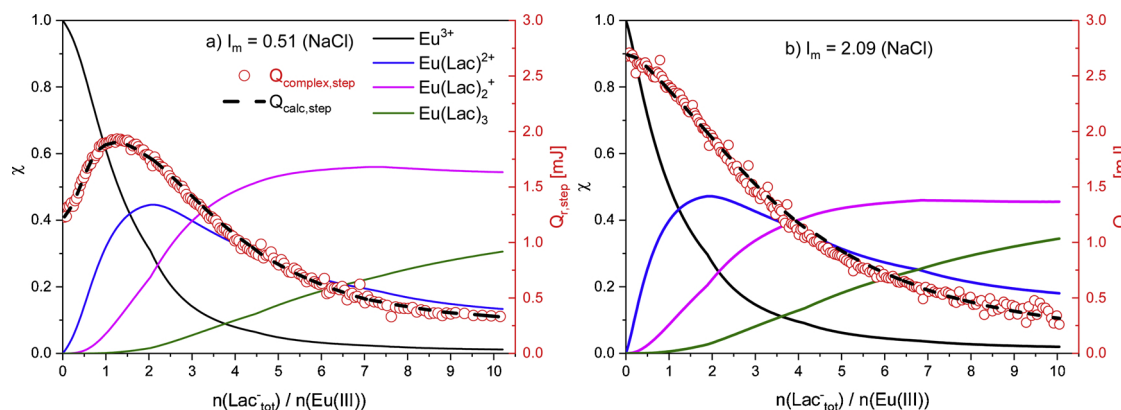


Fig. 3. Calorimetric titrations of Eu(III) with lactate system at two different ionic strengths using the Thermometric 2277 Thermal Activity Monitor. **Symbols:** Net stepwise complexation heat ($Q_{\text{complex,step}}$) vs. R_L : **a)** $[\text{Eu}^{3+}]_0 = 10.02 \times 10^{-3}$ mol kg^{-1} H_2O , $[\text{H}^+]_0 = 5.08 \times 10^{-3}$ mol kg^{-1} H_2O , $[\text{Lac}^-]_{\text{tit}} = 101.7 \times 10^{-3}$ mol kg^{-1} H_2O , $[\text{H}^+]_{\text{tit}} = 2.5 \times 10^{-3}$ mol kg^{-1} H_2O , $I_m = 0.51$ mol kg^{-1} H_2O (NaCl), **b)** $[\text{Eu}^{3+}]_0 = 10.1 \times 10^{-3}$ mol kg^{-1} H_2O , $[\text{H}^+]_0 = 1.09 \times 10^{-3}$ mol kg^{-1} H_2O , $[\text{Lac}^-]_{\text{tit}} = 95.7 \times 10^{-3}$ mol kg^{-1} H_2O , $[\text{H}^+]_{\text{tit}} = 5 \times 10^{-3}$ mol kg^{-1} H_2O , $I_m = 2.09$ mol kg^{-1} H_2O (NaCl). **Dashed line:** Calculated stepwise complexation heat ($Q_{\text{calc,step}}$). **Solid lines:** calculated molar fractions of the $[\text{Eu}(\text{Lac})_n]^{3-n}$ species ($n = 0, 1, 2, 3$). I_m = molal ionic strength (mol kg^{-1} H_2O).

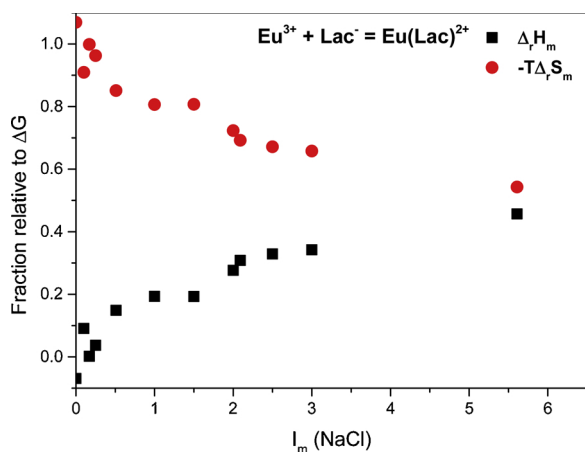


Fig. 4. Thermodynamic functions of the formation of $[\text{Eu}(\text{Lac})_2]^{2+}$. Fractions of $\Delta_r H_{m,1}$ and $-T\Delta_r S_{m,1}$ relative to $\Delta_r G_{m,1}$ as function of I_m .

isothermal calorimetric titrations. Two selected calorimetric titrations, for $I_m = 0.51$ mol kg^{-1} H_2O (left) and 2.09 mol kg^{-1} H_2O (right) (NaCl), are presented in Fig. 3. The net stepwise reaction heat $Q_{\text{complex,step}}$, which is the experimentally measured stepwise reaction heat $Q_{r,\text{step}}$ subtracted by the heat of protonation of lactate, is reported together with the relative speciation of Eu(III) lactate complexes, vs. the ligand to metal ratio (R_L). The speciation is calculated with the program

Hyperquad 2006 using the stability constants given in Table 2 [21]. Under all experimental conditions net positive values are observed for $Q_{\text{complex,step}}$, showing that the conditional reaction enthalpies ($\Delta_r H_{m,n}$) are exothermic. The comparison of the two heat curves in Fig. 4 shows a significant difference for R_L below 1.0: at $I_m = 0.51$ mol kg^{-1} H_2O the initially generated heat starts at 1.36 mJ, increases to a maximum of 1.93 mJ at $R_L \sim 1.2$ and decreases at higher R_L . At $I_m = 2.09$ mol kg^{-1} H_2O the initial heat is distinctively higher (2.68 mJ) and decreases continuously over the entire titration range. This is a strong indication that at lower ionic strength the reaction enthalpies are in general less exothermic and become more exothermic with increasing ionic strength.

The $\Delta_r H'_{m,n}$ ($n = 1, 2, 3$) of the Eu(III) lactate complexes ($[\text{Eu}(\text{Lac})_n]^{3-n}$, $n = 1, 2, 3$) are obtained by fitting the experimental heat using the corresponding $\log \beta'_{m,n}$ values and the $\log \beta'_{m, \text{HLac}}$ and $\Delta_r H'_{m, \text{HLac}}$ of the lactate protonation (see Table 2 and 3). The excellent agreement between the experimental data and the calculated curves (dashed lines in Fig. 3) is a strong proof of the excellent consistency of the calorimetric and potentiometric results. The resulting $\Delta_r H'_{m,n}$ and $\Delta_r S'_{m,n}$ are listed in Table 5 together with the $\Delta_r G'_{m,n}$ calculated from the data given in Table 2.

In case of the first complexation reaction, an extended set of values for several ionic strengths was obtained by the use of the ITC 200 micro titration calorimeter. These values are in good agreement with the values determined with the Thermometric 2277 Thermal Activity Monitor. This shows that the ITC 200 calorimeter with the smaller cell

Table 5

Enthalpies ($\Delta_r H_{m,n}$), entropies ($\Delta_r S_{m,n}$) and free energies of formation ($\Delta_r G_{m,n}$) of $[\text{Eu}(\text{Lac})_n]^{3-n}$ complexes ($n = 1, 2, 3$). Thermodynamic values at $I_m = 0 \text{ mol kg}^{-1} \text{ H}_2\text{O}$ are listed in the first row of each section. $I_m = \text{molal ionic strength (mol kg}^{-1} \text{ H}_2\text{O)}$, $\sigma = \text{confidence interval}$.

Reaction	I_m (NaCl) mol kg ⁻¹ H ₂ O	$\Delta_r H_m \pm 3\sigma \text{ kJ}\cdot\text{mol}^{-1}$	$\Delta_r S_m \pm 3\sigma \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$	$G_m \pm 3\sigma \text{ kJ}\cdot\text{mol}^{-1}$
$\text{Eu}^{3+} + \text{Lac}^- \rightleftharpoons \text{Eu}(\text{Lac})^{2+}$	0.00	1.65 ± 0.90	71.2 ± 6.38	-19.85 ± 2.80
	0.10*	-1.47 ± 0.80	49.4 ± 1.00	-16.19 ± 1.10
	0.17 ⁺	-0.03 ± 0.16	52.1 ± 3.15	-15.54 ± 1.10
	0.25 ⁺	-0.56 ± 0.18	48.7 ± 3.09	-15.07 ± 1.10
	0.51*	-2.12 ± 0.50	40.7 ± 2.18	-14.24 ± 1.15
	1.00 ⁺	-2.64 ± 1.75	37.0 ± 2.01	-13.65 ± 1.15
	1.50 ⁺	-2.60 ± 0.06	36.5 ± 3.66	-13.48 ± 1.15
	2.00 ⁺	-3.73 ± 1.28	32.7 ± 0.44	-13.49 ± 1.15
	2.09*	-4.16 ± 0.23	31.4 ± 5.60	-13.50 ± 1.90
	2.50 ⁺	-4.47 ± 0.11	30.6 ± 6.01	-13.59 ± 1.90
	3.00 ⁺	-4.71 ± 0.27	30.4 ± 5.47	-13.76 ± 1.90
5.61*	-6.89 ± 0.40	27.5 ± 5.03	-15.08 ± 1.90	
$\text{Eu}^{3+} + 2 \text{Lac}^- \rightleftharpoons \text{Eu}(\text{Lac})_2^+$	0.00	-1.51 ± 1.10	112.9 ± 7.05	-35.14 ± 3.20
	0.10*	-4.92 ± 0.30	79.6 ± 2.68	-28.64 ± 1.10
	0.51*	-6.43 ± 0.30	65.4 ± 3.02	-25.90 ± 1.20
	2.09*	-9.38 ± 0.60	50.1 ± 1.68	-24.30 ± 1.10
	5.61*	-17.07 ± 0.50	29.6 ± 2.01	-25.90 ± 1.10
	$\text{Eu}^{3+} + 3 \text{Lac}^- \rightleftharpoons \text{Eu}(\text{Lac})_3$	0.00	-10.65 ± 1.50	112.8 ± 9.73
0.10*		-15.25 ± 1.60	66.9 ± 2.68	-35.20 ± 2.40
0.51*		-16.50 ± 1.50	54.1 ± 3.69	-32.63 ± 2.60
2.09*		-19.47 ± 1.50	41.7 ± 2.68	-31.89 ± 2.30
5.61*		-30.63 ± 2.90	7.90 ± 3.36	-32.97 ± 1.90

$p = 1 \text{ bar (atm)}$; $T = 293 \text{ K (r.t.)}$, *Thermometric 2277 Thermal Activity Monitor, ⁺ ITC 200.

Standard uncertainties for temperature, pressure and molality are $u(T) = \pm 1 \text{ K}$, $u(p) = 0.5 \text{ kPa}$ and $u(m) = \pm 10^{-5} \text{ mol kg}^{-1} \text{ H}_2\text{O}$.

volume is well suited to study 1:1 complexes with an experimental effort comparable to the Thermometric 2277 calorimeter. For thermodynamic investigations of higher complexes, however, several measurements with variable metal ion to ligand ratio are necessary. This is due to the small sample volume of the ITC200, which restricts the range of ligand to metal ratio in a single titration experiment. The data in Table 5 shows negative $\Delta_r H_{m,n}$ and positive $\Delta_r S_{m,n}$ values, which both favor the formation of the $[\text{Eu}(\text{Lac})_n]^{3-n}$ ($n = 1, 2, 3$) complexes. Similarly, to the protonation of lactate (see above) a distinct decrease of both values with increasing I_m is observed. No literature data on conditional reaction enthalpies for the formation of Eu(III) lactate complexes in NaCl ionic medium are available for a direct comparison. A comparison can be made with conditional thermodynamic data determined in NaClO₄ medium. Tian et al determined the $\Delta_r H'$ and $\Delta_r S'$ values of the formation of Eu(III) lactate complexes in 1.0 M NaClO₄, using microcalorimetric titration.¹⁸ The given values for the formation of $[\text{Eu}(\text{lac})]^{2+}$ ($\Delta_r H'_1 = -2.14 \pm 0.77 \text{ kJ mol}^{-1}$, $\Delta_r S'_1 = 46 \pm 3 \text{ J mol}^{-1} \text{ K}^{-1}$) are in very good agreement with those of the present work. Furthermore, a comparison with the analogous Eu(III) glycolate complexes is made. Choppin et al used solvent extraction at different temperatures to determine the conditional enthalpy and entropy of the formation of $[\text{Eu}(\text{gly})]^{2+}$ in 2.0 mol L⁻¹ NaClO₄ [26]. The yielded $\Delta_r H'_1 = -2.2 \text{ kJ mol}^{-1}$ and $\Delta_r S'_1 = 40.6 \text{ J mol}^{-1} \text{ K}^{-1}$ are in agreement with the values of the present work within the error range. Kitano et al applied microcalorimetry to study the thermodynamics of the formation of $[\text{Eu}(\text{gly})_n]^{3-n}$ ($n = 1, 2, 3$) complexes in 1.0 mol L⁻¹ NaClO₄ [32]. The given $\Delta_r H'_1 = -4.0 \pm 0.1 \text{ kJ mol}^{-1}$ is slightly lower compared to the present results, whereas the $\Delta_r S'_1 = 35.4 \pm 0.4 \text{ J mol}^{-1} \text{ K}^{-1}$ is in good agreement.

The $\Delta_r H_{m,n}$ are extrapolated to $I_m = 0 \text{ mol kg}^{-1} \text{ H}_2\text{O}$ using the enthalpy specific SIT model (see eq 7). The resulting standard state reaction enthalpies and entropies ($\Delta_r H_{m,n}^0$ and $\Delta_r S_{m,n}^0$) are given in Table 5. Both $\Delta_r H_{m,n}^0$ and $\Delta_r S_{m,n}^0$ are higher than the conditional data which is in agreement with the trend observed with the ionic strength (see Table 5). This effect is in particular pronounced for the first complexation step and results in a positive enthalpy of reaction at $I_m = 0 \text{ mol kg}^{-1} \text{ H}_2\text{O}$. Thus, the formation of the $[\text{Eu}(\text{Lac})]^{2+}$ complex is an endothermic process under standard state conditions and the

experimentally observed exothermicity is attributed to the interaction with the ionic matrix.

A comparison is made with data given by Barkleit et al. [20] The authors report values of $\Delta_r H_{m,n}^0$ and $\Delta_r S_{m,n}^0$ for the formation of the three successive Eu(III) lactate complexes which are slightly higher than the results of the present work. The difference may rise from the fact that the values obtained by Barkleit et al are determined by fitting of $\log \beta_{m,n}^0(T)$ with the integrated Van't Hoff equation. Data generated by this approach is known to be in general more prone to errors as the given $\Delta_r H_{m,n}^0$ values are averaged over the studied temperature range (283–343 K). [33]

The fractional amounts of $\Delta_r H_{m,n}$ and $-T\Delta_r S_{m,n}$ contributing to $\Delta_r G_{m,n}$ are displayed in Fig. 4 for the first complexation reaction as a function of the ionic strength. As for the protonation reaction of lactate, the driving force of the complexation of Eu(III) with lactate changes significantly with the ionic strength. At standard state condition the complexation reaction is largely entropy-driven with a small reaction enthalpy. As I_m increases, the contribution of the entropic term to the complex stability decreases while the enthalpic contribution increases.

However, the reaction enthalpy remains the dominant contribution to the driving force of the reactions in the studied temperature range. A possible explanation of this result is given in the literature. [30,31,34] In general, the enthalpy of a complexation reaction in aqueous solution is determined mainly by the following processes. First, the reacting species are partially dehydrated which requires energy. Second, the reactants bind to each other and energy is released. Finally, the released water molecules are "solvated" in the aqueous medium. In the case of weak to medium strong ligands (e.g. carboxylates) the energy required for the desolvation (process 1) and the release of energy by complexation (process 2) often cancels each other out, leading to reaction enthalpies around zero. The decrease of $\Delta_r H_{m,n}$ with the ionic strength is therefore explained by a decreasing energy required for the partial dehydration of the reacting species (process 1). At higher I_m ions of the background electrolyte tend to accumulate around the reacting ions leading to a decreased charge density. This decreases the binding energy of the solvating water molecules and lowers the energy needed to separate them from the reacting ion. Therefore, the energy required for process 1 is lower at higher I_m and the resulting overall reaction

Table 6

Sum of the enthalpy specific binary interaction coefficients $\Delta\epsilon_{0n,L}$ for the formation of $[\text{Eu}(\text{Lac})_n]^{3-n}$ complexes ($n = 1, 2, 3$). σ = confidence interval.

Reaction	$\Delta\epsilon_{0n,L} \cdot 10^{-3} \pm 3\sigma \text{ kg mol}^{-1} \text{ K}^{-1}$
$\text{Eu}^{3+} + \text{Lac}^- \rightleftharpoons \text{Eu}(\text{Lac})^{2+}$	0.94 ± 0.14
$\text{Eu}^{3+} + 2 \text{Lac}^- \rightleftharpoons \text{Eu}(\text{Lac})_2^+$	1.44 ± 0.58
$\text{Eu}^{3+} + 3 \text{Lac}^- \rightleftharpoons \text{Eu}(\text{Lac})_3$	2.28 ± 0.69

$p = 1 \text{ bar (atm)}$; $T = 293 \text{ K (r.t.)}$.

Standard uncertainties for temperature, pressure and molality are $u(T) = \pm 1 \text{ K}$, $u(p) = 0.5 \text{ kPa}$ and $u(m) = \pm 10^{-5} \text{ mol kg}^{-1} \text{ H}_2\text{O}$.

enthalpy becomes more exothermic.

Application of the enthalpy specific SIT equation (Eq. (7)) yields the $\Delta\epsilon_{0n,L}$ values for the formation of the different Eu(III)-lactate complexes. The results are summarized in Table 6.

As no values of $\Delta\epsilon_{0n,L}$ are available in the literature, the binary enthalpy specific interaction coefficients ($\epsilon_{1(X, \text{Na}^+/\text{Cl}^-)}$) are not accessible.

5. Summary and conclusion

The present work is a detailed study on the influence of the ionic strength on the thermodynamics of the complexation of Eu(III) by lactate. The conditional stability constants and the thermodynamic functions ($\log \beta^n$, $\Delta_r H_{m,n}^0$, $\Delta_r S_{m,n}^0$) of the protonation of lactate and of the formation of the $[\text{Eu}(\text{Lac})_n]^{3-n}$ ($n = 1, 2, 3$) complexes were determined by potentiometric and calorimetric titrations. $\log \beta_{m,n}^0$ and $\Delta_r H_{m,n}^0$ were extrapolated to $I_m = 0 \text{ mol kg}^{-1} \text{ H}_2\text{O}$ with the SIT approach, yielding the thermodynamic standard state data. Moreover, the SIT specific binary ion interaction coefficients of the different ionic species with Na^+ and Cl^- as well as the enthalpy specific $\Delta\epsilon_{0n,L}$ values were determined. Endothermic $\Delta_r H_{m,n}^0$ values for the lactate protonation and for the formation of the first $[\text{Eu}(\text{Lac})]^{2+}$ complex were obtained, while the reactions at experimental ionic strength conditions showed slightly exothermic reaction enthalpies. For all reactions a distinct decrease of the reaction enthalpy (which favor the metal-complex formation) was observed with increasing ionic strength. The reaction entropies on the other hand decrease with the ionic strength. The variations of both $\Delta_r H_{m,n}^0$ and $\Delta_r S_{m,n}^0$ with I_m lead to a distinct change of the driving force of the reactions: at low I_m , the reactions are mainly entropy driven. As I_m increases the contribution of the enthalpy augments, resulting in reactions which are almost equally driven by entropy and enthalpy.

The present work contributes to a profound understanding of the complexation behavior of trivalent lanthanides with lactate. In particular, the effect of ionic strength on the conditional enthalpies and entropies of the complexation reactions is examined in detail by isothermal titration calorimetry and potentiometric measurements. Due to the similarities in the chemical behavior of trivalent lanthanides and actinides these data may be of high importance to describe the

geochemical behavior of trivalent actinides in nuclear waste repositories in deep geological clay formations.

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