Complexation of gluconic acid with Nd(III) in acidic solutions: A thermodynamic study

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Abstract

Thermodynamic properties of gluconic acid (HGH_4(aq)) complexation with Nd(III) have been studied in acidic solutions at 25 °C and 1.0 M $NaClO_4$ by potentiometry, spectrophotometry and calorimetry. Three Nd(III)/gluconate complexes were identified in solutions of pC_H 2.5–4.5. The formation constants and the complexation enthalpies are: $\log \beta_1 = 2.55 \pm 0.05$ and $\Delta H_1^\circ = -(8.22 \pm 0.23)$ kJ mol^{-1} for $Nd(GH_4)^{2+}$, $\log \beta_2 = 4.45 \pm 0.05$ and $\Delta H_2^\circ = -(15.3 \pm 0.4)$ kJ mol^{-1} for $Nd(GH_4)_2^+$, and $\log \beta_3 = 5.60 \pm 0.15$ and $\Delta H_3^\circ = -(24.6 \pm 0.6)$ kJ mol^{-1} for $Nd(GH_4)_3$(aq). The thermodynamic parameters indicate that gluconic acid, like other α-hydroxycarboxylic acids, forms stronger complexes with Nd(III) than simple monocarboxylic acids, likely by the participation of the α-hydroxyl group during complexation. The same type of binding appears to occur with Ca^{2+} and NpO_2^+ as the 1:1 stability constants are linearly correlated with the effective cationic charges of the metal cations.
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1. Introduction

The complexation of gluconic acid ($CH_2OH(CHOH)_4COOH$) with *f*-elements is of interest because of its past application for industrial separations, for example, in the nuclear fuel cycle. The presence of gluconic acid in high-level radioactive waste tanks could enhance the solubility of lanthanides and actinides by forming soluble complexes, affecting their behavior during waste processing. To develop strategies for radioactive waste treatment, thermodynamic data on gluconate complexation with lanthanides and actinides are needed.

Several studies on the complexation of gluconic acid with lanthanides [1–8] and actinides [9,10] can be found in the literature. Stability constants were reported in these studies, but no other thermodynamic properties (e.g., enthalpies) were provided. Also, these studies were rarely focused on acidic

conditions partly due to the complication of gluconic acid lactonization at low pC_H. Even though a few studies for Ln(III)/gluconate systems [3,4,6] were conducted in acidic solutions, the results are not consistent. Since waste processing may require the thermodynamic data of lanthanides and actinides over a broad pC_H range (from acidic to basic), we have studied the complexation of gluconate with Nd(III) at relatively low pC_H (2.5–4.5) with consideration of the lactonization effect. Thermodynamic parameters, including stability constants, enthalpies, and entropies of Nd(III)/gluconate complexation, were obtained in solutions of 1.0 M $NaClO_4$ at 25 °C.

In this paper, gluconic acid ($CH_2OH(CHOH)_4COOH$) refers to D-gluconic acid derived from natural D-glucose. To be consistent with the notations in the literature, gluconic acid, gluconate and glucono-lactone are denoted by HGH_4(aq), GH_4^{-1} and L(aq), respectively, where the first H refers to the carboxylic acid hydrogen and H_4 refers to the four hydrogens on the secondary alcohols [12,13]. Also, glycolic acid ($CH_2OHCOOH$) was used for comparison. In the notation of glycolic acid (HGH), the first H refers to the carboxylic acid hydrogen and the last H refers to the hydrogen on the alcohol.

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This work is a continuation of our effort to investigate the complexation of gluconate with the actinides in different oxidation states. In this work, Nd(III) is studied as the chemical analog of trivalent actinides such as Am(III) and Cm(III). Based on these data, the impact of the effective charges on the complexation is discussed, providing insight into the complexation behavior of gluconate with "hard acid" cations.

2. Experimental

2.1. Chemicals

All chemicals are reagent grade or higher. Distilled and boiled water was used in preparations of all solutions. The stock solution of gluconate was prepared by weighing and dissolving in a volumetric flask an appropriate amount of sodium gluconate purchased from Acros Chemical Company. The sodium gluconate was used without further purification.

The Nd(III) stock solution in $HClO_4$ ($C_{Nd} \sim 1.0$ M) was prepared by dissolving solid neodymium oxide (Nd_2O_3) in $HClO_4$ solution under low heating. The concentration of Nd(III) in the solution was determined by complexometry using EDTA (Merck). Gran's potentiometric method [14] was used to determine the concentration of $HClO_4$ in the Nd(III) stock solution. The ionic strength of all the solutions used in potentiometry, spectrophotometry and calorimetry was adjusted to 1.0 M at 25 °C by adding appropriate amounts of $NaClO_4$ as the background electrolyte.

2.2. Potentiometry

Potentiometric experiments were carried out at Lawrence Berkeley National Laboratory (LBNL) to determine the formation constants of Nd(III)/gluconate complexes. Details of the titration setup have been provided elsewhere [15,16].

A Metrohm pH meter (Model 713) equipped with a Ross combination pH electrode (Orion Model 8102) was used to measure the electromotive force (*EMF*). The original electrode filling solution (3.0 M potassium chloride) was replaced with 1.0 M sodium chloride to avoid clogging of the electrode frit glass septum due to the precipitation of $KClO_4$. The *EMF* of the glass electrode in the acidic region can be expressed by Eq. (1):

$$E = E^0 + \frac{RT}{F} \ln[H^+] + \lambda_H[H^+] \tag{1}$$

where *R* is the gas constant, *F* 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 λ_H. These parameters allowed the calculation of hydrogen ion concentrations from the *EMF*'s in the subsequent titration that immediately followed. Corrections for the electrode junction potential of the hydroxide ion were not necessary in the acidic region. Multiple titrations were conducted with solutions of different concentrations of Nd(III). The formation constants were calculated by using the program Hyperquad [17] to simultaneously regress all the data from the multiple titrations.

To minimize the effect of the lactonization, sodium gluconate or freshly acidified sodium gluconate was used as a titrant for each run.

2.3. Spectrophotometry

Spectrophotometric titrations were conducted on a Cary-5G UV/Visible/Near IR spectrophotometer (Varian Inc.) at LBNL to determine the stability constants of Nd(III)/gluconate complexes. A quartz cuvette with a 1.0 cm optical pathlength was used and the temperature was maintained at 25 °C by a 1 × 1 peltier system. An absorption spectrum was measured under the following default instrumental settings: (1) double beam mode, (2) full slit height, (3) 24 nm/min scan rate, (4) 0.2 nm data interval, (5) 0.5 s average time and (6) 2.0 nm spectral bandwidth (SBW). It is noteworthy that the default SBW is not within the optimized range for the Nd(III) spectrum measurements.

For the Nd(III) absorption peak with the effective bandwidth of 10 nm, the optimized SBW should be set below 1.0 nm [18]. However, experimental testing demonstrated that this default SBW caused only minimal distortion in the spectra. Such minimal distortion cannot affect the fitting results in this work because all titration spectra were collected under the same default settings.

For each titration, a number of Nd(III) spectra in the wavelength range from 550 to 620 nm were collected as the Nd(III) solution was titrated with gluconate. The solution of each titration point had equilibrated at least 2 days before the spectrum was measured; previous work (not shown) demonstrated that this time was sufficient for the lactonization equilibrium. In this case, the chemical model could include the lactonization during the calculation of the stability constants. In the data treatment, all the absorption spectra were regressed with an assumed chemical model by Hyperquad [17], resulting in the stability constants and the molar absorptivities of Nd(III) species. The chemical model was defined with assistance of the result from factor analysis [17,19] of the spectra by Hyperquad. This result gives the number of significant absorbing species present in the titration solutions and thus, provides important speciation information for the system.

2.4. Calorimetry

Calorimetric titrations were conducted on an isoperibol solution calorimeter (Model ISC-4285, Calorimetry Sciences Corp.) at LBNL to determine the enthalpy of gluconate complexation with Nd(III). The performance of the calorimeter was tested by measuring the enthalpy of protonation of tris(hydroxymethyl)-aminomethane (THAM) at various temperature. The results (in kJ mol^{-1}) are -47.7 ± 0.3 (25 °C), -46.8 ± 0.2 (40 °C), -45.8 ± 0.5 (55 °C), and -45.2 ± 0.5 (70 °C), which compared well with the values in the literature: -46.0 ± 0.3 at 45 °C and -46.2 ± 0.3 at 70 °C [20]; -46.81 ± 0.02 at 35 °C and -46.0 ± 0.02 at 50 °C [21].
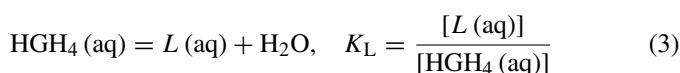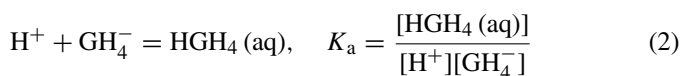
Multiple titrations were carried out for this system. For each titration run, freshly made gluconate titrant was used, and *n* experimental values of the total heat produced in the reaction vessel ($Q_{ex,j}$, $j = 1-n$) were calculated as a function of the volume of the added titrant. These values were corrected for the heat of dilution of the titrant ($Q_{dil,j}$), which was 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 values of $Q_{r,j}$, in conjunction with the titration conditions, the protonation constant and enthalpy from the literature [11] and the complexation constants calculated from potentiometry, were used to calculate the enthalpies by the computer program MQ90 [22].

3. Results and discussion

3.1. Formation constants (β) of Nd(III)/gluconate complexes

3.1.1. Potentiometry

Gluconate protonation and subsequent lactonization are expressed by Eqs. (2) and (3) below:

$$H^+ + GH_4^- = HGH_4 \text{ (aq)}, \quad K_a = \frac{[HGH_4 \text{ (aq)}]}{[H^+][GH_4^-]} \tag{2}$$

$$HGH_4 \text{ (aq)} = L \text{ (aq)} + H_2O, \quad K_L = \frac{[L \text{ (aq)}]}{[HGH_4 \text{ (aq)}]} \tag{3}$$

Protonation/deprotonation (Eq. (2)) is usually rapid and equilibrium can be reached within seconds. On the other hand, literature data [23–25] indicate that lactonization of gluconic acid (Eq. (3)) is negligible in solutions of $pC_H > 5.0$, and occurs slowly in solutions of $pC_H < 5.0$. The first-order rate constant of lactonization was determined at 20–22 °C to be 3.8×10^{-5} s^{-1} at pC_H 2.4 [24] and 1.7×10^{-5} s^{-1} at pC_H 4.5 [25], corresponding to a reaction time of 7.3 and 16 h at pC_H 2.5 and 4.5, respectively.
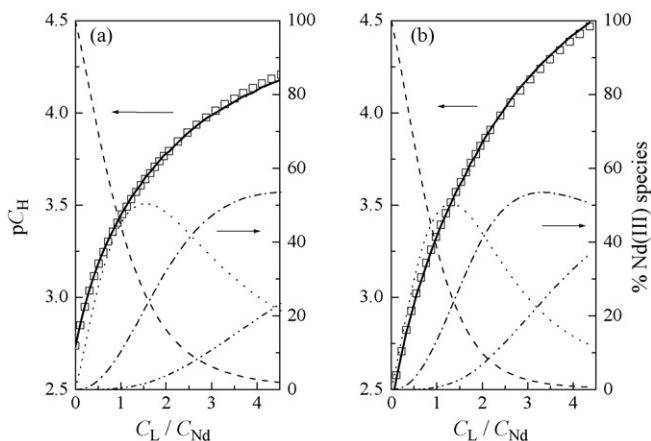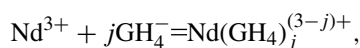
Fig. 1. Potentiometric titrations of Nd(III)/gluconate complexation: $t = 25\,^\circ$C, $I = 1.0$ M NaClO$_4$. For titrations (a) and (b), ($\square$) experimental pC_H; (solid lines) fitted pC_H. Cup solutions: titration (a) $V^0 = 31.50$ mL, $C_{Nd}^0 = 0.01454$ M, $C_H^0 = 0.001795$ M; titration (b) $V^0 = 32.00$ mL, $C_{Nd}^0 = 0.02863$ M, $C_H^0 = 0.003731$ M. Titrant: titration (a) $C_L = 0.9524$ M, $C_H = 0.04696$ M; titration (b) $C_L = 1.000$ M, $C_H = 0.0000$ M. For speciation, dash line, dotted line, dash-dot line and dash-dot-dot line represent the calculated percentages of Nd^{3+}, Nd(GH$_4$)$^{2+}$, Nd(GH$_4$)$_2{}^+$ and Nd(GH$_4$)$_3$(aq), respectively.

Using those kinetic data and our experimental conditions, we estimated the maximum extent of lactonization in 30 min to be 5% at pC_H 2.4 and 2% at pC_H 4.5. Taking advantage of the difference in the kinetics between protonation and lactonization, we have obtained the protonation constant (log $K_a = 3.30 \pm 0.10$ in Table 3) using relatively fast potentiometric titrations [11]. In this work, we have again conducted relatively fast potentiometric titrations to determine the formation constants of

Nd(III)/gluconate complexes, using a freshly made gluconate titrant (p$C_H > 4.5$). The titrations were performed from low pC_H (~2.5) to high pC_H (~4.5). The time interval between data points is 60 s, sufficient to achieve steady *EMF* reading after each addition, and the titrations were completed within 30 min.

Fig. 1 shows two representative potentiometric titrations. The starting solutions were designed with different pC_H values. The higher one (pC_H ~2.8, Fig. 1(a)) was expected to decrease the formation of lactones and the lower one (pC_H ~2.5, Fig. 1(b)) to provided more titration points for determination of the first step constant. As can be seen from Fig. 1, the data fitting is agreeable in both cases. Using the protonation constant (log $K_a = 3.30 \pm 0.10$) determined previously [11], the data were fitted by Hyperquad with the formation of three complex species shown in Eq. (4). The calculated formation constants are log $\beta_1 = 2.55 \pm 0.05$, log $\beta_2 = 4.45 \pm 0.05$, and log $\beta_3 = 5.60 \pm 0.15$ (Table 1):

$$\text{Nd}^{3+} + j\text{GH}_4{}^- = \text{Nd(GH}_4)_j^{(3-j)+},$$

$$\beta_j = \frac{[\text{Nd(GH}_4)_j^{(3-j)+}]}{[\text{Nd}^{3+}][\text{GH}_4{}^-]^j}, \quad j = 1, 2, 3 \tag{4}$$

3.1.2. Spectrophotometry

The spectrophotometric titrations were carried out in a different way where sufficient time was given for all the reactions, including protonation, lactonization and complexation, to achieve equilibrium. The solution conditions were similar to those in potentiometry, e.g., pC_H range 2.5–4.5. In the data treat-

Table 1
Thermodynamic parameters of gluconate complexation with Nd(III) ($I = 1.0$ M NaClO$_4$ and $t = 25\,^\circ$C) and comparative data

Reaction	log ((±3σ)	ΔG° (kJ mol^{-1})	ΔH° (±3σ) (kJ mol^{-1})	ΔS° (±3σ) (J K^{-1} mol^{-1})	Ref.
Nd(III)/gluconate					
Nd^{3+} + GH$_4{}^-$=Nd(GH$_4$)$^{2+}$	2.55 ± 0.05, 2.59 ± 0.05[a]	−14.6	−(8.22 ± 0.23)	21 ± 1	
Nd^{3+} + 2GH$_4{}^-$=Nd(GH$_4$)$_2{}^+$	4.45 ± 0.05, 4.52 ± 0.07[a]	−25.4	−(15.3 ± 0.4)	34 ± 1	This work
Nd^{3+} + 3GH$_4{}^-$=Nd(GH$_4$)$_3$(aq)	5.60 ± 0.15, 5.53 ± 0.07[a]	−32.0	−(24.6 ± 0.6)	25 ± 2	
Nd(III)/glycolate[b]					
Nd^{3+} + GH$^-$=Nd(GH)$^{2+}$	2.50 ± 0.10	−14.3	−5.0 ± 0.1	31.1 ± 0.4	
Nd^{3+} + 2GH$^-$=Nd(GH)$_2{}^+$	4.31 ± 0.08	−24.6	−9.2 ± 0.2	51.6 ± 0.7	[27]
Nd^{3+} + 3GH$^-$=Nd(GH)$_3$(aq)	5.6 ± 0.3	−32	−14.1 ± 0.2	60 ± 1	
Nd(III)/acetate[b]					
Nd^{3+} + A$^-$=Nd(A)$^{2+}$	1.92 ± 0.04	−11.0	7.1	60.6	
Nd^{3+} + 2A$^-$=Nd(A)$_2{}^+$	3.00 ± 0.07	−17.1	14	104	[27]
Nd^{3+} + 3A$^-$=Nd(A)$_3$(aq)	3.60 ± 0.08	−20.5	18	130	
Literature for Ln(III)/gluconate					
Pr^{3+} + GH$_4{}^-$=Pr(GH$_4$)$^{2+}$	2.78 ± 0.03	(pC_H 2.0–4.2; $t = 25\,^\circ$C			[6]
Pr^{3+} + 2GH$_4{}^-$=Pr(GH$_4$)$_2{}^+$	5.57 ± 0.03	and $I = 0.1$ M)			
Nd^{3+} + HGH$_4$=Nd(GH$_4$)$^{2+}$ + H$^+$	−1.06	(p$C_H < 4.2$; $t = 32\,^\circ$C			[4]
		and I not defined)			
Nd^{3+} + GH$_4{}^-$=Nd(GH$_4$)$^{2+}$	2.66 ± 0.03	(pC_H 2.0–3.0; $t = 25\,^\circ$C			[3]
Nd^{3+} + 2GH$_4{}^-$=Nd(GH$_4$)$_2{}^+$	4.70 ± 0.09	and I not defined)			

σ in the table indicates the standard deviation.
[a] Those stability constants were determined by the spectrophotometric titrations.
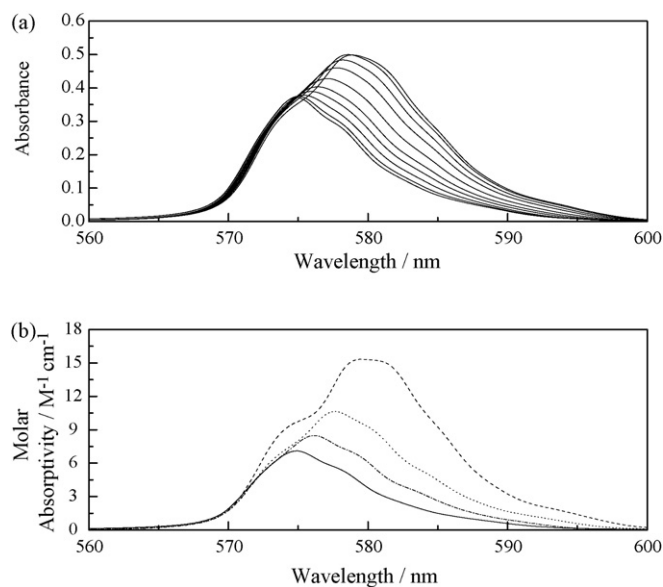[b] The data for those two systems refer to the conditions of $t = 25\,^\circ$C and $I = 2.0$ M.

Fig. 2. (a) Spectrophotometric titrations of Nd(III)/gluconate complexation: $t = 25\,^{\circ}C$, $I = 1.0\,M$ NaClO$_4$. Cuvette solution: $C_{Nd}^0 = 0.05248\,M$, $C_H^0 = 0.005652\,M$, $V^0 = 2.5\,mL$. Titrant: $C_{NaGH4} = 0.9501\,M$, $C_H = 0.0501\,M$. (b) Resolved molar absorbance spectra of Nd(III) species in gluconate solution. Solid line: Nd^{3+}, dotted-dash line: Nd(GH$_4$)$^{2+}$, dot line: Nd(GH$_4$)$_2{}^+$, dash line: Nd(GH$_4$)$_3$(aq).

ments, lactonization along with protonation and complexation was included in the chemical model by using the lactonization constant ($\log K_L = -(0.54 \pm 0.04)$) determined in the early work [25]. Fig. 2(a) shows a representative series of absorption spectra obtained during a titration. Factor analysis [17,19] of the spectra by Hyperquad indicated that there are four Nd(III) species that have significant absorbance in the visible region. Therefore, the complexation model was defined with the reactions used in the potentiometry (Eq. (4)). With our previously measured constants for protonation ($\log K_a = 3.30 \pm 0.10$) [11] and lactonization ($\log K_L = -(0.54 \pm 0.04)$) [25], this conceptual model described our experimental data very well. The resolved molar absorptivities of Nd(III) species are depicted in Fig. 2(b). The calculated formation constants are $\log \beta_1 = 2.59 \pm 0.05$, $\log \beta_2 = 4.52 \pm 0.07$, and $\log \beta_3 = 5.53 \pm 0.07$ (Table 1). Comparison of those constants from potentiometry and spectrophotometry reveals that they are mutually consistent. This suggests that lactonization, under the potentiometric conditions, has little effect on the determination of potentiometry.

3.1.3. Comparison to literature data

Representative literature data [3,4,6] for gluconate complexation with lanthanides in acidic solutions are listed in Table 1, including complexation patterns and stability constants, which were determined by potentiometry. The results indicate divergent interpretations of the observed Ln(III)/gluconate behavior under similar experimental conditions. Kostromina [3] and Giroux et al. [6] agreed on the formation of 1:1 and 1:2 Ln(III) gluconate complexes, but the values for the 1:2 complex do not agree. Panda and Patnaik [4] considered only a 1:1 Ln(III) gluconate complex under their experimental conditions. These

differences may be partially explained by lactonization, which the authors did not consider. It is interesting that the 1:1 and 1:2 formation constants obtained from this work are close to Kostromina's values (Table 1), although Kostromina did not consider the formation of the 1:3 complex. We have explicitly included consideration of the 1:3 complex based on the mutual consistency among our potentiometric, spectrophotometric and calorimetric (discussed below) results.

3.2. Enthalpy of Nd(III)/gluconate complexation

The experimental conditions used in calorimetry and the values of reaction heat measured are summarized in Table 2.

Table 2
Stepwise heat of reaction in the calorimetric titrations

Run 1		Run 2	
$V_{titr.}$ (mL)	Q_r (J)	$V_{titr.}$ (Ml)	Q_r (J)
0.000	0.000	0.000	0.000
0.077	0.482	0.077	0.448
0.156	0.48	0.156	0.458
0.235	0.445	0.235	0.428
0.315	0.471	0.314	0.436
0.394	0.459	0.394	0.409
0.473	0.419	0.473	0.382
0.552	0.411	0.552	0.379
0.631	0.408	0.631	0.334
0.711	0.383	0.710	0.322
0.790	0.346	0.790	0.291
0.869	0.34	0.869	0.268
0.948	0.334	0.948	0.251
1.028	0.294	1.027	0.227
1.107	0.268	1.106	0.209
1.186	0.26	1.186	0.184
1.265	0.246	1.265	0.187
1.344	0.234	1.344	0.181
1.424	0.213	1.423	0.139
1.503	0.198	1.503	0.138
1.582	0.177	1.582	0.124
1.661	0.176	1.661	0.120
1.740	0.156	1.740	0.124
1.820	0.144	1.819	0.099
1.899	0.139	1.899	0.090
1.978	0.142	1.978	0.092
2.057	0.121	2.057	0.088
2.136	0.103	2.136	0.077
2.216	0.120	2.215	0.078
2.295	0.100	2.295	0.077
2.374	0.104	2.374	0.057
2.453	0.095	2.453	0.073
2.532	0.080	2.532	0.066
2.612	0.091	2.611	0.064
2.691	0.071	2.691	0.048
2.770	0.091	2.770	0.052
2.849	0.055	2.849	0.040
2.929	0.058	2.928	0.059
3.008	0.074	3.007	0.038
3.087	0.065	3.087	0.051
3.166	0.043	3.166	0.039

$I = 1.0\,M$ NaClO$_4$, $t = 25\,^{\circ}C$. Titrant: $C_{NaGH4} = 0.9776\,M$, $C_H = 0.07760\,M$. Cup solution: $V^0 = 20.40\,mL$ (Run 1), 20.50 (Run 2); $C_M/C_H/C_L$ in mM: 17.96/1.933/0 (Run 1), 22.33/2.404/0 (Run 2).
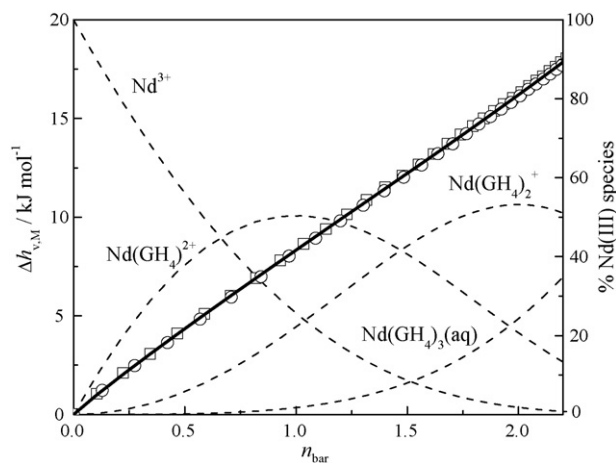
Fig. 3. $\Delta h_{v,M}$ as a function of n_{bar}, the average ligand number, for the calorimetric titrations of Nd(III)/gluconate complexation: $t = 25\,^\circ C$, $I = 1.0\,M$ NaClO$_4$. Titrant: $C_{NaGH4} = 0.9776\,M$, $C_H = 0.0776\,M$. Cup solution: $V^0 = 20.4\,mL$ ($\bigcirc$), 20.5 mL ($\square$); $C_{Nd}^0 = 0.01796\,M$ ($\bigcirc$), 0.02233 M ($\square$); $C_H^0 = 0019331\,M$ ($\bigcirc$), 0.002404 M ($\square$). ($\bigcirc$/$\square$): experimental data (left y-axis); (solid line) calculated. Dashed lines: speciation of Nd(III) species in the titrations (right y-axis).

Fig. 4. $\log\beta_1$ vs. pK_a. Correlation between the formation constants of the 1:1 Nd(III) monocarboxylate complexes and the pK_a values of the monocarboxylic acids. (1) Glycolate, (2) 2-hydroxypropanoate, (3) 2-hydroxy-2-methylpropanoate. $I = 1.0\,M$, $t = 20$–$25\,^\circ C$. Data except for gluconate are from [27].

The conditions were established to be similar to those used in the potentiometric titrations. The reaction heat observed at the jth addition of the titrant, $Q_{r,j}$, is a function of the enthalpy of complexation and the change in speciation after titrant addition:

$$Q_{r,j} = \sum \Delta n_i \Delta H_i^\circ \qquad (5)$$

where Δn_i is the change of the amount of the ith species in moles after the jth addition, while ΔH_i° is the enthalpy of formation of the ith species. In the calculation of enthalpies of complexation, the quantity $\Delta h_{v,M}$ is defined as Q_r/n_M and used as the error-carrying variable (Q_r is the overall reaction heat and n_M is the number of moles of Nd(III) in the cup). The enthalpies of complexation were calculated to be $\Delta H_1^\circ = -(8.22 \pm 0.23)\,kJ\,mol^{-1}$ for Nd(GH$_4$)$^{2+}$, $\Delta H_2^\circ = -(15.3 \pm 0.4)\,kJ\,mol^{-1}$ for Nd(GH$_4$)$_2^+$, and $\Delta H_3^\circ = -(24.6 \pm 0.6)\,kJ\,mol^{-1}$ for Nd(GH$_4$)$_3$(aq) (Table 1). Two representative calorimetric titrations are shown in Fig. 3 as the plot of $\Delta h_{v,M}$ versus n_{bar}, the average ligand number. Using these values and the formation constants of Nd(GH$_4$)$^{2+}$, Nd(GH$_4$)$_2^+$ and Nd(GH$_4$)$_3$(aq) obtained from the potentiometry, the curves simulating the calorimetric titrations were calculated and are shown to be in excellent agreement with the experimental data in Fig. 3. Ttitrations with different concentrations of Nd(III) coincide very well, indicating the absence of polynuclear Nd(III) species.

3.3. $\log\beta - pK_a$ correlation for Nd(III)/monocarboxylate complexation

As a hard acid cation, the interaction of Nd^{3+} with carboxylate ligands in aqueous solution is expected to be ionic and electrostatic in nature [26]. This means that the stability constants of Nd(III) carboxylate complexes may correlate with the protonation constants of the ligands, because the
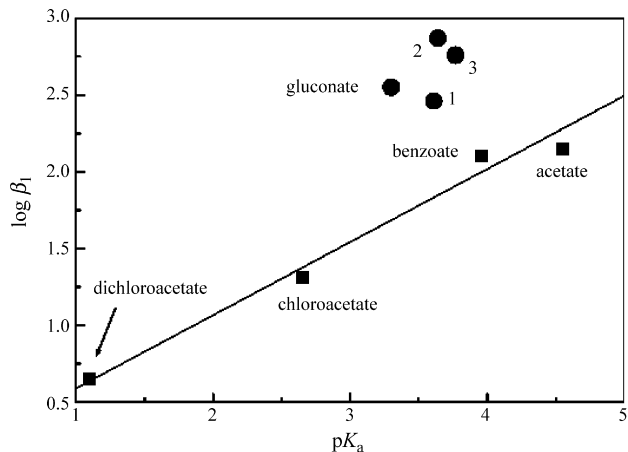
protonation of carboxylates is also predominantly an electrostatic interaction. Fig. 4 shows the relationship between the formation constants of the 1:1 Nd(III) carboxylate complexes and the pK_a of the ligand. The data for simple monocarboxylates (acetate, benzoate, chloroacetate and dichloroacetate) show a strong linear correlation. However, the stability constants of the Nd(III) complexation with gluconate and several α-hydroxycarboxylates (glycolate, 2-hydroxypropanoate, 2-hydroxy-2-methylpropanoate) are not correlated, and have values greater than that expected from the relationship observed for the monocarboxylates. The increased stability constants may result from the participation of the α-hydroxyl group to form a chelate complex with Nd(III).

Comparison of the enthalpies of complexation between simple carboxylate complexes and α-hydroxycarboxylate complexes could provide further insight into the coordination modes. The complexation of Nd(III) with simple carboxylates (e.g., acetate) is endothermic, and therefore, entropy driven (Table 1), resulting from the energy required for dehydration of the cation and the anion, and the disorder gained when dehydration occurs. However, the complexation of Nd(III) with glycolate, an α-hydroxycarboxylic acid, is exothermic (Table 1), implying that the hydroxyl group participates in the complexation, resulting in a more favorable enthalpy of complexation. The hydroxyl group may be less hydrated than the carboxylate group so that less energy is required to dehydrate the hydroxyl group than the carboxylate group. This discussion may also apply to complexation by gluconic acid. The exothermic nature of the Nd(III)/gluconate complexation (Table 1) suggests that the hydroxyl group of gluconic acid plays a role in the coordination as the enhanced stability constant of the complex indicates.

The thermodynamic observation for the participation of the hydroxyl group into the complexation is also in agreement with Giroux et al.'s work [7], where ^{13}C NMR data confirmed the involvement of α-hydroxyl group of gluconate in the coordination to Pr(III).

Table 3
Thermodynamic parameters of gluconate protonation and its complexation with other metal cations

Reaction	$\log K_a$ (or β) ($\pm 3\sigma$)	ΔG° (kJ mol^{-1})	ΔH° ($\pm 3\sigma$) (kJ mol^{-1})	ΔS° ($\pm 3\sigma$) (J K^{-1} mol^{-1})	Ref.
$H^+ + GH_4^- = HGH_4$	3.30 ± 0.10	-18.8	$-(4.03 \pm 0.07)$	50 ± 1	[11]
$Ca^{2+} + GH_4^- = Ca(GH_4)+$	1.21 ± 0.05	-6.91			This work
$NpO_2^+ + GH_4^- = NpO_2(GH_4)(aq)$	1.48 ± 0.03	-8.45	$-(7.42 \pm 0.13)$	3.5 ± 0.4	[11]
$NpO_2^+ + 2GH_4^- = NpO_2(GH_4)_2^-$	2.14 ± 0.09	-12.2	$-(12.1 \pm 0.5)$	0.4 ± 1.5	[11]

$I = 1.0$ M NaClO$_4$ and $t = 25\,^\circ$C.

3.4. $\log \beta - Z_{eff}$ correlation

Table 3 summarizes the measured thermodynamic parameters of gluconate protonation [11] and its complexation with Ca^{2+} and NpO$_2^+$ [11] at 25 °C and 1.0 M NaClO$_4$. The formation constant of the Ca(II)/gluconate complex, $\log \beta_1 = 1.21 \pm 0.05$, was determined at p$C_H$ range of 1.5–2.5 by "batch" potentiometric titrations (data not shown) with consideration of lactonization.

Because the f-elements exhibit ionic interactions with hard base (e.g., oxygen-donor) ligands as discussed above, the stability constants for a given ligand should be correlated with the effective cationic charges of the ions. Using the Born equation, Choppin and Rao demonstrated through complexation studies with the fluoride anion (F$^-$) that the effective cationic charge of the NpO$_2^+$ cation is nominally 2.2 [28]. When included with the simple spherical cations Ca^{2+} and Nd^{3+}, they form a series of increasing cationic charges from Ca^{2+} to NpO$_2^+$ to Nd^{3+}. As shown in Fig. 5, such a correlation is observed for the 1:1 complexes with both acetate (data from [27]) and gluconate, where the logarithm of the formation constants increases linearly with the effective charges of the cations. These observations suggest that gluconate complexation with Ca^{2+}, NpO$_2^+$, and Nd^{3+} follows a similar coordination mode for all three cations, despite the fact that the neptunyl cation is a dioxo species and the other two are spherical.
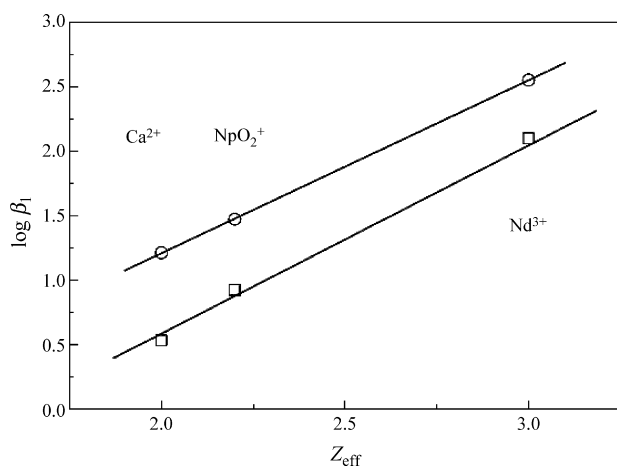
4. Summary

In acidic solutions (pC_H $2.5 - 4.5$), gluconate forms three Nd(III) complexes, Nd(GH$_4$)$^{2+}$, Nd(GH$_4$)$_2^+$ and Nd(GH$_4$)$_3$(aq). The formation constants and the enthalpies were determined by potentiometry, spectrophotometry and calorimetry. The stability constants of the Nd(III)/gluconate complexes are higher than those expected from a $\log \beta - pK_a$ relationship for simple monocarboxylates based on the electrostatic model. This suggests that the α-hydroxyl group may participate in complexation. The interpretation of the enthalpy data also supports this observation. The linear correlation of $\log \beta$ for the 1:1 complexes of gluconate with Ca^{2+}, NpO$_2^+$, and Nd^{3+} and their effective cationic charge, Z$_{eff,}$ provides an evidence that the coordination modes for these cations with gluconate are similar.

Acknowledgments

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jallcom.2007.01.034.

Fig. 5. $\log \beta_1$ vs. Z_{eff}. Correlation between the 1:1 formation constants of acetate gluconate with the cations (Ca^{2+}, NpO$_2^+$ and Nd^{3+}) and the effective charges of these cations. (□) The data of acetate complexation with those cations at $I = 1.0$ M and $t = 25$ °C, obtained from the literature [27]. (○) The data of gluconate complexation with those cations at $I = 1.0$ M NaClO$_4$ and $t = 25$ °C, determined by this group.

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