

Thermodynamic Studies of the Complexation between Neodymium and Acetate at Elevated Temperatures

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Complexation of neodymium (III) with acetate in 2.2 mol·kg⁻¹ NaClO₄ solution was studied at elevated temperatures (45 and 70°C) by potentiometry, calorimetry, and optical spectroscopy. The formation constants of the consecutive complexes, Nd(OOCCH₃)²⁺, Nd(OOCCH₃)₂⁺, and Nd(OOCCH₃)₃, and the molar enthalpies of complexation at these temperatures were determined. The stability of the three complexes increases with increased temperatures, because of increased positive entropy change at higher temperatures, which exceeds the increased values of the positive (endothermic) enthalpy. The molar heat capacity changes of complexation $\Delta C_{p,m}(ML_j)$ (J·K⁻¹·mol⁻¹) for Nd(OOCCH₃)_j^{(3-j)+} in the temperature range from 25 to 70°C were calculated to be: 102 ± 13 (j = 1); 122 ± 19 (j = 2); and 239 ± 27 (j = 3). The effect of temperature on the complexation is discussed in terms of the electrostatic model.

KEY WORDS: Neodymium; acetate; complexation; formation constant; enthalpy; entropy; heat capacity.

1. INTRODUCTION

Although a considerable number of stability constants of lanthanide and actinide complexes with inorganic and organic ligands have been published,⁽¹⁾ the coordination chemistry of lanthanides and actinides remains an active and challenging subject of study at both the fundamental and applied levels. At the fundamental level, many aspects concerning the nature of lanthanide and actinide complexes, including the coordination number, the hydration number, and the

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nature of bonding (*e.g.*, covalent *vs.* ionic, and inner sphere *vs.* outer sphere), are not fully understood.⁽²⁾ At the applied level, recent activities in the environmental management of nuclear wastes have stimulated significant interest in the studies of the coordination chemistry of lanthanides and actinides in complicated matrices and under conditions relevant to nuclear wastes.

Currently, large quantities of nuclear wastes from decades of plutonium production are stored in underground tanks. There is an urgent need to develop technologies to process and dispose of these high-level wastes in a repository in a safe and economic manner. Lanthanides (from fission) and actinides (from neutron capture and radioactive decay) are important components in the nuclear wastes, which exist in an extremely complex matrix of organic materials (*e.g.*, carboxylates and aminocarboxylates) and highly concentrated electrolytes (*e.g.*, nitrates and nitrites). In addition, the temperature of the tank wastes and the waste forms in the repository can be significantly higher than the ambient temperature due to the decay energy of the radioactivity. For example, the temperature in the waste tanks ranges from ambient to over 90°C^(3,4) while that in the waste repository could vary from 100 to 300°C, depending on waste loading and geothermal conditions.⁽⁵⁾ Successful development of waste processing and disposal technologies thus relies on accurate data on the chemical behavior of lanthanides and actinides under these conditions. However, the majority of the thermodynamic data on the formation of lanthanide and actinide complexes are for 25°C with very limited information on complexation at other temperatures. As a result, it is difficult to predict the speciation of lanthanides and actinides in the storage tanks and in waste processing where the temperature is significantly above 25°C.

One method to calculate the formation constants at variable temperatures is based on the integration of the van't Hoff isochore:⁽⁶⁾

$$\ln \beta_{T_2} - \ln \beta_{T_1} = \int_{T_1}^{T_2} \Delta H_m / (RT^2) dT \quad (1)$$

where β_T is the formation constant of the complex at the Kelvin temperature T and ΔH_m is the molar enthalpy of the complexation. If the expression of ΔH_m as a function of temperature is not available, an accurate calculation of β_{T_2} by Eq. (1) is not possible. In this case, one approach of approximation is to assume that ΔH_m remains constant in the temperature range from T_1 to T_2 . Thus,

$$\ln \beta_{T_2} = \ln \beta_{T_1} - \Delta H_{m,T_1} (1/T_2 - 1/T_1) / R \quad (2)$$

Since the formation constants and molar enthalpy of many complexation reactions at 25°C are available in the literature,⁽¹⁾ Eq. (2) is used to estimate the formation constants at other temperatures. This approach may provide reasonable estimates if the dependence of ΔH_m on temperature over the range between T_1 and T_2 is insignificant. However, it cannot be used if ΔH_m changes significantly

as a function of temperature. In particular, the estimated values can be greatly in error if the temperature range of interest is wide. To provide more reliable prediction of the speciation of lanthanides and actinides in the waste tanks and in the waste repository where the temperature is significantly higher than 25°C, there is a need either to directly measure the complex formation constants at the specific temperature or to determine the variation of ΔH_m as a function of temperature in the temperature range of interest.

The dependency of the enthalpy of complexation on the temperature can be expressed as

$$d(\Delta H_m)/dT = \Delta C_{p,m} \quad (3)$$

where $\Delta C_{p,m}$ is the difference of the heat capacities of the products and reactants at temperature T (which can also be a function of temperature). If $\Delta C_{p,m}$ of the complexation is known, the molar enthalpy of complexation as a function of temperature can be expressed as (Kirchhoff's Law)⁽⁶⁾

$$\Delta H_{m,T} = \Delta H_{m,298} + \int_{298}^T \Delta C_{p,m} dT \quad (4)$$

Numerical tables of empirical and theoretical expressions of $C_{p,m}$ for a number of substances are available in the literature, allowing the exact integration in Eq. (4) for the systems involving these substances. However, such information on $C_{p,m}$ does not exist for the complexation of lanthanides and actinides and, consequently, the complexation of lanthanides and actinides at higher temperatures cannot be predicted with reliance.

In recent years, significant progress has been made in the development of theoretical models to predict the thermodynamic properties of aqueous species at variable temperatures and pressures.⁽⁷⁻¹⁹⁾ Among these, the conceptual model developed and modified by Helgeson and co-workers [the Helgeson-Kirkham-Flowers equation of state⁽¹¹⁻¹³⁾] has been applied to geothermal conditions.⁽¹¹⁻¹⁹⁾ By this model, the standard partial molal property of an aqueous species is viewed as the sum of its intrinsic counterpart and contributions by electrostriction collapse of the local solvent structure and by solvation of the species in solution. The contribution from ion solvation is of electrostatic nature and derived theoretically by the Born equation,⁽²⁰⁾ while the contributions from the intrinsic and solvent-collapse terms are determined semi-empirically by regression procedures with available experimental data at variable temperatures. Using the modified HKF equations of state, Tanger *et al.*⁽¹⁵⁾ and Shock *et al.*⁽¹⁶⁻¹⁹⁾ calculated the thermodynamic properties of a number of common aqueous species at high temperatures and pressures and predicted the constants of the equilibria involving these species. The modified HKF equations of state have considerably improved the accuracy in predictions of thermodynamic properties of aqueous species in geochemical processes at high temperatures and pressures. However, these have not been applied to the complex

system of high-level tank wastes. The parameters for actinide species that need to be determined by regression procedures with experimental data do not exist. As a result, reliable experimental data on the complexation of actinides in solutions of high ionic strength at variable temperatures are still needed.

To extend the thermodynamic database for the complexation of lanthanides and actinides to higher temperatures, we have initiated investigations on the complexation of lanthanides and actinides with a series of organic ligands by potentiometry and calorimetry at variable temperatures. The ligands include monocarboxylic acids (*e.g.*, acetic acid) and polycarboxylic acids (*e.g.*, malonic, iminodiacetic, and oxodiacetic acids). Some of these ligands are present in the tank wastes; others may not exist in the tank wastes but are of relevance in waste processing and/or metal transport in the repository. This paper summarizes the results of the complexation of neodymium with acetate at variable temperatures. Complexation of lanthanides with acetate has been extensively studied at 25°C by various techniques including potentiometry, spectrophotometry, calorimetry, ion exchange, and solvent extraction, but only a limited number of studies have been conducted at variable temperatures.⁽²¹⁻²⁴⁾ Choppin and Schneider determined the formation constants of the monoacetate complexes of trivalent Ce, Eu, and a few actinides by solvent extraction in a temperature range between 0° and 55°C.⁽²¹⁾ Ding *et al.*⁽²²⁾ obtained stability constants of neodymium acetate complexes in 0.1 mol·kg⁻¹ NaCl at temperatures up to 70°C by potentiometry. Wruck *et al.*⁽²³⁾ determined the stability constants of Nd-acetate complexes in 2.2 mol·kg⁻¹ NaClO₄ from 20 to 70°C by laser-induced photoacoustic spectroscopy. More recently, Wood *et al.*⁽²⁴⁾ determined the stability constants of Nd-acetate complexes in 0.1 mol·kg⁻¹ NaCl from 25 to 225°C by potentiometry and derived the enthalpy of complexation from the potentiometric titration data. In most of these studies, only the formation constants are directly determined experimentally. In the present study, the formation constants of three Nd-acetate complexes, Nd(OOCCH₃)_j^{(3-j)+} where *j* = 1, 2, and 3, and the corresponding enthalpy values were experimentally determined at 45 and 70°C by potentiometry and calorimetry. These data, in conjunction with the data at 25°C from the literature,^(1,25) allow the calculation of the $\Delta C_{p,m}$ of complexation.

2. EXPERIMENTAL SECTION

2.1. Chemicals

All chemicals were reagent grade or higher. Sodium acetate from Aldrich was recrystallized twice from ethanol + H₂O in the form of NaOOCCH₃(H₂O)₃. Sodium perchlorate was recrystallized twice from water.

Distilled and deionized water was used in preparations of all the solutions. Prior to use, the water was boiled and stored in the absence of air after cooling.

Preparation of alkaline solutions was performed under a nitrogen atmosphere to avoid contamination with carbon dioxide. Sodium hydroxide solutions free of carbonate were prepared from a saturated solution (about 50% by weight). The sodium hydroxide solutions were standardized with potassium hydrogen phthalate (Aldrich, ACS Acidimetric grade). Acetate buffer solutions were prepared by adding appropriate amounts of NaOH to acetic acid solutions immediately prior to use. The perchloric acid solutions were standardized potentiometrically with tris(hydroxymethyl) aminomethane (Aldrich, ultrapure grade). A stock solution of neodymium perchlorate was prepared by dissolving neodymium oxide (Aldrich, 99.99%) in perchloric acid. The amount of perchloric acid was in excess with respect to the stoichiometric ratio of 3:1 ([perchlorate]:[Nd]) to avoid hydrolysis of neodymium. The concentrations of neodymium and perchloric acid in the stock solution were determined by complexometry with EDTA⁽²⁶⁾ and by Gran's potentiometric method,⁽²⁷⁾ respectively.

2.2. Potentiometry

The potentiometric and calorimetric measurements were carried out at $45 \pm 0.1^\circ\text{C}$ and $70 \pm 0.1^\circ\text{C}$. The ionic strength was adjusted to $2.0 \text{ mol}\cdot\text{dm}^{-3}$ at 25°C by adding appropriate amounts of the stock solution of sodium perchlorate.

The potentiometric apparatus consists of a 100 cm^3 glass cell with a lid. Both the cell and the lid are water-jacketted so that the cell temperature can be maintained at the desired temperatures by water circulating from a constant temperature bath. The measurements of electromotive force (emf) were conducted with a Metrohm pH meter (Model 654) equipped with an Ingold 405-60-S7 combination glass electrode (for measuring pH in a temperature range up to 125°C). The original electrode filling solution ($3.0 \text{ mol}\cdot\text{dm}^{-3}$ KCl) was replaced with a $2.0 \text{ mol}\cdot\text{dm}^{-3}$ NaClO_4 solution to avoid clogging of the electrode frit glass septum by precipitation of KClO_4 . The electrode was standardized before each titration by titrating standard perchloric acid solution with standard NaOH solution. The calculated hydrogen ion concentrations were used to convert the emf readings to hydrogen ion concentrations. All the emf data were corrected for a small contribution from the contact junction potential E_{j,H^+} of the hydrogen ion. Corrections for the contact junction potential of hydroxide ion were not necessary in these experiments.

The emf data were collected on a computer-controlled potentiometric apparatus at intervals determined by the data collection criterion, *i.e.*, the drift of emf (ΔE) is less than 0.1 mV for 2 min.⁽²⁸⁾ Usually, this criterion was satisfied within 5 min after each addition of the titrant. At least three titrations with different metal or ligand concentrations were conducted for each system. A few titrations were repeated to check the reproducibility.

In the studies of acetate protonation, the potentiometric titrations were conducted in two ways: (1) solutions of HClO_4 ($0.4\text{--}1\text{ mol-dm}^{-3}$) were placed in the cup and titrated with sodium acetate; (2) solutions of sodium acetate (0.02 mol-dm^{-3}) and HClO_4 ($0.03\text{--}0.04\text{ mol-dm}^{-3}$) were placed in the cup and titrated with NaOH . In the studies of neodymium acetate complexation, the potentiometric titrations were conducted with $\text{Nd}(\text{ClO}_4)_3$ ($0.01\text{--}0.03\text{ mol-dm}^{-3}$) in the cup titrated with solutions of either sodium acetate or sodium acetate + perchloric acid. Multiple runs were conducted at each temperature with different neodymium or acetate concentrations. The computer program Superquad⁽²⁹⁾ was used to calculate the protonation constants $K_{\text{H,M}}$ of acetate and the stability constants $\beta_{\text{j,M}}$ of neodymium acetate complexes on the molarity scale.

To compare stability data at different temperatures, the constants calculated on the molarity scale were converted to the values on the molality scale as suggested by Grenthe *et al.*⁽³⁰⁾ Since the protonation and complex stability constants at 45 and 70°C are obtained from the potentiometric data referring to the additions, volumes, and concentrations at 25°C, such conversion can be accomplished by Eq. (5):

$$K_{\text{H,m}} = K_{\text{H,M}}d_{298} \quad (5a)$$

$$\beta_{\text{j,m}} = \beta_{\text{j,M}}(d_{298})^j \quad (5b)$$

where d_{298} ($=1.149\text{ g-cm}^{-3}$) is the density of 2.0 mol-dm^{-3} NaClO_4 in water at 25°C.⁽²³⁾ This solution, equivalent to a solution of 2.2 mol-kg^{-1} NaClO_4 , is chosen as the reference solution for the calculation of the stability constants on the molality scale.

2.3. Calorimetry

The calorimetric titrations were conducted with a variable-temperature titration calorimeter operated by a computer. The calorimetric apparatus, described in detail in a previous publication,⁽³¹⁾ was immersed in a Tronac water bath controlled by a Tronac Model PTC-36 precision temperature controller. The Tronac bath has a volume of 95 dm^3 and maintains the temperature to $\pm 0.0005\text{ K}$. The performance of the calorimeter was previously tested by measuring the enthalpy of protonation of tris(hydroxymethyl)aminomethane (TRIS) at 45 and 70°C.⁽³¹⁾ The values obtained compare very well with those in the literature.

The calorimetric measurements were conducted by incremental additions of the titrant ($0.1\text{--}0.5\text{ cm}^3$ per addition) to the solution in the reaction vessel. The titrant solution was allowed to reach the temperature of the experiment by residence in a coiled polypropylene tube (3 m long, 1-mm i.d.) immersed in the thermostatic bath prior to delivery to the reaction vessel. A Radiometer ABUSO autoburette was used for delivery. The mass of the titrant solution delivered was

calculated from the volume of the addition and the density of the reference solution ($2.2 \text{ mol}\cdot\text{kg}^{-1} \text{ NaClO}_4$) at the experimental temperature (the densities of $2.2 \text{ mol}\cdot\text{kg}^{-1} \text{ NaClO}_4$ are $1.138 \text{ g}\cdot\text{cm}^{-3}$ at 45°C and $1.125 \text{ kg}\cdot\text{dm}^{-3}$ at 70°C , respectively). To determine the enthalpy change of acetate protonation at 45 and 70°C , acetate buffer ($0.04 \text{ mol}\cdot\text{dm}^{-3}$ acetic acid + $0.02 \text{ mol}\cdot\text{dm}^{-3}$ sodium acetate) was placed in the cup and titrated with $0.1 \text{ mol}\cdot\text{dm}^{-3}$ perchloric acid. Each titration was repeated three times at each temperature. To determine the enthalpy change of complexation, titrations were conducted with different neodymium or acetate concentrations at 45°C (eight runs) and 70°C (seven runs). For each titration run, n experimental values of the total heat produced in the reaction vessel ($Q_{\text{ex},j}$, $j = 1$ to n) were calculated as a function of the mass of the added titrant. These values were corrected for the heat of dilution of the titrant ($Q_{\text{dil},j}$), which was determined in separate runs. The net reaction heat at the j th point ($Q_{\text{r},j}$) was obtained from the difference: $Q_{\text{r},j} = Q_{\text{ex},j} - Q_{\text{dil},j}$. The quantity Δh_v , the total heat per mole of proton (in protonation titrations) or metal (in complexation titrations), was calculated by dividing the net reaction heat by the number of moles of proton or metal in the calorimeter vessel. The enthalpy changes of the acetate protonation and neodymium acetate complexation were calculated with the computer program LETAGROP KALLE with Δh_v as the error-carrying variable.^(32,33)

2.4. Optical Spectroscopy

Absorption spectra of Nd–acetate solutions were obtained on a Varian Cary-5G spectrophotometer equipped with a 1×1 Peltier automatic temperature controller. Quartz cells with 1.0-cm optical length were used.

3. RESULTS AND DISCUSSION

3.1. Protonation of Acetate

The acetate protonation constants at 45 and 70°C , determined by potentiometric titrations, were used to calculate the enthalpies of protonation from the calorimetric titrations at the same temperatures. The calculated protonation constants, Gibbs free energy, enthalpy, and entropy are summarized in Table I, together with the corresponding values at 25°C from the literature.^(1,25)

The data in Table I indicate that the protonation constant of acetate remains almost constant in the temperature range from 25 to 70°C , which is the result of the compensation of changes in the enthalpy (ΔH_m) and entropy ($T\Delta S_m$) terms. As is typical of many carboxylic acids,⁽¹⁾ the enthalpy of protonation of acetate is small (from zero to a few $\text{kJ}\cdot\text{mol}^{-1}$) and changes from slightly exothermic at lower temperatures (between 25 and 45°C) to slightly endothermic at higher

Table I. Acetate Protonation Constants and Corresponding Thermodynamic Parameters^a $I = 2.2\text{ m}$ Na(ClO₄)

$T(^{\circ}\text{C})$	$\log K_{H,M}$	$\log K_{H,m}$	$-\Delta G_{H,m}$ (kJ·mol ⁻¹)	$\Delta H_{H,m}$ (kJ·mol ⁻¹)	$\Delta S_{H,m}$ (J·K ⁻¹ ·mol ⁻¹)	$T\Delta S_{H,m}$ (kJ·mol ⁻¹)	Reference
25	4.80 ± 0.01	4.86 ± 0.01	27.74 ± 0.06	-3.01 ± 0.16	82.9 ± 0.7	24.73 ± 0.20	1,25
45	4.76 ± 0.01	4.82 ± 0.01 4.75 ± 0.06 ^b	29.36 ± 0.06	-2.74 ± 0.05	83.7 ± 0.4	26.62 ± 0.11	This work 23
70	4.82 ± 0.01	4.88 ± 0.01 4.81 ± 0.07	32.05 ± 0.07	+0.92 ± 0.06	96.1 ± 0.4	32.97 ± 0.13	This work 23

^aThe protonation constant $K_H = [\text{HL}]/([\text{H}^+][\text{L}^-])$, where L stands for acetate. $K_{H,M}$ and $K_{H,m}$ represent the protonation constants on the molarity and the molality scales, respectively. All error limits represent 1σ .

^bValue obtained by interpolation of the data from Ref. 23.

temperatures (70°C). By contrast, the entropy term increases from 24.73 kJ·mol⁻¹ at 25°C to 32.97 kJ·mol⁻¹ at 70°C.

Using a modified HKF equation of state, Shock⁽¹⁷⁾ calculated the standard partial molar thermodynamic properties of a series of aqueous carboxylic acids and predicted their protonation constants as functions of temperature and pressure. The predicted thermodynamic constants of acetate protonation ($\log K$) by Shock are 4.76 (25°C), 4.79 (50°C), and 4.85 (75°C), which is in good agreement with the experimental values from the present study.

3.2. Complexation of Neodymium with Acetate

3.2.1. Formation Constants and Gibbs Free Energy

A representative set of potentiometric titration data at 70°C is shown in Fig. 1 as a plot of \bar{n} vs. $\log[L]$ for the neodymium acetate system, where \bar{n} is the average number of acetate ions bound to each neodymium as calculated by the relation

$$\bar{n} = \{C_L - [L](1 + K_{H,M}[H^+])\} / C_M \quad (6)$$

In Eq. (6), C_L and C_M are the concentrations of total acetate and total neodymium in solution and $[L]$ is the concentration of free acetate. Similar plots are obtained at 45°C.

The analysis of the potentiometric data by the Superquad program⁽²⁹⁾ indicates that, at 45 and 70°C, neodymium forms at least three successive mononuclear complexes according to equilibrium (7).



The calculated formation constants and Gibbs free energy of complexation are summarized in Table II and a potentiometric titration curve calculated with these

constants shown in Fig. 1. The consistency between the calculated curve and the experimental points indicates that the potentiometric titration data are accurately represented by the formation of the three consecutive mononuclear complexes.

Table II shows that the formation constants (β_1 , β_2 , and β_3) increase with temperature, which is consistent with the trend for β_1 and β_2 observed by others.⁽²¹⁻²⁴⁾ Among the data from the literature, those from Ref. 23 are for Nd(III) and at the same ionic strength as in this study, allowing direct comparison. As shown in Table II, the formation constants of the first two complexes, $\text{Nd}(\text{OOCCH}_3)_2^{2+}$ and $\text{Nd}(\text{OOCCH}_3)_2^+$, from Ref. 23 are in good agreement with the present data at 45 and 70°C. The data from the present study are consistent with the presence of the third complex, but this complex was not reported in Ref. 23 in spite of the wide concentration range of acetate used in both studies. This may reflect that the photoacoustic spectra of $\text{Nd}(\text{OOCCH}_3)_2^+$ and $\text{Nd}(\text{OOCCH}_3)_3$ were sufficiently similar that they could not be resolved in Ref. 23.

Since the Nd-O bonds in the Nd-acetate complexes are expected to be ionic, the Gibbs free energy of complexation can be expressed by a modified Born equation⁽³⁴⁻³⁶⁾

$$\Delta G_m = Ne^2 Z_+ Z_- / (0.1 \epsilon d_{12}) - RT \nu \ln 55.51 + RT \Sigma \ln f(I) \quad (8)$$

where ΔG_m is in $\text{J}\cdot\text{mol}^{-1}$ and the symbols are explained in Ref. 36. Combining

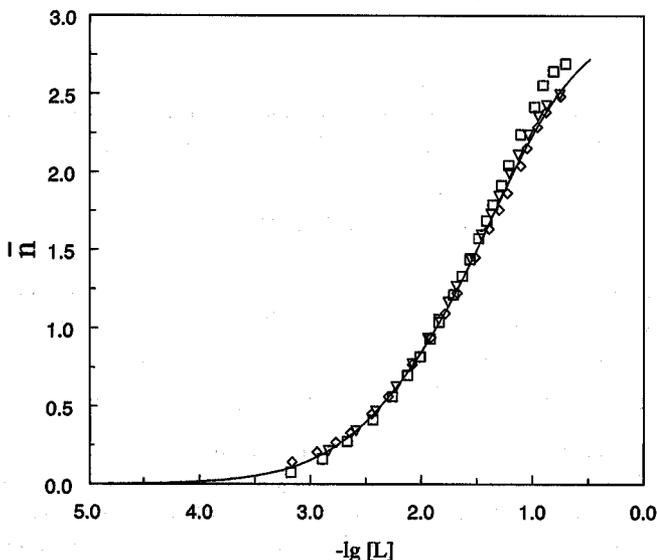


Fig. 1. Complex-formation function for neodymium acetate at 70°C. Detailed information on the titrations is shown in Table AI in the Appendix. The curve was calculated using the formation constants in Table II.

Table II. Formation Constants and Corresponding Thermodynamic Parameters^a for Neodymium–Acetate Complexation $I = 2.2\text{ m Na}(\text{ClO}_4)$

j	$\log\beta_{j,M}$	$\log\beta_{j,m}$	$-\Delta G_{H,m}$ (kJ·mol ⁻¹)	$\Delta H_{H,m}$ (kJ·mol ⁻¹)	$\Delta S_{H,m}$ (J·K ⁻¹ ·mol ⁻¹)	$T\Delta S_{H,m}$ (kJ ⁻¹ ·mol ⁻¹)	Reference
$T = 25^\circ\text{C}$							
1	1.92 ± 0.04	1.98 ± 0.04 2.10 ± 0.04	11.30 ± 0.23	7.1 ± 0.03	66.0 ± 0.4	18.4 ± 0.1	1,25 24 ^b
2	3.02 ± 0.05	3.14 ± 0.05 3.76 ± 0.05	17.98 ± 0.28	14.6 ± 0.16	107 ± 2	32.6 ± 0.6	1,25 24
3	3.58 ± 0.08	3.76 ± 0.08	21.46 ± 0.46	18.4 ± 0.46	130 ± 4	39.9 ± 1.2	1,25
$T = 45^\circ\text{C}$							
1	2.05 ± 0.03	2.11 ± 0.03 $\sim 2.0 \pm 0.03^c$ 2.18^c	12.9 ± 0.2	9.1 ± 0.3	69 ± 2	22.0 ± 0.4	This work 23 24
2	3.40 ± 0.05	3.52 ± 0.05 $\sim 3.4^c$ 3.76^c	21.4 ± 0.3	17.5 ± 0.4	122 ± 3	38.9 ± 0.7	This work 23 24
3	4.36 ± 0.09	4.54 ± 0.09	27.7 ± 0.7	23.6 ± 0.5	163 ± 4	51 ± 1	This work
$T = 70^\circ\text{C}$							
1	2.24 ± 0.01	2.30 ± 0.01 $2.0\text{--}2.4$ 2.33	15.11 ± 0.07	11.7 ± 0.2	78 ± 1	26.8 ± 0.3	This work 23 24
2	3.65 ± 0.03	3.77 ± 0.03 $3.6\text{--}3.9$ 3.90	24.8 ± 0.2	20.1 ± 0.4	131 ± 2	44.9 ± 0.6	This work 23 24
3	4.71 ± 0.10	4.89 ± 0.10	32.1 ± 0.7	29.2 ± 0.5	178 ± 3	61 ± 1	This work

^a $\beta_{j,M} = [\text{ML}_j]/([\text{M}][\text{L}]^j)$, where M and L stand for neodymium and acetate, respectively. All error limits represent 1σ .

^bData from Ref. 24 are for $I = 0.1\text{ m NaCl}$.

^cValues obtained by interpolation of the data from Refs. 23 and 24.

Eq. (8) and the empirical expression for ε by Gurney⁽³⁷⁾ and Wyman *et al.*⁽³⁸⁾ ($\varepsilon = \varepsilon_0 \exp(-T/\vartheta)$, where $\varepsilon_0 = 305.7$; $\vartheta = 219\text{ K}$ for water), it is possible to estimate the dependence of the complexation constant on temperature:

$$\partial(\log \beta)/\partial T = Ne^2 Z_+ Z_- / (0.2303 R d_{12}) (1/T - 1/\vartheta) / (\varepsilon T) \quad (9)$$

For a complex formation between a cation and an anion in water, $Z_+ Z_- < 0$. Thus, $\partial(\log \beta)/\partial T > 0$, if $T > \vartheta$. Since $\vartheta = 219\text{ K}$ and is far below the freezing point of water, the formation constants of such complexes will always increase as the temperature is elevated in the whole accessible temperature range of aqueous solution. This is consistent with the trend of the formation constants from this study (Table II) and others that cover a temperature range up to 500 K.^(24,39) For the formation of the first Nd–acetate complex [$Z_+ = 3$, $Z_- = -1$ and $d_{12} \approx 2.5 \times 10^{-8}\text{ cm}^2$],

$\Delta \log \beta_1$ is estimated by Eq. (9) to be 0.1 (from 25 to 45°C) and 0.25 (from 25 to 70°C). These values are in good agreement with the experimental results in Table II.

Although the $f-f$ transitions of lanthanides are usually insensitive to the nature of the coordinated ligands because of the shielding effect on the f electrons by the outer electrons of the ion, a few absorption bands do exhibit significant sensitivity.⁽⁴⁰⁻⁴⁷⁾ It was proposed that "such hypersensitivity" could be due to coulombic correlation of dipoles induced in the ligands by the transition quadrupole moment of the metal ion.^(41-43,48) For example, the changes in the absorption spectrum of Nd(III), the hypersensitive $^4I_{9/2} \rightarrow ^4G_{5/2}, ^2G_{7/2}$ transition, in particular, have been used to provide insight into the coordination environment of the Nd³⁺ ion in aqueous solutions.^(45,49,50) Choppin *et al.*⁽⁴⁹⁾ found that the $^4I_{9/2} \rightarrow ^4G_{5/2}, ^2G_{7/2}$ transition of Nd(III) was greatly intensified as the total acetate concentration was increased. From the experimental data, the oscillator strengths for this transition were calculated to be 7.9×10^{-6} (for Nd³⁺), 9.5×10^{-6} [for Nd(OOCCH₃)₂⁺], and 46×10^{-6} [for Nd(OOCCH₃)₂⁺] at an ionic strength of 2.0 M. No information on the third complex, Nd(OOCCH₃)₃, was obtained because the total acetate concentration was lower than 0.12 M.⁽⁴⁹⁾ To extend the study to higher acetate concentrations, where the third complex becomes significant, and to variable temperatures, we have collected the absorption spectra of Nd-acetate solutions ($C_{\text{acetate}}/C_{\text{Nd}} = 0, 4, 8, 16, 28, \text{ and } 40$) at 25 and 70°C (Fig. 2). Using the stability constants in Table II, speciation diagrams corresponding to these solutions were calculated as shown in Fig. 3. As shown in Fig. 2, the $^4I_{9/2} \rightarrow ^4G_{5/2}, ^2G_{7/2}$ transition was significantly intensified as $C_{\text{acetate}}/C_{\text{Nd}}$ was increased from 0 to 40, in a similar fashion at 25 and at 70°C. Attempts to deconvolute the spectra and calculate the oscillator strengths for individual species were not successful. However, when the peak area (normalized against the peak area in the absence of acetate) was plotted against $C_{\text{acetate}}/C_{\text{Nd}}$, our data indicated that the intensity of the $^4I_{9/2} \rightarrow ^4G_{5/2}, ^2G_{7/2}$ transition was enhanced by the complexation more significantly at 70 than at 25°C (Fig. 4a). Based on the generalization by Henrie *et al.*,⁽⁴⁵⁾ this difference implies that there are a greater number of coordinated acetate ligands around Nd³⁺ at 70 than at 25°C when the ratio of $C_{\text{acetate}}/C_{\text{Nd}}$ is constant. In other words, the difference in the enhancement of intensity between 25 and 70°C suggests that the Nd-acetate complexation is stronger at higher temperatures. This is consistent with the trend in the thermodynamic constants obtained by potentiometry (Table II). Figure 4b indicates that the peak area is proportional to the average number of acetate ligands around Nd³⁺ at both temperatures.

3.2.2. Enthalpy and Entropy of Complexation

The experimental data of the calorimetric titrations at 45 and 70°C are shown in Fig. 5. The values of \bar{n} were calculated using the formation constants in

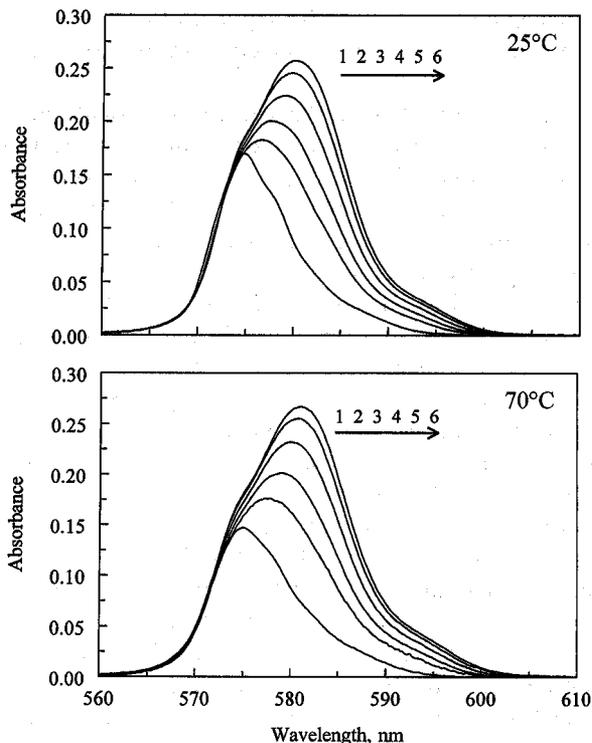


Fig. 2. Absorption spectra of Nd-acetate solutions (the hypersensitive ${}^4I_{9/2} \rightarrow {}^4G_{5/2}, {}^2G_{7/2}$ transition) at 25 and 70°C. Optical length: 1.0 cm, $I = 2.0 \text{ mol-dm}^{-3} \text{ NaClO}_4$; pH = 4.7, $[\text{Nd(III)}]_{\text{total}} = 0.025 \text{ mol-dm}^{-3}$, ratios of $C_{\text{acetate}}/C_{\text{Nd}}$ for spectra 1-6 are 0, 4, 8, 16, 28, and 40, respectively.

Table II and the analytical concentrations of Nd(III), H^+ , and acetate in solution at each step of the titration. In the calculation of Δh_v , the heat due to the protonation or deprotonation of acetate has been subtracted from the total reaction heat. From these data, the enthalpies of complexation for the three consecutive neodymium acetate complexes were calculated by the LETAGROP KALLE program⁽³²⁾ and are listed in Table II. To test the reliability of the obtained enthalpy and the formation constants, simulated calorimetric titration curves at 45 and 70°C were, in turn, calculated and are shown in Fig. 5. The curves are in good agreement with the experimental points, reflecting the mutual consistency of the calorimetric and potentiometric data on the complexation of neodymium with acetate (Table II), as well as the reliability of the data on acetate protonation (Table I).

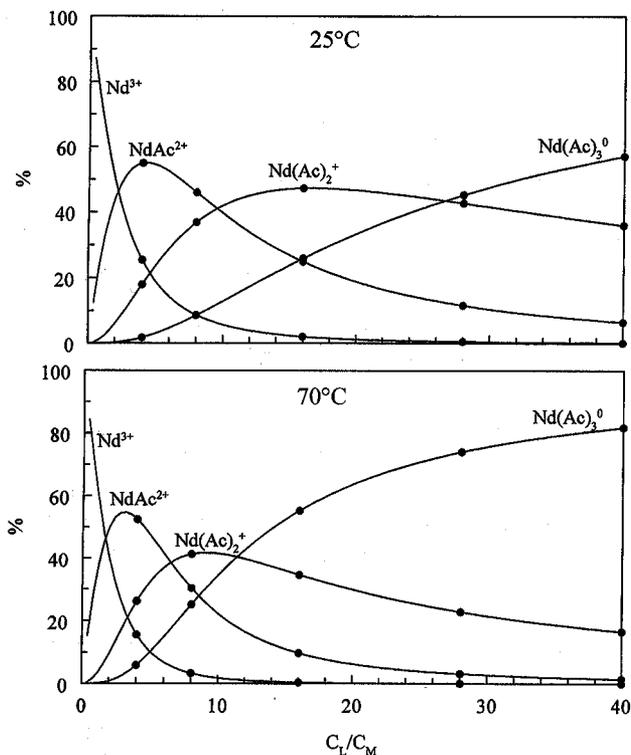


Fig. 3. Speciation diagram of the Nd-acetate solutions at 25 and 70°C. $I = 2.0 \text{ mol-dm}^{-3} \text{ NaClO}_4$; $\text{pH} = 4.7$; $[\text{Nd(III)}]_{\text{total}} = 0.025 \text{ mol-dm}^{-3}$. Solid symbols represent the speciation at $C_{\text{acetate}}/C_{\text{Nd}} = 4, 8, 16, 28, \text{ and } 40$.

Some regularities concerning the complexation enthalpy and entropy can be drawn from the data in Table II. (1) In the temperature range from 25 to 70°C, both the enthalpy and entropy of complexation are positive, indicating that the complexation is entropy driven. This is consistent with the previous observation at 25°C by Choppin and Friedman⁽⁵¹⁾ that the lanthanide-acetate complexation is stabilized by the favorable entropy factor predominating over the unfavorable enthalpy effect. (2) The entropy term $T\Delta S_m$ increases more significantly than the enthalpy as the temperature is increased, resulting in larger contributions from the entropy to the Gibbs free energy ΔG_m and more stable complexes at higher temperatures. These regularities are expected for hard acid-hard base interactions⁽⁵²⁾ ($T\Delta S_m$ is positive and dominant, while ΔH_m contributes little or unfavorably to the stability).

As shown in Table II and Fig. 6, the formation of all three neodymium-acetate complexes is endothermic and becomes increasingly endothermic as the

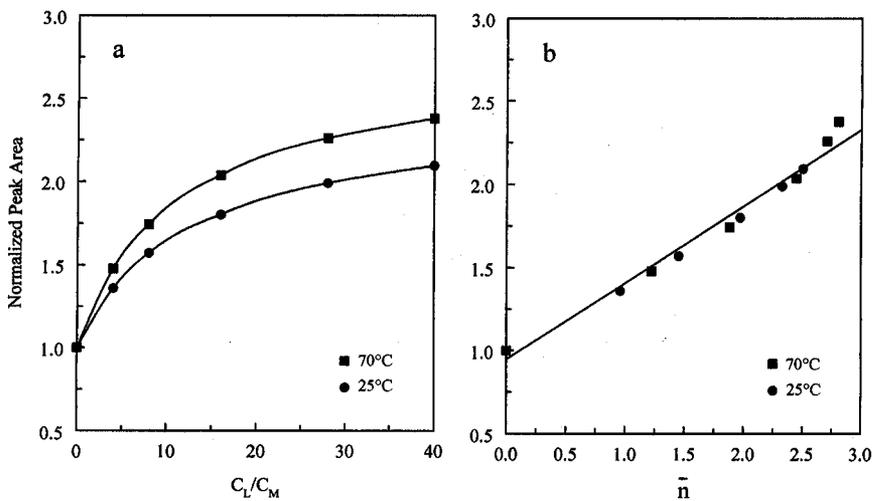


Fig. 4. Normalized peak area for the ${}^4I_{9/2} \rightarrow {}^4G_{5/2}, {}^2G_{7/2}$ transition of Nd(III) vs. $C_{\text{acetate}}/C_{\text{Nd}}$ (Fig. 4a) and \bar{n} (Fig. 4b) at 25 and 70°C.

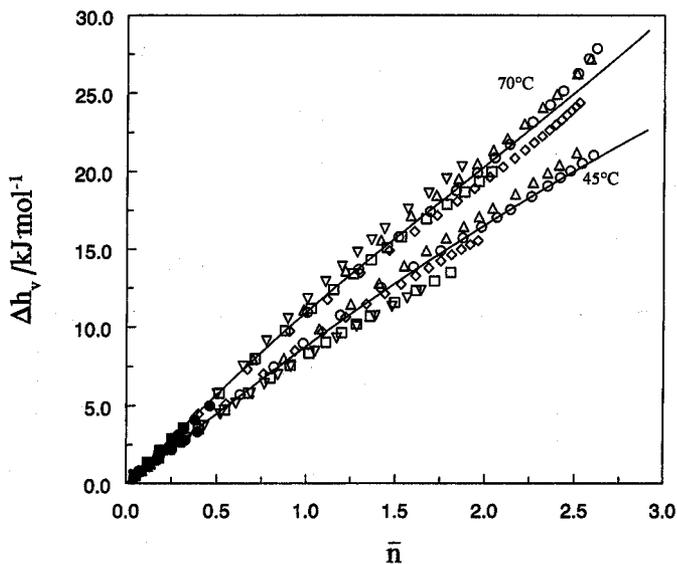


Fig. 5. Total enthalpy changes per mole of neodymium as a function of \bar{n} . Detailed information on the titrations is shown in Table AII in the Appendix. The curves were calculated using the formation constants and the molar enthalpies in Table II.

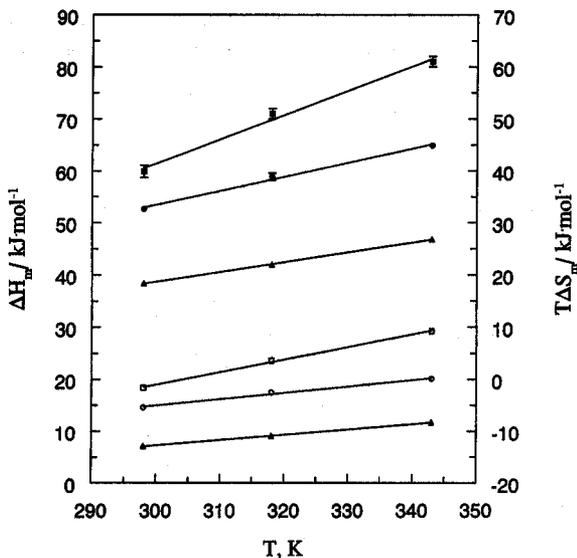


Fig. 6. Thermodynamic functions (open symbol: ΔH_m , left y axis; solid symbol: $T\Delta S_m$, right y axis) for neodymium acetate complexation at variable temperatures (Δ : ML; \circ : ML₂; \square : ML₃). The slopes of ΔH_m vs. T are: (102, 122, 239) J·mol⁻¹·K⁻¹ for $j = 1, 2,$ and $3,$ respectively. Error bars ($\pm 1\sigma$) smaller than ± 1 kJ·mol⁻¹ are not shown in the figure.

temperature is elevated. The molar enthalpy for the formation of all the three complexes can be fit with linear equations, the slopes of which correspond to the changes in the heat capacity of the complexation $\Delta C_{p,m}(\text{ML}_j)$. In the temperature range from 25 to 70°C, values of $\Delta C_{p,m}$ (J·K⁻¹·mol⁻¹) for the three complexes are all positive and independent of temperature (102 ± 13 , 122 ± 19 , and 239 ± 27 for ML, ML₂, and ML₃, respectively). It is noteworthy to point out that $\Delta C_{p,m}(\text{ML}_3)$ is significantly larger than $\Delta C_{p,m}(\text{ML}_1)$ and $\Delta C_{p,m}(\text{ML}_2)$, implying that the reactions where a complete charge neutralization occurs are most affected by a temperature change.

Data in Table II indicate that the entropy of complexation also becomes increasingly positive as the temperature is increased. As shown in Fig. 6, the increase in the entropy term $T\Delta S_m$ is more than enough to compensate the increase in the enthalpy, resulting in a more negative free energy of complexation and more stable complexes. The increase of entropy with temperature could be the consequence of a more disordered bulk water structure at higher temperatures due to perturbation by thermal motion. In the process of complexation, the solvating

water molecules are released to an already expanded and more disordered bulk solvent.⁽⁵³⁾ As a result, the net gain in the complexation entropy is larger at higher temperatures.

APPENDIX

The Appendix contains detailed information on the experimental conditions of the titrations shown in Figs. 1 and 5.

Table A1. Representative Potentiometric Titrations (Fig. 1) of Acetate Complexation with Nd(III) at 70°C (Ionic strength = 2.0 M)

Symbol	Initial cup solution			Titrant
	V (ml)	[Nd(ClO ₄) ₃], mM	[HClO ₄], mM	
□	30	10.67	20.05	1.054 M NaAc
▽	30	17.78	20.05	1.054 M NaAc
◇	30	18.20	17.23	1.489 M NaAc/ 0.511 M HAc

Table AII. Representative Calorimetric Titrations (Fig. 5) of Acetate Complexation with Nd(III) at 45 and 70°C (Ionic strength = 2.0 M)

Symbol	Initial cup solution			Titrant	
	V (ml)	[Nd(ClO ₄) ₃], mM	[HClO ₄], mM	[NaAc], M	[HAc], M
<i>T</i> = 45°C					
△	50	30.47	11.24	1.489	0.511
○	50	9.75	3.46	1.489	0.511
▽	50	30.47	11.64	0.531	0.531
□	50	20.11	8.68	0.531	0.531
◇	50	9.75	6.77	0.531	0.531
▲	50	30.30	1.76	0.0513	0.0513
■	50	20.06	1.65	0.0513	0.0513
●	50	12.12	1.31	0.0513	0.0513
<i>T</i> = 70°C					
○	50	10.66	11.77	1.489	0.511
△	50	21.33	13.81	1.489	0.511
◇	50	30.47	20.81	1.489	0.511
□	50	10.66	5.52	0.531	0.531
▽	50	21.33	10.63	0.531	0.531
●	50	10.66	0.90	0.0513	0.0513
■	50	21.33	0.88	0.0513	0.0513

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