

The aqueous geochemistry of the rare earth elements and yttrium. Part X. Potentiometric determination of stability constants of acetate complexes of La³⁺, Nd³⁺, Gd³⁺ and Yb³⁺ at 25-70 °C and 1 bar

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Abstract - The stability constants of acetate (Ac⁻) complexes of four trivalent REE (rare earth element) ions (La³⁺, Nd³⁺, Gd³⁺ and Yb³⁺) were determined in aqueous NaCl solutions at temperatures from 25-70 °C and ionic strengths from 0.1 to 2.0 mol kg⁻¹ via a potentiometric method. At the relatively low total acetate concentrations employed in this study (≤0.02 m), only the first acetate complex, LnAc²⁺ (where Ln³⁺ represents any trivalent REE ion) was required to fit the data. The data obtained are adequately described by the following equations:

$$\log Q_1(\text{La}^{3+}) = 7.081 - 1326/T + 125.2/I/T - 1.892 \times 10^{-4} \cdot T \cdot \exp(I) - 6 \cdot A_\gamma \cdot I^{1/2}/(1+I^{1/2})$$

$$\log Q_1(\text{Nd}^{3+}) = 6.671 - 1108/T + 141.5/I/T - 1.856 \times 10^{-4} \cdot T \cdot \exp(I) - 6 \cdot A_\gamma \cdot I^{1/2}/(1+I^{1/2})$$

$$\log Q_1(\text{Gd}^{3+}) = 7.092 - 1258/T + 166.5/I/T - 2.239 \times 10^{-4} \cdot T \cdot \exp(I) - 6 \cdot A_\gamma \cdot I^{1/2}/(1+I^{1/2})$$

$$\log Q_1(\text{Yb}^{3+}) = 8.196 - 1659/T + 137.4/I/T - 1.146 \times 10^{-4} \cdot T \cdot \exp(I) - 6 \cdot A_\gamma \cdot I^{1/2}/(1+I^{1/2})$$

where Q_1 is the conditional stability constant for the association reaction $\text{Ln}^{3+} + \text{Ac}^- \leftrightarrow \text{LnAc}^{2+}$, I is the ionic strength in mol kg⁻¹, T is the temperature in Kelvin and A_γ is the Debye-Hückel limiting slope. Conditional stability constants measured in this study at 25 °C and at ionic strengths ≤ 1.0 mol kg⁻¹ were in good agreement (generally less than ±0.2 log unit difference) with most values reported previously in the literature for NaClO₄ media, suggesting that competition from chloride complexation was negligible. However, stability constants determined in NaCl solutions of higher concentrations (2.0 mol kg⁻¹) were typically lower (by more than 0.2 log unit for La³⁺) than those reported in the literature for NaClO₄ solutions of the same ionic strength, suggesting that the influence of chloride complexation is significant at this NaCl concentration.

Stability constants obtained in this study were extrapolated to 250 °C using an isocoulombic approximation, and were found to be in fair agreement (within ±0.2 log unit) with the few experimental data available at elevated temperatures. However, our extrapolated values are orders of magnitude greater than previously published theoretical estimates of these constants at 100-250 °C. Our stability constants, combined with additional thermodynamic data from the literature, should permit quantitative modeling of the influence of acetate on REE mass transfer in a variety of geologic environments and fine-tuning of models designed to predict REE-acetate stability constants at elevated temperatures and pressures.

1. INTRODUCTION

Rare earth elements (REE) and Nd isotopes increasingly are being employed as tracers of processes occurring during the formation and diagenesis of sedimentary rocks, and the genesis of petroleum and base-metal deposits (e.g., Mississippi Valley-Type) that these rocks may contain (Scherer and Seitz, 1980; Graf, 1984; Banner et al., 1988a,b; Dorobek and Filby, 1988; McLennan, 1989; Bock et al., 1994; McDaniel et al., 1994; Ohr et al., 1994; Kontak and Jackson, 1995). The REE are usually considered to be relatively immobile, and it is generally held that normalized REE patterns and Nd isotope ratios, which are used widely as petrogenetic tracers, are comparatively immune to changes during weathering, diagenesis, metamorphism and hydrothermal alteration. However, a number of studies have documented dis-

turbance of Nd isotope and REE systematics by fluid-mediated processes in sedimentary rocks (Bock et al., 1994; McDaniel et al., 1994; Ohr et al., 1994; Kontak and Jackson, 1995). Mobility, and particularly fractionation, of the REE in aqueous fluids can greatly complicate the use of these elements as tracers. Assessment of the degree of mass transfer of the REE by aqueous fluids in any given geological environment requires accurate stability constants for relevant REE complexes and solubility products for relevant REE-bearing phases, but such data are often unavailable or of uncertain quality.

The mobility of the REE in hydrothermal solutions also is relevant to the safe disposal and effective remediation of nuclear waste materials in geological environments. The REE are produced during the fission of uranium and plutonium (Rard 1988), and are

analogues of trivalent elements of the actinide series (Moeller et al. 1965; Choppin 1983). Moreover, a method which is being evaluated for disposal of Pu from dismantled nuclear warheads involves the production of a waste form containing Pu and the REE gadolinium (Gd) which acts as a neutron moderator to prevent criticality. Thus, data are required to evaluate the solubility of Gd and Pu under the P-T conditions of burial of the waste.

Acetate occurs in high concentrations in some oil-field brines (up to 10,000 ppm; Willey et al., 1975; Carothers and Kharaka, 1978) and in sediments affected by seafloor hydrothermal fluids (Martens, 1990). It is a product of thermal degradation of more complex organic matter (Surdam et al., 1984; Kawamura et al., 1986), and can persist metastably in aqueous solution for geologically long periods of time at temperatures between 100 and 200 °C (Kharaka et al., 1983; Drummond and Palmer, 1986; Palmer and Drummond, 1986; Bell et al., 1993). Acetate also is produced by corn roots and the roots of grasses and herbs, and occurs in soil solutions in concentrations of $2\text{--}5 \times 10^{-3} \text{ mol L}^{-1}$ (Bruckert, 1970; Sposito, 1989). Carboxylate ligands such as acetate may also be present in mixed nuclear-organic wastes such as those occurring at Oak Ridge, Tennessee and Maxey Flats, Kentucky (cf. Means et al., 1978; Cleveland and Rees, 1981). Furthermore, acetate can be used as an analogue of monocarboxylate groups in general, both in individual low-molecular weight ligands and in complex humic and fulvic acids (Wood, 1996; 2000).

The points discussed in the preceding paragraph suggest that acetate is a potentially important ligand for the transport of metals in geological environments, and acetate complexes of the following metals have been studied at elevated temperatures: Al^{3+} (Fein, 1991; Bénézeth et al., 1994; Palmer and Bell, 1994), Zn^{2+} (Hennet et al., 1988; Yang et al., 1989; Giordano and Drummond, 1991), Fe^{2+} (Palmer and Drummond, 1986; 1988; Palmer and Hyde, 1993), Mg^{2+} (Semmler et al., 1990; Fein, 1991), Ca^{2+} (Fein, 1991; Seewald and Seyfried, 1991) and Pb^{2+} (Hennet et al., 1988; Giordano, 1989; Yang et al., 1989). Acetate complexes of the REE have been investigated using potentiometric, spectrophotometric, calorimetric, ion-exchange and solvent extraction techniques (e.g., Sonesson, 1958a,b; 1959; 1960; Grenthe, 1962; 1964; Manning and Monk, 1962; Kolat and Powell, 1962; Kovar and Powell, 1966; Archer and Monk, 1964; 1966; Choppin and Schneider, 1970; Antipenko et al., 1973; Gruzdev and Ermolaev, 1974; Bukietynska et al., 1977; 1981a,b; Daniele et al., 1985; Ilnitskaya and Ternovaya, 1988), and these studies are in reasonably good agreement (cf. review by Wood, 1993). However, the above studies are re-

stricted to low temperatures (20–25 °C) and, although they collectively cover a range of ionic strength from <0.1 to 2.0 mol L^{-1} , individual studies have dealt generally with only a single ionic strength, making problematic the extrapolation of the conditional stability constants to infinite dilution. Because of the lack of experimentally measured values at elevated temperatures and pressures, Shock and Koretsky (1993) estimated the stability constants of REE-acetate complexes using the modified Helgeson-Kirkham-Flowers (HKF) equation. Recently, Deberdt et al. (1998; 2000) measured the stability constants of La^{3+} -, Gd^{3+} - and Yb^{3+} -acetate complexes at temperatures up to 80 °C, and Wood et al. (2000) determined the stability constants of Nd^{3+} -acetate complexes in $0.1 \text{ mol kg}^{-1} \text{ NaCl}$ from 25 to 225 °C. Both Deberdt et al. (1998; 2000) and Wood et al. (2000) used potentiometric methods. Also, Wruck et al. (1997) determined stability constants of Nd^{3+} -acetate complexes from 20 to 70 °C by means of photoacoustic spectroscopy and conventional spectrophotometry. Because the ranges of ionic strengths and/or temperatures covered in these studies are somewhat restricted, additional measurements are warranted.

This paper is the tenth in a series of contributions to improved understanding of the aqueous geochemistry of the REE (Wood, 1990a,b; Wood, 1993; Wood and Williams-Jones, 1994; Wood et al., 1995; Gammons et al., 1996; van Middlesworth and Wood, 1998; Gammons and Wood, 2000; Wood et al., 2000). Here we report the potentiometric determination of the stability constants of the monoacetato (LnAc^{2+}) complexes of La^{3+} , Nd^{3+} , Gd^{3+} and Yb^{3+} in 0.1, 0.2, 1.0 and $2.0 \text{ mol kg}^{-1} \text{ NaCl}$ from 25 to 70 °C at 1 bar. Preliminary results of this investigation were reported by Ding et al. (1998). The potentiometric measurements were conducted in a different manner from those of either Deberdt et al. (1998; 2000) or Wood et al. (2000), and should provide an independent check on their results.

2. METHODOLOGY

2.1. Theoretical

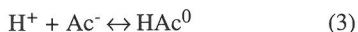
In this study, cumulative stability constants (β_n) are defined with respect to the following generalized relations:



$$\beta_n = \frac{a_{\text{LnAc}_n^{3-n}}}{a_{\text{Ln}^{3+}} a_{\text{Ac}^-}^n} \quad (2)$$

where Ln^{3+} is any trivalent REE ion, Ac^- is the acetate ion, a_i is the activity of species i , and n is the ligand

number and is assumed to range from 1 to 4. The potentiometric method employed is based on the fact that, complexation of free acetate with Ln^{3+} according to reaction (1) above will decrease the free acetate activity, causing the proton association reaction of acetate:



to shift to the left, thus liberating protons. Therefore, complex formation can be monitored by measuring the pH of a solution containing REE and acetate, when neutralized by stepwise addition of a strong base (see Baes and Mesmer, 1976 and Martell and Motekaitis, 1992).

In this study, we carried out our experiments at a constant ionic strength maintained by the addition of NaCl. As a result, activity coefficients are maintained approximately constant, and we can define a conditional, cumulative stability constant according to the following expression:

$$Q_n = \frac{m_{\text{LnAc}_n}^{3-n}}{m_{\text{Ln}^{3+}} m_{\text{Ac}^-}^n} \quad (4)$$

These conditional stability constants are truly constant only at the ionic strength at which they were determined. Determination of conditional stability constants at a series of ionic strengths permits the determination of the stability constant at infinite dilution by extrapolation to zero ionic strength. In this study we define pH_m to be the negative logarithm of the stoichiometric hydrogen ion molality, i.e., $\text{pH}_m = -\log m_{\text{H}^+}$. The convention employed is that H^+ is not complexed by the chloride ion and ion-pairing is treated implicitly by the activity coefficient model used.

We have carried out these experiments in NaCl medium as recommended by Millero (1992), rather than NaClO_4 or Na-trifluoromethanesulfonate media, so that the stability quotients determined would be directly applicable to natural hydrothermal fluids, which are dominated by NaCl. Furthermore, REE-chloride complexes are known to be relatively weak at the temperatures employed in this investigation (Wood, 1990a,b; Gammons et al., 1996 and this volume). As will be seen below, our results indicate that chloride complexation was insignificant in our lower-ionic strength experiments but not at the highest NaCl concentration employed.

Measurements by Sonesson (1958b) indicate that small amounts of polynuclear acetate complexes are formed by the heavy REE at high REE concentration. However, they are not expected to be important at the low total REE concentrations employed in our experiments. The potentiometric study of Nd-acetate complexes by Wood et al. (2000) confirmed that polynuclear species are not significant at REE concentrations of $0.005 \text{ mol kg}^{-1}$, the concentration em-

ployed in the present study, so such species were not considered in the treatment of our data.

2.2. Materials

All chemicals used in the experiments were reagent grade, or better, and all solutions were prepared with $18\text{-M}\Omega\text{-cm}$ deionized, degassed water. The following stock solutions were prepared: 1) $0.097 \text{ mol kg}^{-1}$ HCl, prepared from concentrated HCl (37 wt %, Mallinckrodt), and standardized by titration against certified 0.1 N NaOH (Fisher); 2) $0.0966 \text{ mol kg}^{-1}$ NaOH, which was prepared from 50 wt % NaOH (Fisher) and standardized against the $0.097 \text{ mol kg}^{-1}$ HCl by titration; and 3) $4.868 \text{ mol kg}^{-1}$ NaCl, which was prepared from A.C.S. grade crystals (Fisher), standardized against silver nitrate by titration using a chloride-ion selective electrode as endpoint detector. The above three stock solutions of HCl, NaOH, and NaCl were sparged with argon and stored under positive argon pressure in 20-L polyethylene containers to exclude CO_2 . Solutions were transferred by positive argon pressure to minimize contact with air. Stock solutions of REE chlorides, prepared from hydrated crystalline solids (Alfa Aesar), were standardized by acidimetric titration of the eluent obtained by passing an aliquot of the REE stock solution through a cation-exchange column (Dowex 50WX2-200 ion-exchange resin in H^+ form, Aldrich). Excess acid was required in the REE stock solutions to prevent hydrolysis. In our case, sufficient concentrated HCl was added to the stock solution to keep the pH near 2. A stock solution of $0.196 \text{ mol kg}^{-1}$ sodium acetate, which was prepared from A.C.S. grade crystals (Sigma Chemical Co.), was standardized against $0.097 \text{ mol kg}^{-1}$ HCl by titration.

2.3. Potentiometric Measurements

The stability constants of La^{3+} , Nd^{3+} , Gd^{3+} , and Yb^{3+} complexes with acetate were determined at ionic strengths of 0.1, 0.2, 1.0 and 2.0 mol kg^{-1} and at temperatures of 25, 40, 50, 60, and $70 \text{ }^\circ\text{C}$. The maximum total acetate and REE concentrations employed were 0.02 and $0.005 \text{ mol kg}^{-1}$, respectively. Separate experiments to measure the ionization constants of acetic acid were conducted over the same range of temperature and ionic strength. All titrations were repeated at least twice. The procedure employed closely follows that described by Martell and Motekaitis (1992) and is described briefly below. Additional details of the titration procedure are given by Ding (1999).

The experiments were conducted using two jacketed glass reaction vessels. One of these vessels

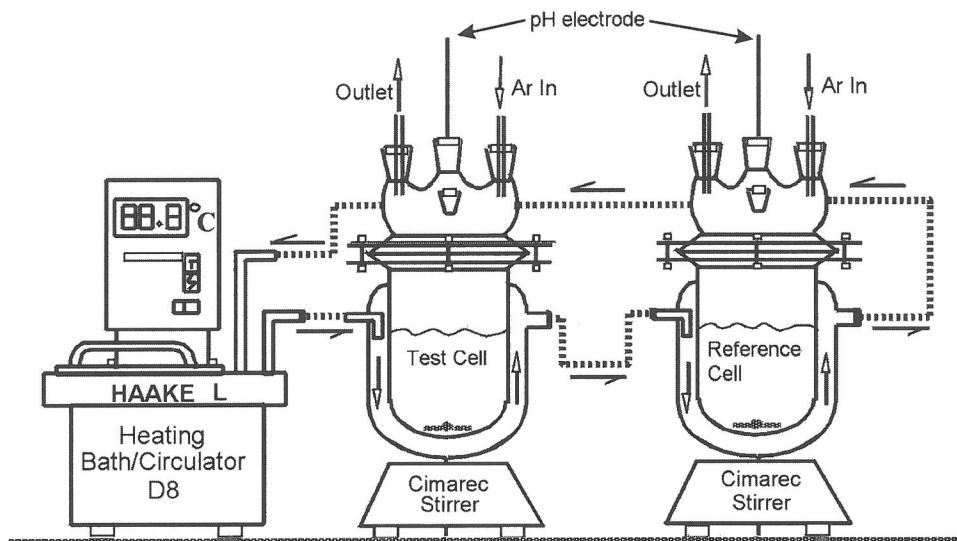


Figure 1: Schematic diagram of the apparatus employed in this study for potentiometric titrations. The reference cell is used for calibration of the pH electrode and contained solutions with precisely known concentrations of NaCl and strong acid or base. The test cell was used for the stability constant measurements and contained solutions with precisely known concentrations of LnCl_3 , NaCl, HCl and NaAc. After calibration in the reference cell (as described in the text), the electrode was transferred immediately into the test cell and the measurement of stability constants was initiated.

served as the reference cell in which the pH electrode was calibrated, and the other served as the test cell in which the stability constants were determined. The apparatus used to carry out the potentiometric titrations is illustrated schematically in Figure 1. The caps for each reaction vessel have five openings to allow a combination glass pH electrode (Orion, ROSS), PEEK (polyetheretherketone) tubing (the titrant inlet), a mercury thermometer, and gas inlet and outlet tubes to be introduced into the cell. Ultra-pure (99.99%) argon was continually bubbled through the cells to exclude CO_2 . Before being introduced into the reaction cells, the argon was passed through a polyethylene drying tube containing ASCARITE II (to absorb any traces of CO_2) and bubbled through an aqueous solution at the same ionic strength and a temperature near that of the reaction cell (to inhibit evaporation of water from the cell). A 0.8-mm thick Teflon gasket was used to effect a seal between each cell and its lid. The temperature was controlled by circulation of thermostatted water through the jacket of the cell using a circulating water bath (Haake Model D8). The desired temperature could be maintained throughout the titration experiment to within ± 0.05 °C. The solutions were mixed thoroughly during titration by means of a Teflon-coated magnetic stirring bar. When not in use,

the glass electrode was stored in a NaCl solution containing $0.001 \text{ mol kg}^{-1} \text{ H}^+$ with a similar ionic strength to that of the next experiment.

At the start of each experiment, weighed amounts of reference solution (containing a known amount of HCl) and test solution (containing known amounts of LnCl_3 , HCl, NaCl and acetate) were placed into the calibration and test cells, respectively, using polyethylene transfer pipettes. After sealing the cells, air was removed by sparging with water-saturated Ar and the solutions were allowed to attain thermal equilibrium. The potential of the glass-electrode in the calibration cell was monitored with a pH meter (Radiometer Copenhagen Model PHM84). Once a stable cell potential was attained ($< 0.01 \text{ mV/min}$), the potential was recorded. Then, a precise amount of standard base was titrated into the cell to change its pH a known amount, and a second potential reading was taken once a stable value was attained. This procedure was repeated until a calibration curve of mV vs. calculated pH_m , containing 5-10 points, was obtained. Then the electrode was transferred immediately to the test cell and measurement of the stability constant was begun. The measured potential was converted to pH_m of the test solutions using the calibration curve described above. This calibration procedure is based on the Nernst Equation:

$$E = E^o + E_{LJ} + \frac{RT}{2.3025F} pH_m \quad (5)$$

where E is the measured potential, E^o is a constant depending on the glass and reference electrodes, E_{LJ} is the liquid junction potential, R is the gas constant and F is Faraday's constant. If E^o and E_{LJ} together are constant in both the calibration cell and the test cell, then a calibration plot of potential vs. pH_m can be used to determine the pH_m of the test cell during stability constant measurements.

Calibration was conducted under the same conditions of ionic strength and temperature as the test cell. The major ion compositions in the calibration and test cells were made as similar as possible to minimize liquid junction and activity coefficient effects. The ionic strength of the solution and the concentration of the titrant-base were also matched to avoid changes in ionic strength during titration. Thus, we believe the E_{LJ} term in equation (5) to be small and constant in our experiments. Therefore, no explicit corrections were made for liquid-junction effects.

During both calibration and stability constant measurements, the titrant solution (NaOH) was transferred by volume using a syringe pump (KD Scientific, Model 210) which was connected via PEEK tubing to the cell. This syringe pump is capable of delivering volumes down to 0.001 mL, and was calibrated by weighing amounts of deionized water delivered. In initial experiments it was found that addition of the base titrant to the test solution caused local supersaturation with respect to solid REE hydroxide, which then precipitated and could not be redissolved. This problem was eliminated by employing PEEK tubing with a very fine inner diameter, relatively slow titrant addition rates, a relatively low concentration of NaOH in the titrant and vigorous mixing in the cell.

During titrations of REE-bearing solutions with NaOH, eventually a pH was reached where precipitation of $Ln(OH)_3$ was observed. This precipitation usually occurred where the rate of change of pH with titrant concentration suddenly increased. Once precipitation occurred, the titration was stopped, and several data points taken prior to precipitation were deleted from the data set to insure that hydrolysis did not affect the results.

2.4. Determination of Conditional Stability Constants

Conditional stability constants of REE-acetate complexes and dissociation constants of acetic acid were obtained from the titration data in this study using the program "BEST" provided by Martell and Motekaitis (1992). This program obtains the best-fit stability constants for a system by minimizing the

Table 1. Comparison of dissociation quotients of acetic acid in aqueous NaCl media measured in this study with those of Mesmer et al. (1989).

Ionic strength (mol kg ⁻¹)	T(°C)	log Q ¹	log Q ²	Diff.
0.1	25	-4.52	-4.54	-0.02
	30	-4.54	-4.54	-0.00
	40	-4.54	-4.55	-0.01
	50	-4.54	-4.56	-0.02
	60	-4.58	-4.58	0.00
	70	-4.58	-4.60	-0.02
0.2	25	-4.50	-4.50	-0.00
	40	-4.49	-4.50	-0.01
	50	-4.52	-4.51	0.01
	60	-4.53	-4.53	0.00
	70	-4.55	-4.54	0.01
1.0	25	-4.49	-4.49	-0.00
	40	-4.47	-4.48	-0.01
	50	-4.48	-4.47	0.01
	60	-4.49	-4.48	0.01
	70	-4.49	-4.48	0.01
2.0	25	-4.61	-4.61	0.00
	40	-4.58	-4.57	0.01
	50	-4.57	-4.56	0.01
	60	-4.56	-4.55	0.01
	70	-4.56	-4.55	0.01

¹This study – average uncertainty is ± 0.03 log units.

²Mesmer et al. (1989) – average uncertainty is ± 0.02 log units.

sum of the squares of the differences between calculated and measured pH for all the points in the titration, i.e., the standard error (see Martell and Motekaitis, 1992 for details). Raw titration data are input into "BEST", and calculated stability constants are output, in volume and molarity (mol L⁻¹) units. All concentrations and conditional stability constants reported in this paper are given in molality units (mol kg⁻¹). Conversions between weight and volume, and molarity and molality were accomplished using the density of aqueous sodium chloride solutions (calculated using the expression of Fabuss et al., 1966), assuming that, because NaCl is the dominant component in solution, the density of the solution is equal to the density of an NaCl solution of the same concentration. Additional data required by "BEST" are the dissociation products of water, which have been reported by Busey and Mesmer (1978).

In order to determine the number and identity of species present in the titration experiments, a number of models containing various combinations of the species $LnAc^{2+}$, $LnAc_2^+$, $LnAc_3^0$ were fit to the titration data. The best fit was deemed to be the one that minimized the overall standard error of the fit using the fewest species. Moreover, for a species to be included in the model, it had to account for a significant percent-

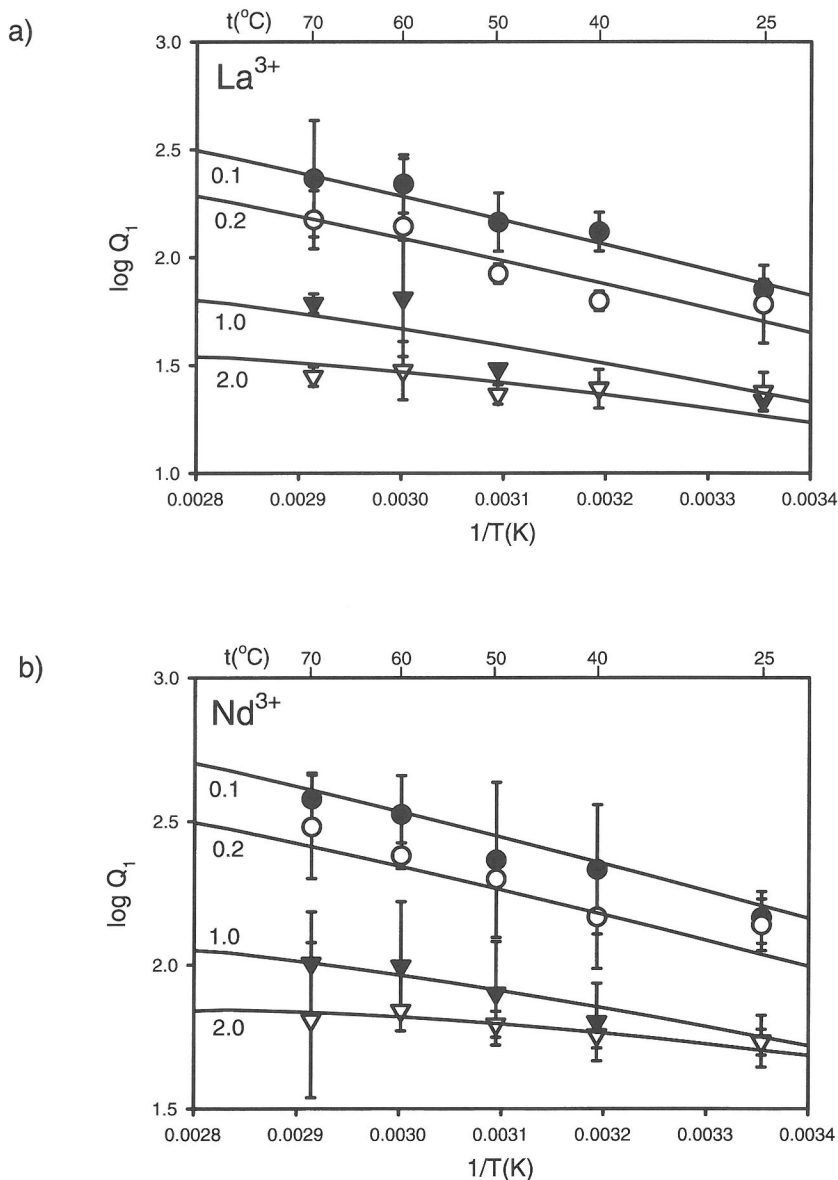


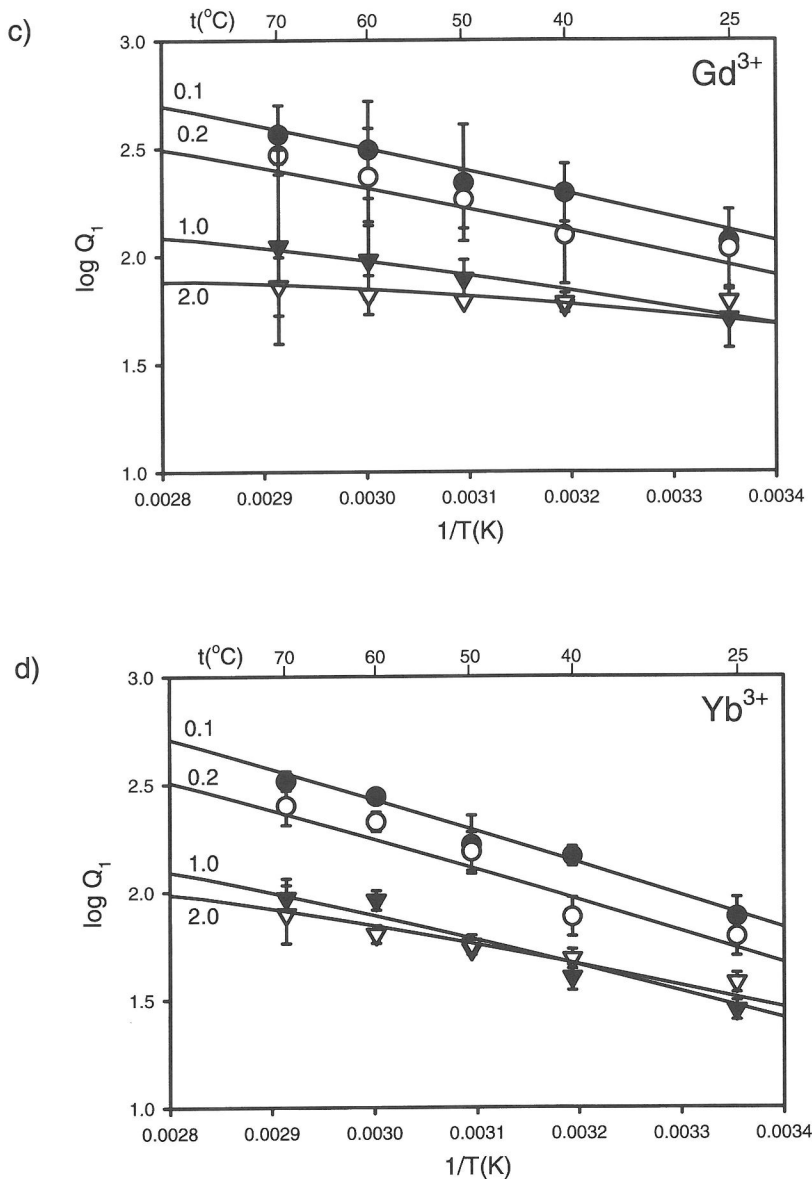
Figure 2: Plots of $\log Q_1$ vs. $1/T(K)$ for Ln^{3+} -acetate complexes in NaCl solutions at various ionic strengths (in mol kg⁻¹). The error bars represent three standard deviations about the mean of at least two replicates. The solid curves are the predicted values of $\log Q_1$ calculated from equations (7-10) in the text, which represent global fits to all the stability constant data for each REE: a) La³⁺; b) Nd³⁺;

age of the total REE present over at least some portion of the titration and the standard error of the conditional stability constant for the species had to be relatively small. The details on the mechanism by which the best fit stability constants are calculated by "Best" are given in Martell and Motekaitis (1992).

3. RESULTS

3.1. Conditional Dissociation Constants of Acetic Acid

The conditional dissociation constants of acetic acid in NaCl media were measured in this study as a

Figure 2 (continued): c) Gd^{3+} ; d) Yb^{3+} .

check on our experimental methodology and data reduction procedures. The results of these measurements are given in Table 1, where they are compared to the results of Mesmer et al. (1989). It can be seen that the two sets of measured dissociation quotients are in excellent agreement at all temperatures. This agreement suggests that our experimental apparatus and procedures are capable of yielding high-quality conditional equilibrium constants.

3.2. Conditional Stability Constants of REE-Acetate Complexes

Under all experimental conditions and for all REE studied, only the monoacetato complex, $LnAc^{2+}$, was required to fit the titration data. Other complexes such as $LnAc_2^+$ were too low in concentration to measure accurately at the acetate concentrations studied. This was particularly evident because, on fitting a two-

Table 2. Unsmoothed conditional stability constants for LnAc^{2+} in NaCl solutions obtained in this study at various temperatures and ionic strengths.

t (°C)	I (mol kg ⁻¹)	La	Nd	Gd	Yb
25	0.1	1.85±0.05	2.17±0.09	2.07±0.05	1.88±0.09
	0.2	1.78±0.18	2.14±0.09	2.03±0.18	1.79±0.09
	1.0	1.34±0.05	1.73±0.09	1.71±0.14	1.45±0.05
	2.0	1.38±0.09	1.73±0.05	1.79±0.02	1.58±0.05
40	0.1	2.12±0.09	2.33±0.22	2.29±0.14	2.16±0.05
	0.2	1.80±0.05	2.17±0.18	2.09±0.22	1.88±0.09
	1.0	1.39±0.02	1.80±0.14	1.77±0.02	1.60±0.14
	2.0	1.39±0.09	1.76±0.05	1.78±0.05	1.69±0.05
50	0.1	2.16±0.14	2.37±0.27	2.34±0.27	2.22±0.14
	0.2	1.92±0.05	2.30±0.02	2.26±0.14	2.19±0.09
	1.0	1.48±0.02	1.90±0.18	1.89±0.09	1.73±0.02
	2.0	1.36±0.05	1.79±0.05	1.79±0.02	1.75±0.05
60	0.1	2.34±0.14	2.52±0.14	2.49±0.22	2.44±0.02
	0.2	2.14±0.32	2.38±0.05	2.37±0.22	2.33±0.05
	1.0	1.81±0.27	2.00±0.22	1.98±0.18	1.96±0.05
	2.0	1.48±0.14	1.84±0.02	1.82±0.09	1.80±0.04
70	0.1	2.37±0.27	2.58±0.09	2.56±0.14	2.52±0.05
	0.2	2.17±0.14	2.48±0.18	2.47±0.09	2.40±0.09
	1.0	1.79±0.05	2.01±0.18	2.04±0.45	1.97±0.09
	2.0	1.45±0.05	1.81±0.27	1.86±0.14	1.90±0.14

Errors given represent three standard deviations from the mean of two or more replicate measurements.

Table 3. Values of $\log \beta_1$ for REE-acetate complexes at zero ionic strength calculated in this study from equations (7-10).

t(°C)	La	Nd	Gd	Yb
25	2.58	2.90	2.81	2.60
40	2.79	3.08	3.00	2.86
50	2.92	3.18	3.13	3.03
60	3.04	3.28	3.24	3.18
70	3.15	3.38	3.35	3.32

Average uncertainty is ±0.1 log units.

For each REE studied, an equation of the following form was fit to the entire set of conditional stability constants:

$$\log Q_1 = A + B/T + C \cdot I/T + D \cdot T \cdot \exp(I) + \frac{\Delta Z_1^2 \cdot A_\gamma I^{1/2}}{(1+I)^{1/2}} \quad (6)$$

where A_γ is the Debye-Hückel limiting slope (taken from Ananthaswamy and Atkinson, 1984), I is the ionic strength in mol kg⁻¹, T is the temperature in Kelvin, ΔZ_1^2 is the change in the charges squared for the complexation reaction (here $\Delta Z_1^2 = -6$), and A , B , C and D are fit parameters. The first two terms in equation (6) are of the van't Hoff type. The last term represents the Debye-Hückel contribution to activity coefficients. The remaining two terms were found, after an exhaustive search, to provide the overall best fit to the stability constant data as judged by the standard error of fit and examination of the residuals. The best fit A , B , C and D parameters were obtained using the Marquardt-Levenberg least squares algorithm in Sigmaplot® (Jandel Scientific). The resulting equations for the conditional stability constants for each of the REE studied are:

$$\log Q_1(\text{La}^{3+}) = 7.081 - 1326/T + 125.2 \cdot I/T - 1.892 \times 10^{-4} \cdot T \cdot \exp(I) - 6 \cdot A_\gamma I^{1/2}/(1+I)^{1/2} \quad (7)$$

$$\log Q_1(\text{Nd}^{3+}) = 6.671 - 1108/T + 141.5 \cdot I/T - 1.856 \times 10^{-4} \cdot T \cdot \exp(I) - 6 \cdot A_\gamma I^{1/2}/(1+I)^{1/2} \quad (8)$$

$$\log Q_1(\text{Gd}^{3+}) = 7.092 - 1258/T + 166.5 \cdot I/T - 2.239 \times 10^{-4} \cdot T \cdot \exp(I) - 6 \cdot A_\gamma I^{1/2}/(1+I)^{1/2} \quad (9)$$

$$\log Q_1(\text{Yb}^{3+}) = 8.196 - 1659/T + 137.4 \cdot I/T - 1.146 \times 10^{-4} \cdot T \cdot \exp(I) - 6 \cdot A_\gamma I^{1/2}/(1+I)^{1/2} \quad (10)$$

The solid curves in Figure 2 represent the fit to the conditional stability constant data provided by the above equations. It can be seen that equations (7-10) fit the majority of the data within their respective uncertainties, and almost all the data within ±0.1 log units. Smoothed values of the stability constants at 25-70 °C and infinite dilution, calculated from equations (7-10), are given in Table 3.

species model (LnAc^{2+} and LnAc_2^+) to the data and calculating the distribution of species based on the stability quotients obtained, it was found that the maximum percentage of total REE for the second complex was always very low (≤0.18%) and the standard error for the estimate of Q_2 was often larger than the value of Q_2 itself. Clearly, at the acetate concentrations employed in this study, the diacetate and higher complexes were present in insufficient quantity to obtain their conditional stability constants. Thus, we report conditional stability constants only for the monoacetate LnAc^{2+} complex.

The unsmoothed, conditional stability constants for the LnAc^{2+} complexes (i.e., Q_1) determined in this study are given as a function of temperature and ionic strength in Table 2. In each case the quoted error represents three standard deviations from the mean of replicate measurements. The temperature and ionic strength dependencies of the stability constants are also shown in Figure 2. For the most part, the measured conditional stability constants increase steadily with increasing temperature. However, for La, Nd and Gd, $\log Q_1$ values are nearly independent of temperature at $I = 2.0$ mol kg⁻¹. It is also evident that, in general, the conditional stability constants increase with decreasing ionic strength. However, the difference in conditional stability constants at $I = 1.0$ and $I = 2.0$ mol kg⁻¹ is relatively small, especially for Gd and Yb.

Table 4. Thermodynamic data obtained in this study for the formation of LnAc²⁺ complexes at zero ionic strength and 25°C.

Property	La	Nd	Gd	Yb
$\Delta G_{r,298.15}^0$ (kJ mol ⁻¹)	-14.7±0.6	-16.6±0.6	-16.0±0.6	-14.8±0.6
$\Delta H_{r,298.15}^0$ (kJ mol ⁻¹)	25.1±2.4	20.9±1.4	23.7±1.5	31.6±1.8
$\Delta S_{r,298.15}^0$ (J mol ⁻¹ K ⁻¹)	133±10	126±7	133±7	153±4
$\Delta H_{r,298.15}^0$ (kJ mol ⁻¹) ¹	21.0	—	17.2	23.9

¹Deberdt et al. (1998, 2000)Table 5. Values of log Q₁ reported in the literature for 20-25°C.

Source	t(°C)	Medium	La	Nd	Gd	Yb
Sonesson (1958a)	20	2.0 mol L ⁻¹ NaClO ₄	1.56	1.90	1.84	ND
Sonesson (1958b)	20	2.0 mol L ⁻¹ NaClO ₄	ND	ND	ND	1.64
Sonesson (1959)	20	1.0 mol L ⁻¹ NaClO ₄	ND	ND	1.82	ND
Kolat & Powell (1962)	20	0.1 mol L ⁻¹ NaClO ₄	2.02	2.22	2.16	2.03
Archer & Monk (1964)	25	infinite dilution	2.55	2.67	ND	2.56
Archer & Monk (1966)	25	infinite dilution	ND	ND	ND	2.45
Kovar & Powell (1966)	25	0.1 mol L ⁻¹ NaClO ₄	1.82	2.11	2.02	1.84
Migal' & Chebotar (1967)	25	2.0 mol L ⁻¹ NaClO ₄	1.54	ND	ND	ND
Migal' & Chebotar (1970)	?	2.0 mol L ⁻¹ NaClO ₄	ND	1.90	ND	ND
Migal' et al. (1971)	?	0.5 mol L ⁻¹ NaClO ₄	1.35	1.93	ND	ND
Gruzdev & Ermolaev (1974)	20	2.0 mol L ⁻¹ NaClO ₄	ND	1.80	ND	ND
Bukietynska et al. (1977)	21	2.0 mol L ⁻¹ NaClO ₄	ND	1.83	ND	ND
Bukietynska et al. (1981a)	21	2.0 mol L ⁻¹ NaClO ₄	ND	1.81	ND	ND
Bukietynska et al. (1981b)	21	2.0 mol L ⁻¹ NaClO ₄	ND	1.93	ND	ND
Bukietynska & Mondry (1984)	21	2.0 mol L ⁻¹ NaClO ₄	1.66	1.93	1.96	ND
Daniele et al. (1985)	25	0.25 mol L ⁻¹	1.74	ND	ND	ND
Ternovaya (1985)	20	1.0 mol L ⁻¹ KCl	1.4	1.76	1.70	1.20
Wood (1993)	25	infinite dilution	2.24	2.52	2.43	2.24
Wruck et al. (1997)	20	2.2 mol L ⁻¹ NaClO ₄	ND	1.90	ND	ND
Deberdt et al. (1998)	25	infinite dilution	2.20	ND	ND	ND
Deberdt et al. (2000)	25	infinite dilution	ND	ND	2.52	2.32
Wood et al. (2000)	25	0.1 mol L ⁻¹ NaCl	ND	2.1	ND	ND
This study	25	infinite dilution	2.58	2.90	2.81	2.60
This study ¹	25	0.09 mol L ⁻¹ NaCl	1.90	2.23	2.14	1.93
This study ¹	25	0.19 mol L ⁻¹ NaCl	1.73	2.06	1.98	1.76
This study ¹	25	0.98 mol L ⁻¹ NaCl	1.38	1.76	1.73	1.48
This study ¹	25	2.03 mol L ⁻¹ NaCl	1.26	1.70	1.70	1.50

¹The conditional stability constants obtained in this study have been converted to molar units for the purpose of comparison with values obtained in the literature. ND= not determined.

Thermodynamic quantities ($\Delta G_{r,298}^0$, $\Delta H_{r,298}^0$, and $\Delta S_{r,298}^0$) for reaction (1) at 25 °C and infinite dilution are given in Table 4. The values of $\Delta G_{r,298}^0$ were obtained from the formula:

$$\Delta G_{r,298}^0 = \frac{-\log \beta_{1,298}}{2.3025R(298.15)} \quad (11)$$

Where R is the ideal gas constant (8.314 J mol⁻¹ K⁻¹) and $\beta_{1,298}$ is the stability constant given in Table 3 for reaction (1) at 25 °C and infinite dilution. The enthalpy of reaction was obtained by differentiating equations (7-10) according to the relation:

$$\left(\frac{\partial \log \beta_1}{\partial T} \right) = \frac{\Delta H_{r,298}^0}{2.3025RT^2} \quad (12)$$

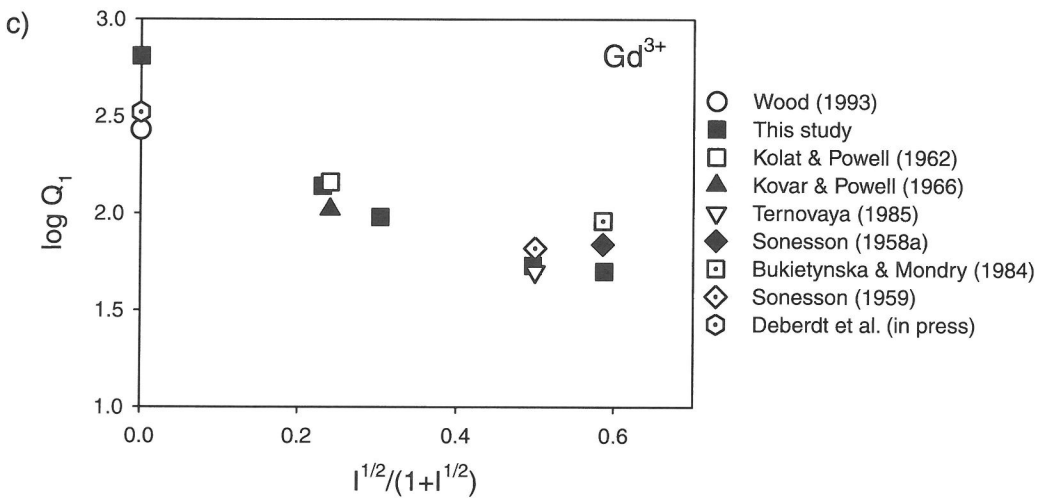
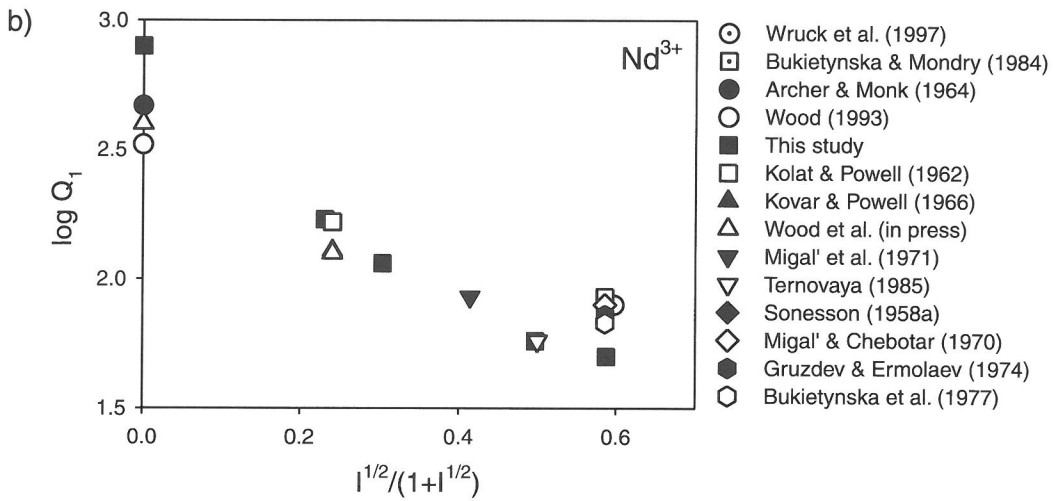
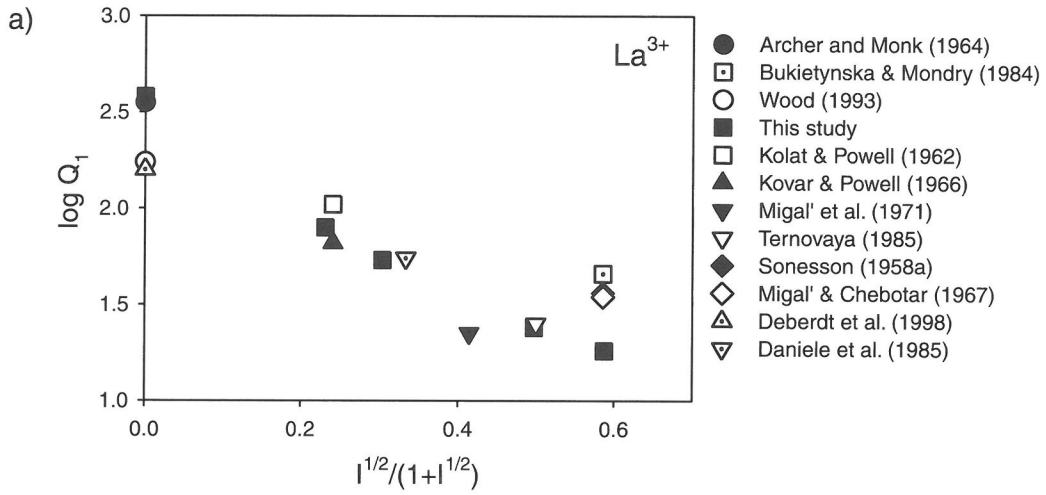
To apply equation (12), the ionic strength was set equal to zero in equations (7-10) and the resulting expressions were differentiated with respect to temperature. Finally, $\Delta S_{r,298}^0$ was obtained from the expression:

$$\Delta S_{r,298}^0 = \frac{\Delta H_{r,298}^0 - \Delta G_{r,298}^0}{T} \quad (13)$$

4. DISCUSSION

4.1. Comparison to Previous Work

The conditional stability constants obtained in this study at 25 °C are compared with those reported in the literature at 20-25 °C in Figure 3. Details of



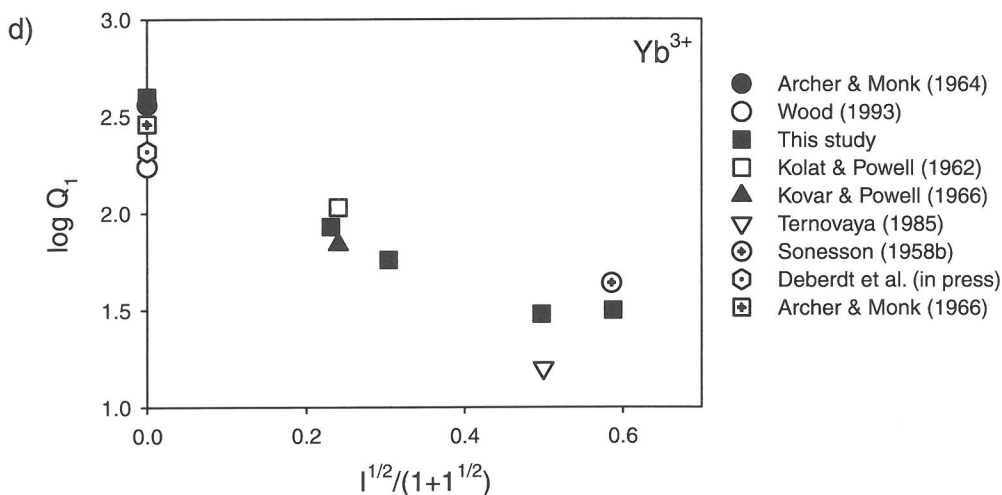


Figure 3: Comparison of $\log Q_1$ values for Ln^{3+} -acetate complexes determined in this study with those reported previously in the literature at 20–25 °C, plotted as a function of ionic strength ($I^{1/2}/(1+I^{1/2})$): a) La^{3+} ; b) Nd^{3+} ; c) Gd^{3+} ; d) Yb^{3+} . Values of conditional stability constants and ionic strengths from this study have been converted from mol kg^{-1} to mol L^{-1} units for the purpose of comparison. The average uncertainty for most of the data depicted is less than or equal to ± 0.1 log units.

the values from the literature are given in Table 5. In both Figure 3 and Table 5, we have converted our concentrations and stability constants to molar (mol L^{-1}) units for comparison with the literature values which are given almost exclusively in these units. Note that we did not include previously published data in the fitting process described above, primarily because our experiments were conducted in NaCl solutions, whereas most experiments reported in the literature to date were conducted in NaClO_4 solutions. Independent comparison of our stability constants with those determined in non-complexing perchlorate media should permit assessment of the degree to which chloride complexation of the REE may have occurred.

Figure 3 shows that, in general, our results at finite ionic strengths agree very well with those in the literature when comparison is made at the same ionic strength. In particular, our data for all four REE at 0.1 mol L^{-1} ionic strength agree to within 0.1 log unit with those of Kolat and Powell (1962) and Kovar and Powell (1966), with our conditional stability constants falling between those reported by the latter two authors. Moreover, our data at 1.0 mol L^{-1} ionic strength are nearly identical to those of Ternovaya (1985) at the same ionic strength, with the exception of the datum for Yb. The agreement among our results and those reported in the literature is particularly notable because the majority of the results reported previously have been determined in non-complexing NaClO_4 media,

whereas ours were determined in NaCl media. The agreement among the data obtained in these two media suggest that chloride complexation is quite weak at room temperature and the lower ionic strengths (NaCl concentrations) considered, in concordance with the known weak complexation of the trivalent REE with chloride under these conditions (cf. Wood, 1990a,b; Gammons et al., 1996 and this volume). However, at 2 mol kg^{-1} ionic strength, there is a discrepancy between our results and those obtained in NaClO_4 media. This discrepancy is greatest for La^{3+} , but decreases with atomic number. For Yb^{3+} , our stability quotient at 2 mol kg^{-1} is in good agreement with that determined in the landmark study by Sonesson (1958b). There are several reasons why we believe that the observed discrepancy is a result of the competing effect of chloride complexation at the highest ionic strength: 1) the discrepancy is only apparent at the highest concentrations of chloride investigated; 2) the direction of the discrepancy is compatible with the effect of chloride complexation. As shown by Wood et al. (2000), if chloride complexation occurs, stability quotients for REE-acetate complexes calculated neglecting chloride complexation will be underestimated; and 3) the discrepancy decreases on going from La^{3+} to Yb^{3+} , consistent with the apparent decrease in the stability of chloride complexes along the REE series (Wood, 1990a). Furthermore, the relatively weak temperature dependence of the stability quotients for La- and Nd-acetate complexes at $I = 2.0$

mol kg⁻¹ may be explained by the fact that the temperature dependencies of REE–acetate and –chloride complexes are quite similar (Wood et al., 2000), such that the two offset one another.

The agreement among the results at infinite dilution is more variable. For La³⁺ at infinite dilution (Fig. 3a), the stability constant of this study agrees well with the value determined by Archer and Monk (1964). On the other hand, the result of Deberdt et al. (1998) agrees more closely with the value extracted by Wood (1993) via a Pitzer treatment of all the available literature data. However, the value determined in this study is more than 0.3 log units greater than that of Deberdt et al. (1998). For Nd³⁺ (Fig. 3b), the value determined in this study is considerably larger than any of the values determined by Archer and Monk (1964), Wood (1993), or Wood et al. (2000), all of which are relatively close. For Gd³⁺ (Fig. 3c) the values from Wood (1993) and Deberdt et al. (2000) are relatively close, but our value is more than 0.2 log units greater. Finally, for Yb³⁺ (Fig. 3d) the values from this study and Archer and Monk (1964, 1966) are similar, falling within 0.20 log units of one another, whereas the values of Wood (1993) and Deberdt et al. (2000) are lower.

The discrepancies noted among values of log β_1 are most likely due to uncertainties in the activity coefficients of highly charged species such as the trivalent REE. Figure 3 demonstrates that the agreement among log Q_1 values determined at finite ionic strengths is generally much better than that among log β_1 values at infinite dilution. Moreover, quite different methods of extrapolation to infinite dilution were employed in each of these studies. For example, Archer and Monk (1964; 1966) employed the Davies equation to correct their constants to infinite dilution. On the other hand, Wood (1993) used the data of Kovar and Powell (1966) at 0.1 mol kg⁻¹ ionic strength and those of Sonesson (1958a,b) at 2.0 mol kg⁻¹ ionic strength combined with a modification of the Pitzer equations proposed for REE complexes by Millero (1992). Deberdt et al. (1998; 2000) obtained log β_1 values at infinite dilution by applying the extended Debye–Hückel equation to calculate activity coefficients for their low, but variable ionic strength solutions. Wood et al. (2000) estimated the value of log β_1 for Nd using the extended Debye–Hückel equation recommended by Helgeson (1969). Finally, our study is the only one in which the constants were determined over a range of ionic strengths and extrapolated semi-empirically to infinite dilution.

As mentioned in the Introduction, there are relatively few data available in the literature on the stability constants of REE–acetate complexes at elevated temperature. However, in the next few paragraphs we

compare our data to those from the relatively few studies reported in the literature conducted at temperatures greater than 25 °C. Our data for stability constants at elevated temperatures are compared to those determined by Deberdt et al. (1998, 2000) in Figures 4a,b,c. In general, the data exhibit similar trends with respect to temperature, but the stability constants of Deberdt et al. (1998, 2000) are consistently lower than ours by 0.2–0.4 log units. As discussed in the preceding paragraph, the discrepancies shown in Figure 4 most likely arise from differences in the manner in which the results were extrapolated to zero ionic strength.

The conditional stability constants measured by Wruck et al. (1997) for Nd³⁺ as a function of temperature (20–70 °C) in 2.2 mol kg⁻¹ NaClO₄ are more than 0.2 log units higher than those measured by us in 2.0 mol kg⁻¹ NaCl. Similarly, the results of Bukietynska et al. (1981a) for 2.0 mol kg⁻¹ NaClO₄ at temperatures from 0 to 70 °C are 0.3–0.4 log units higher than those of this study for 2.0 mol kg⁻¹ NaCl. These differences between our results in 2.0 mol kg⁻¹ NaCl solution and previous measurements in ~2.0 mol kg⁻¹ NaClO₄ solutions are most likely attributable to the effect of chloride complexation.

The recently reported conditional stability constants for Nd³⁺ in 0.1 mol kg⁻¹ NaCl solutions from 25–225 °C of Wood et al. (2000) are compared with conditional stability constants derived in this study from 25–70 °C in Figure 5. It is apparent that the stability constant determined in this study based on a one-species fit of the experimental data at 25 °C is in good agreement with the corresponding value measured by Wood et al. (2000), but only fair agreement with the data at the higher temperatures. There is a discrepancy of 0.2–0.3 log unit between these two data sets at temperatures greater than 25 °C. The uncertainty in the log Q_1 values of Wood et al. (2000) below 100 °C is on the order of ±0.1 log unit, and therefore the error limits of the two sets of data just overlap or almost overlap. It is interesting to note that, although there was no statistical justification for the introduction of a second Nd–acetate complex to fit our data, Figure 5 shows that the value of log Q_1 is sensitive to whether or not a second complex is included in the speciation model. Log Q_1 values calculated with a two-species model are lower than those calculated using a one-species model, and these values are closer to those of Wood et al. (2000). Nevertheless, because there is no statistical justification for including a second complex in the fit to the titration data, and because the conditional stability constants derived for the second complex have unreasonably large uncertainties and exhibit highly irregular trends with respect to temperature and ionic strength, we report only log Q_1 and log β_1 values obtained from the one-species model in

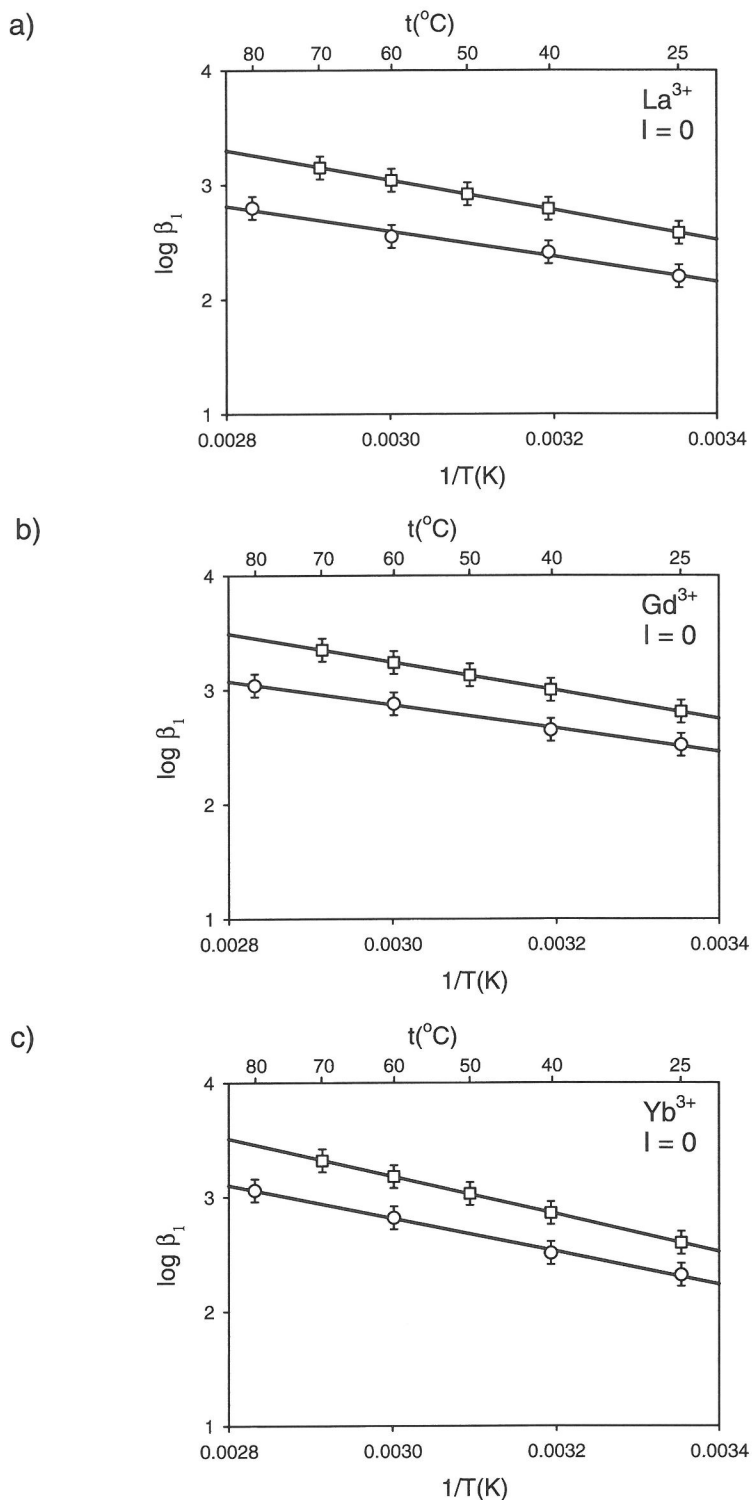


Figure 4: Comparison of $\log \beta_1$ values obtained in this study with those determined by Deberdt et al. (1998, 2000) at various temperatures for: a) La^{3+} ; b) Gd^{3+} ; and c) Yb^{3+} . The open squares are the results of this study and the open circles are the results of Deberdt et al. (1998, 2000). The solid lines are linear least squares fits to the data and are provided as visual aids only.

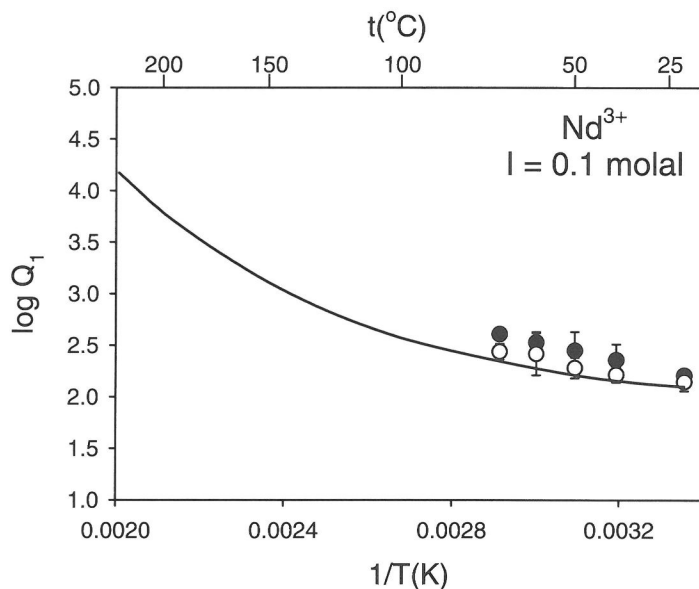


Figure 5: Comparison of $\log Q_1$ values determined in this study for Nd^{3+} in 0.1 mol kg^{-1} NaCl solution with the smoothed values obtained by Wood et al. (2000) in the same medium at various temperatures up to 250°C .

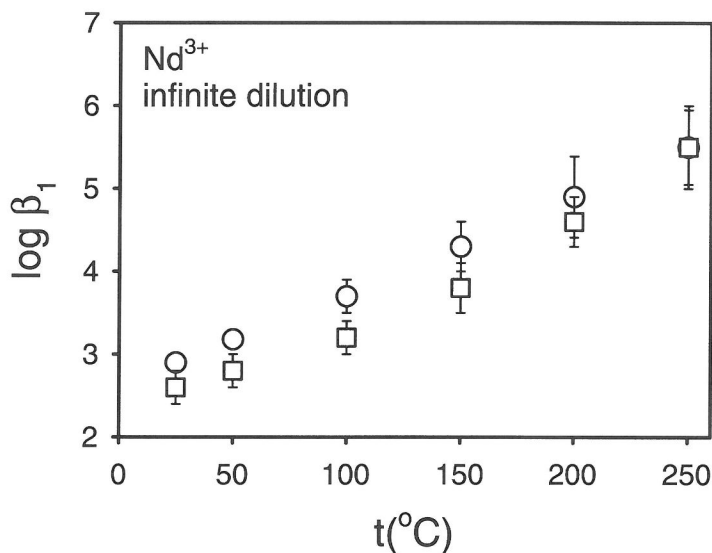


Figure 6: Comparison of stability constants ($\log \beta_1$) at infinite dilution estimated in this study (filled circles) for the first Nd^{3+} - acetate complex at elevated temperatures with those determined by Wood et al. (2000).

this paper. Results of the two-species model fits to the titration data can be found in Ding (1999).

As shown in the preceding paragraphs, our values of $\log Q_1$ and $\log \beta_1$ agree to within the combined experimental errors (± 0.1 - $0.3 \log$ units) with the data of

Deberdt et al. (1998, 2000) and Wood et al. (2000). The agreement among these studies is encouraging because, although all three studies employed a potentiometric method, there are significant differences in the experimental methodology. In this study, we em-

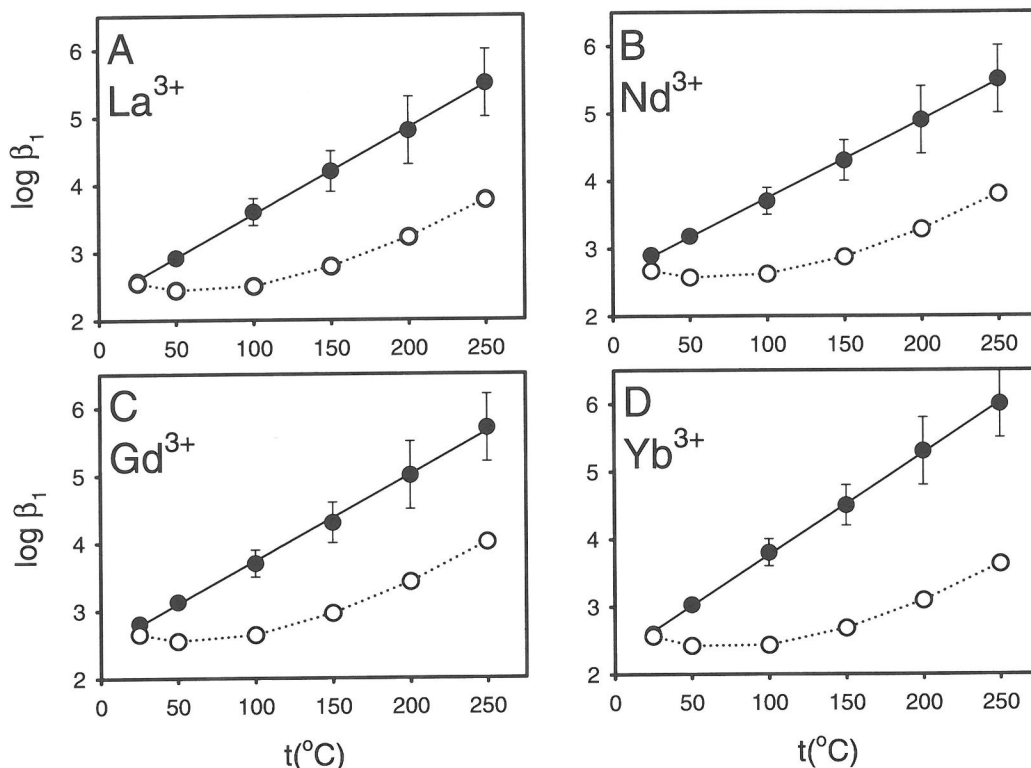


Figure 7: Comparison of stability constants ($\log \beta_1$) at infinite dilution estimated in this study using the isocoulombic approximation (solid circles, solid line) with those estimated by Shock and Koretsky (1993) (open circles, dotted line) for the first acetate complex with: a) La³⁺; b) Nd³⁺; c) Gd³⁺; d) Yb³⁺.

ployed glass electrodes, and titrated NaOH into a solution containing LnCl₃, NaCl, HCl and acetate, holding ionic strength constant throughout the titration. Deberdt et al. (1998, 2000) also used glass electrodes, but titrated a LnCl₃ solution into a sodium acetate/sodium hydroxide buffer solution and ionic strength was low but not constant. Finally, Wood et al. (2000) employed a hydrogen-concentration cell, and titrated a sodium acetate solution into a solution containing LnCl₃, HCl and NaCl, maintaining ionic strength constant throughout.

In Table 4 we compare the enthalpies of complexation calculated by us with those determined by Deberdt et al. (1998, 2000). For La the agreement between the two studies is quite reasonable (i.e., the two results agree within their combined uncertainty). However, for Gd and Yb there is a significant discrepancy, with our values being 5–8 kJ mol⁻¹ higher than those of Deberdt et al. (2000). Although the temperature trends of the stability constants of Gd- and Yb-acetate complexes determined in this study and by Deberdt et al. (2000) are subparallel (Fig. 4), our results exhibit a temperature trend with a slightly

more positive slope than those of Deberdt et al. (2000). It is well known that enthalpies derived from van't Hoff type plots are very sensitive to uncertainties in the $\log K$ values, so these slight differences in slope probably account for the observed differences in enthalpies of complexation.

4.2. Extrapolation of Stability Constants to Higher Temperature

Although we have not derived heat capacity changes for the REE-acetate complexation reactions studied here, examination of Figure 4 suggests that, at infinite dilution over the temperature range investigated, $\Delta C_{p,r,298}^{\circ} \approx 0$. This would suggest that a simple van't Hoff treatment might be used to extrapolate the measured stability constants to higher temperatures. However, there is no reason to believe that $\Delta C_{p,r,298}^{\circ}$ for reaction (1), a non-isocoulombic reaction, would remain near zero over a temperature range greater than the approximately 50 °C range covered in this study. Therefore, in order to extrapolate the stability constants for REE-acetate complexes to higher tem-

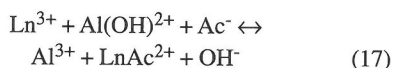
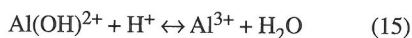
Table 6. Stability constants ($\log \beta_1$) for REE-acetate complexes at elevated temperatures calculated in this study using the isocoulombic method.

t(°C)	La	Nd	Gd	Yb
100	3.6±0.2	3.7±0.2	3.7±0.2	3.8±0.2
150	4.2±0.3	4.3±0.3	4.3±0.3	4.5±0.3
200	4.8±0.5	4.9±0.5	5.0±0.5	5.3±0.5
250	5.5±0.5	5.5±0.5	5.7±0.5	6.0±0.5

perature, the isocoulombic approximation (Lindsay, 1980; Cobble et al., 1982) was used. The complex formation reaction:



is not isocoulombic, but it can be converted to an isocoulombic reaction by addition of other appropriate reactions. In our case, we added reactions (15) and (16) to reaction (14) to obtain reaction (17), which is isocoulombic.



The change of heat capacity of reaction (17) is more likely than that of reaction (14) to remain approximately zero over a wide temperature range. $\log K$ of reaction (17) then can be extrapolated to elevated temperatures using a plot of $\log K$ vs. $1/T$. Values of $\log K$ required for reactions (15) and (16) at elevated temperatures were taken from Palmer and Wesolowski (1993) and Busey and Mesmer (1978), respectively. The uncertainty in the extrapolated values of the stability constants is considerably greater than in the raw experimental data determined here. This is a result of the accumulation of errors resulting from the combination of reactions (14), (15) and (16), as well as potential errors introduced by the isocoulombic approximation. The results of the extrapolation, with estimated uncertainties, are given in Table 6 and compared with the values reported by Wood et al. (2000) in Figure 6. The extrapolated stability constants (this study) are in reasonable agreement with the experimentally derived data (Wood et al., 2000) considering their combined uncertainties. It is particularly interesting that the stability constants from the two studies are nearly identical at 250 °C.

Our extrapolated stability constants are compared with those predicted by Shock and Koretsky (1993) in Figure 7. The values estimated by Shock and Koret-

sky (1993) are lower than ours by several orders of magnitude at temperatures above 50 °C. Deberdt et al. (1998; 2000) and Wood et al. (2000) also found that their experimentally determined stability constants for REE-acetate complexes were higher than the predictions by Shock and Koretsky (1993). Furthermore, our measured and estimated stability constants are in much closer agreement with the experimentally determined values of Deberdt et al. (1998; 2000) and Wood et al. (2000), than are the estimates of Shock and Koretsky (1993). Thus, we believe that the theoretical estimates of Shock and Koretsky (1993) require revision in the light of these new experimental data.

5. CONCLUSIONS

The stability constants of La^{3+} , Nd^{3+} , Gd^{3+} , and Yb^{3+} complexes with acetate have been determined potentiometrically from 25 to 70 °C at ionic strengths of 0.1, 0.2, 1.0 and 2.0 mol kg^{-1} .

Under the conditions of our experiments, complexes higher than the 1:1 complex LnAc^{2+} were not required to fit the data.

The measured conditional stability constants show a mild, positive temperature dependence over the range investigated. The constants decrease with increasing ionic strength.

The measured conditional stability constants for each REE can be represented adequately by an equation of the type: $\log Q_1 = A + B/T + C \cdot I/T + D \cdot T \cdot \exp(I) + \Delta Z_1^2 \cdot A_v \cdot I^{1/2} / (1+I^{1/2})$.

Our conditional stability constants at 25 °C and ionic strengths between 0.1 and 1.0 mol kg^{-1} are in excellent agreement with the conditional stability constants reported in the literature for NaClO_4 media. The similarity of REE-acetate stability constants in chloride and perchlorate media suggests that REE-chloride complexes are very weak under the conditions investigated. However, at 2 mol kg^{-1} ionic strength, the difference between the data obtained here and previous work suggest that chloride complexation has become more important at higher NaCl concentrations.

The experimentally derived stability constants were extrapolated to 250 °C using the isocoulombic approximation. These extrapolated constants are in fair agreement with previously measured values (Wood et al., 2000), but suggest that previous theoretical predictions by Shock and Koretsky (1993) are in need of revision.

Acknowledgments—This paper is dedicated to the memory of Dr. David A. Crerar, who was one of the first geochemists to recognize the importance of dissolved organic matter in the complexation of metals in natural aqueous environments and

was a pioneer in the study of the thermodynamics of metal-organic complexation at elevated temperatures. SAW is indebted to Professor Crerar for the positive influence on his career. Acknowledgment is made to the Donors of the Petroleum Research Fund, administered by the American Chemical Society, and the State Board of Education of Idaho for financial support of this research. Some of the data reduction and preparation of this manuscript were conducted while SAW was on sabbatical leave at Oak Ridge National Laboratory. This sabbatical leave was financially supported by the Geosciences Program of the Office of Basic Energy Research, U.S. Department of Energy under contract DE-AC05-96OR22464 with Lockheed Martin Energy Research Corporation. Reviews by Moira Ridley, Dick Kettler and Tom Giordano resulted in significant improvement of the manuscript and are gratefully acknowledged.

Editorial handling: T.H. Giordano

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