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The first two steps of protonation of HEDTA occur on the diamine nitrogen atoms and are exothermic, while the third step occurs on the oxygen of one carboxylate group and is slightly endothermic. This trend is in good agreement with the enthalpies of protonation directly determined by calorimetry. The energetics of the protonation can be well explained by the difference in the degree of hydration between the amine nitrogen and carboxylate oxygen sites.

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4 **Effect of Temperature on the Protonation of *N*-(2-hydroxyethyl)ethylenediamine-*N,N',N'*-**
5 **triacetic Acid in Aqueous Solutions: Potentiometric and Calorimetric Studies**
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Abstract

The TALSPEAK process (Trivalent Actinide Lanthanide Separations by Phosphorus-reagent Extraction from Aqueous Komplexes) has been demonstrated in several pilot-scale operations to be effective at separating trivalent actinides (An^{3+}) from trivalent lanthanides (Ln^{3+}). However, fundamental studies have revealed undesired aspects of TALSPEAK, such as the significant partitioning of Na^+ , lactic acid, and water into the organic phase, thermodynamically unpredictable pH dependence, and the slow extraction kinetics. In the modified TALSPEAK process, the combination of the aqueous holdback complexant HEDTA (*N*-(2-hydroxyethyl)ethylenediamine-*N,N',N'*-triacetic acid) with the extractant HEH[EHP] (2-ethyl(hexyl) phosphonic acid mono-2-ethylhexyl ester) in the organic phase has been found to exhibit a nearly flat pH dependence between 2.5 and 4.5 and more rapid phase transfer kinetics for the heavier lanthanides. To help understand the speciation of Ln^{3+} and An^{3+} in the modified TALSPEAK, systematic studies are underway on the thermodynamics of major reactions in the HEDTA system under conditions relevant to the process (e.g., higher temperatures). Thermodynamics of the protonation and complexation of HEDTA with Ln^{3+} were studied at variable temperatures. Equilibrium constants and enthalpies were determined by a combination of techniques including potentiometry and calorimetry. This paper presents the protonation constants of HEDTA at 25 – 70°C. The potentiometric titrations have demonstrated that, stepwise, the first two protonation constants decrease and the third one slightly increases with the increase of temperature. This trend is in good agreement with the enthalpy of protonation directly determined by calorimetry. The results of NMR analysis further confirm that the first two protonation reactions occur on the diamine nitrogen atoms, while the third protonation reaction occurs on the oxygen of a carboxylate group. These data, in conjunction with the

thermodynamic parameters of $\text{Ln}^{3+}/\text{An}^{3+}$ complexes with HEDTA at different temperatures, will help to predict the speciation and temperature-dependent behavior of $\text{Ln}^{3+}/\text{An}^{3+}$ in the modified TALSPEAK process.

Key Words: N-(2-hydroxyethyl)ethylenediamine-N,N',N'-triacetic acid; Protonation; Temperature effect; Actinide/lanthanide separations

1 INTRODUCTION

Advanced concepts for closing the nuclear fuel cycle typically include separating the minor actinides (i.e., Np, Am, and Cm) from other fuel components to mitigate their long-term effects on the performance of geological repositories for irradiated fuels. A critical challenge in this regard is separating the trivalent actinides (An^{3+}) from the lanthanide fission products (Ln^{3+}) due to their extremely similar chemical behavior. Effective separations of An^{3+} from Ln^{3+} by the TALSPEAK process (Trivalent Actinide Lanthanide Separations by Phosphorus-reagent Extraction from Aqueous Komplexes) have been demonstrated in pilot-scale operations [1]. The TALSPEAK process uses bis(2-ethylhexyl)phosphoric acid (HDEHP) as the extractant and an aqueous-soluble complexant, diethylenetriaminepentaacetic acid (DTPA, Fig. 1), either to “hold” the actinides in the aqueous phase and prevent their extraction into the organic phase in the conventional TALSPEAK, or to strip the actinides from the organic phase in the so-called “reversed TALSPEAK” approach [2,3]. Because DTPA binds the An^{3+} ions more strongly than the Ln^{3+} ions, the latter are preferably extracted by HDEHP in the presence of DTPA, thereby achieving the separation of An^{3+} from Ln^{3+} .

The efficiency of the TALSPEAK process is affected by a few drawbacks including the less predictable pH dependence, the significant partitioning of Na^+ , lactic acid, and water into the organic phase, and the slow extraction kinetics [4,5]. Recently, a modified TALSPEAK process was proposed in which HDEHP is replaced by its phosphonic acid analog, 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester acid (HEH[EHP]), as the extractant, and DTPA is replaced by N-(2-hydroxyethyl)ethylenediamine-N,N',N'-triacetic acid (HEDTA, Fig. 1) as the aqueous hold-back complexant [4]. Several improvements were observed with the

modified TALSPEAK, including more predictable extraction behavior, faster kinetics, and less dependence on the acidity [5].

Figure 1. DTPA (left) and HEDTA (right).

To help understand the speciation of Ln^{3+} and An^{3+} in the modified TALSPEAK and achieve better control of the process operation, systematic studies are underway on the thermodynamics of major reactions in the HEDTA system under conditions relevant to the process (e.g., higher temperatures). Thermodynamic data on the protonation of HEDTA at variable temperatures (25 – 70°C) are reported in this paper.

2 EXPERIMENTAL

2.1 Chemicals

All chemicals were reagent-grade or higher. Milli-Q water was used in preparations of all solutions. HEDTA ($\geq 98\%$, Sigma-Aldrich) was purchased as the fully protonated acid (H_3L where L^{3-} stands for the fully deprotonated HEDTA anion). A stock solution of H_3L was prepared by dissolving the desired amount of H_3L in the solution of NaClO_4 (99.99%, Sigma-Aldrich). Working solutions of NaOH in NaClO_4 were standardized by titration with potassium

hydrogen phthalate. The ionic strength of all working solutions was maintained at 1.0 mol·L⁻¹ (NaClO₄) at 25°C, and the molar concentrations in this paper were also referred to 25°C.

An HEDTA solution in D₂O (80 mmol·L⁻¹) was prepared for NMR studies. Desired amounts of HEDTA solid and 40% NaOD in D₂O (Cambridge Isotopic Laboratory) were individually weighed into a volumetric flask and D₂O was then added to the mark.

2.2 Potentiometry at variable temperatures

To avoid the problem of water-vapor condensation during the titrations at temperatures above the ambient, potentiometric experiments were carried out using a specially designed vessel for variable-temperature titrations. The potentiometric vessel consists of a 100 mL glass cell with a lid. Both the cell and the lid are water-jacketed so that the cell temperature can be maintained at the desired temperatures by water circulating from a constant temperature bath. Electromotive force (EMF, in millivolts) was measured by a pH meter (Model 713, Metrohm) equipped with a combination pH electrode (6.0259.100 Unitrode, Metrohm). The original 3.0 mol·L⁻¹ KCl salt bridge solution of the electrode was replaced with a 1.0 mol·L⁻¹ sodium chloride solution to avoid formation of insoluble KClO₄ in the electrode joint sleeve that is in contact with the working solution.

All the EMF data were corrected for a small contribution from the contact junction potential of hydrogen or hydroxide ion. Corrections for the contact junction potential of the glass electrode in the acidic and basic regions can be expressed by Eq. 1 and 2.

$$E = E^{\circ} + RT/F \ln[H^{+}] + y_H[H^{+}] \quad (1)$$

$$E = E^{\circ} + RT/F \ln(Q_w/[OH^{-}]) + y_{OH}[OH^{-}] \quad (2)$$

where R is the gas constant, F is the Faraday constant, and T is the temperature in K. $Q_w = [H^+][OH^-]$. The last terms are the electrode junction potentials ($\Delta E_{j,H^+}$ or $\Delta E_{j,OH^-}$) for the hydrogen ion (Eq.1) or the hydroxide ion (Eq.2), assumed to be proportional to the concentration of the hydrogen or hydroxide ions. The electrode was calibrated before each titration by an acid/base titration with standard $HClO_4$ and $NaOH$ solution to obtain the electrode parameters of E° , y_H , and y_{OH} . These parameters allow the calculation of hydrogen ion concentrations from the electrode potential in the subsequent titration.

Usually, three titrations using different H_3L concentrations were conducted at each temperature. 60-100 points were collected for each titration. The protonation constants at different temperatures were calculated using the program *Hyperquad* 2008 [6].

2.3 Microcalorimetry at 25°C

Calorimetric titrations were conducted with an isothermal titration microcalorimeter (TAM III, TA Instruments) at 25 °C. The TAM III system consists of a nanocalorimeter, a removable titration ampoule (1.0 ml) with stirring facilities, and a precision syringe pump for titrant delivery. The performance of the calorimeter has been tested by measuring the enthalpy of protonation of tris(hydroxymethyl)-aminomethane. Before each experiment, a full dynamic calibration was performed. Multiple titrations were conducted with solutions of different concentrations of H_3L . For each titration, n additions were made (usually $n = 50$), resulting in n experimental values of the heat generated in the reaction cell ($Q_{ex,j}$, where $j = 1$ to n). These values were corrected for the heat of dilution of the titrant ($Q_{dil,j}$), which was determined in separate runs. The net reaction heat at the j -th point ($Q_{r,j}$) was obtained from the difference: $Q_{r,j} = Q_{ex,j} - Q_{dil,j}$. These data, in conjunction with the protonation constant obtained by potentiometry, were used to calculate the enthalpy of protonation with the computer program *HypDeltaH* [7].

2.4 NMR spectroscopy

NMR experiments (^1H and COSY) were carried out on a Bruker Avance DPX 300 spectrometer. The spectrometer was operated at 300.13 MHz for the measurement of ^1H signals.

A series of HEDTA solutions with varied pD values (i.e., $-\log[\text{D}^+]$) was measured to probe the HEDTA protonation reactions. The solutions were prepared by titrating the 80 mmol·L $^{-1}$ HEDTA solution in D $_2$ O with a concentrated deuterated acid or base (68% DClO $_4$ in D $_2$ O or 40% NaOD in D $_2$ O, Cambridge Isotopic Laboratory). The pD of each HEDTA solution was determined from the pH measurements with the Metrohm pH meter (Model 713) equipped with a Ross combination pH electrode (Orion Model 8102). Prior to use, the electrode was calibrated with three standard buffer solutions of pH 4.0, 7.0 and 10.0. Values of pD was obtained by using $\text{pD} = \text{pH} + 0.40$ [8].

^1H NMR spectra were obtained for the series of HEDTA solutions, among which a solution with low pH was tested for COSY to help with the assignment of ^1H peaks. The ^1H spectra were recorded with a standard pulse program ZG30, averaging 32 scans for each spectrum. The obtained ^1H spectra were referenced to the solvent peak (HOD, 4.79 ppm).

2D ^1H - ^1H COSY data were collected using the standard Bruker pulse program COSY-45 with the 1502 Hz spectral width in both F2 and F1. The data were recorded using the DQ method with 128 x 2 increments and a total of 8 scans per t_1 increment. The data were processed with the sine weighting function in both dimensions, the extension of the t_1 dimension from 128 real points to 512 real points by zero filling, and the Fourier transformation to give a 0.5K×0.5K real matrix.

3 RESULTS AND DISCUSSION

3.1 Protonation constants of HEDTA at 25-70°C

Potentiometric titrations show that the titration curves ($-\log[H^+]$ vs. the ratio of C_H/C_L) at different temperatures are significantly different, indicating that the effect of temperature is significant on the protonation of HEDTA. Fig. 2 shows a representative set of protonation titrations of HEDTA at different temperatures. As the temperature was increased from 25°C to 70°C, the values of $-\log[H^+]$ at the same C_H/C_L became lower, a clear indication that the protonation of HEDTA became weaker at higher temperatures.

Figure 2. Potentiometric titrations of HEDTA protonation at different temperatures. $I=1.0 \text{ mol}\cdot\text{L}^{-1}$ (NaClO_4). Cup solution: Initial volume 20.00 - 25.00 mL, $C_L=17.32 - 24.31 \text{ mmol}\cdot\text{L}^{-1}$, $C_H=51.96 - 72.93 \text{ mmol}\cdot\text{L}^{-1}$. Titrant: $99.83 \text{ mmol}\cdot\text{L}^{-1}$ NaOH. Negative values of C_H/C_L represent the region where hydroxide is in excess ($-C_H/C_L = C_{OH}/C_L$).

Representative potentiometric titrations at 25°C and 70°C and the fitting curves obtained by using the *Hyperquad* program are shown in Fig. 3. The speciation of the ligand during the course of these titration experiments is superimposed on these plots. From multiple titrations at

each temperature, the protonation constants of HEDTA at different temperatures were calculated and shown in Table 1. Other comparable values at different ionic strengths from the literature have been previously reported [9-11]. To allow the comparison between the equilibrium constants at different temperatures, the constants in molarity should be converted to the constants in molality. According to the literature [12], the equilibrium constant of a reaction in molality (K_m) is related to that in molarity (K_M) by Equation (3).

$$\log K_m = \log K_M + \sum_r \nu_r \log g \quad (3)$$

where $\sum_r \nu_r$ is the stoichiometric coefficient of the reaction (ν_r is positive for products and negative for reactants) and is equal to $-i$ for the protonation reactions ($iH + L = H_iL$). g is the ratio of the values of molality to molarity for the specific ionic medium and varies for different media and concentrations. For $1.0 \text{ mol}\cdot\text{L}^{-1} \text{ NaClO}_4$, $\log g$ is about 0.02 [12]. The converted protonation constants of HEDTA are also shown in Table 1.

Figure 3. Potentiometric titrations of the protonation of HEDTA at 25°C (left) and 70°C (right). $I=1.0 \text{ mol}\cdot\text{L}^{-1} \text{ NaClO}_4$. Cup solution: Initial volume = 24.97 mL (25°C), and 20.15 mL (70°C); $C_L=17.32 \text{ mmol}\cdot\text{L}^{-1}$ (25°C), and $24.31 \text{ mmol}\cdot\text{L}^{-1}$ (70°C). Titrant: $99.83 \text{ mmol}\cdot\text{L}^{-1} \text{ NaOH}$. Symbols: $\circ$ – experimental data ($-\log[\text{H}^+]$), dashed line – fit ($-\log[\text{H}^+]$), solid lines – percentages of HEDTA species relative to the total HEDTA concentration (1: H_3L , 2: H_2L^- , 3: HL^{2-} , 4: L^{3-} , where H_3L stands for the neutral HEDTA).

Table 1 Thermodynamic parameters for the protonation of HEDTA. $\log\beta_{H,M}$ and $\log\beta_{H,m}$ represent the protonation constants in molarity and molality, respectively ($I = 1.0 \text{ mol}\cdot\text{L}^{-1}$ NaClO_4 , standard pressure: $p = 0.1 \text{ MPa}$). The uncertainties of the thermodynamic parameters represent those at 95% confidence level.

Reaction	$t, ^\circ\text{C}$	$\log\beta_{H,M}$	$\log\beta_{H,m}$	$\Delta H, \text{kJ}\cdot\text{mol}^{-1}$
$\text{H}^+ + \text{L}^{3-} = \text{HL}^{2-}$	25.0 ± 0.1	9.14 ± 0.01	9.12 ± 0.01	$-(26.0 \pm 1.7)^a, -(27.8 \pm 0.4)^b$
	40.0 ± 0.1	8.94 ± 0.01	8.92 ± 0.01	
	55.0 ± 0.1	8.69 ± 0.01	8.67 ± 0.01	
	70.0 ± 0.1	8.56 ± 0.01	8.54 ± 0.01	
$2\text{H}^+ + \text{L}^{3-} = \text{H}_2\text{L}^-$	25.0 ± 0.1	14.66 ± 0.01	14.62 ± 0.01	$-(38.3 \pm 3.3)^a, -(49.3 \pm 0.4)^b$
	40.0 ± 0.1	14.34 ± 0.01	14.30 ± 0.01	
	55.0 ± 0.1	13.97 ± 0.02	13.93 ± 0.02	
	70.0 ± 0.1	13.81 ± 0.02	13.77 ± 0.02	
$3\text{H}^+ + \text{L}^{3-} = \text{H}_3\text{L}$	25.0 ± 0.1	17.20 ± 0.01	17.14 ± 0.01	$-(30.3 \pm 4.0)^a, -(46.5 \pm 0.6)^b$
	40.0 ± 0.1	16.95 ± 0.02	16.89 ± 0.02	
	55.0 ± 0.1	16.62 ± 0.02	16.56 ± 0.02	
	70.0 ± 0.1	16.54 ± 0.03	16.48 ± 0.03	

^a Values from Van't Hoff plots, ^b Values from calorimetry at $(25.0 \pm 0.1)^\circ\text{C}$.

As shown in Table 1, the three protonation constants all decrease with the increase of temperature. From the Van't Hoff plot of $\ln\beta_H$ vs. $1/T$ (Fig. 4), the enthalpies of protonation (for the overall reactions shown in Table 1) were calculated from the slopes to be $-(26.0 \pm 1.7) \text{ kJ}\cdot\text{mol}^{-1}$, $-(38.3 \pm 3.3) \text{ kJ}\cdot\text{mol}^{-1}$, and $-(30.3 \pm 4.0) \text{ kJ}\cdot\text{mol}^{-1}$, respectively. Stepwise, the enthalpies of protonation are $-(26.0 \pm 1.7) \text{ kJ}\cdot\text{mol}^{-1}$ (for $\text{H}^+ + \text{L}^{3-} = \text{HL}^{2-}$), $-(12.3 \pm 3.7) \text{ kJ}\cdot\text{mol}^{-1}$ ($\text{H}^+ + \text{HL}^{2-} = \text{H}_2\text{L}^-$), and $+(8.0 \pm 5.9) \text{ kJ}\cdot\text{mol}^{-1}$ ($\text{H}^+ + \text{H}_2\text{L}^- = \text{H}_3\text{L}$). This means that, the first two steps of protonation are exothermic while the third step of protonation is slightly endothermic. In a previous study at $I = 0.1 \text{ mol}\cdot\text{L}^{-1} \text{ NaClO}_4$ [9], very similar enthalpies of protonation for the first two steps (-27.3 , and $-13.8 \text{ kJ}\cdot\text{mol}^{-1}$) but quite different enthalpy of protonation for the third step ($-6.4 \text{ kJ}\cdot\text{mol}^{-1}$) were reported, based on the Van't Hoff plots of the data in the temperature range

of 0 – 60°C. The discrepancy suggests that the uncertainties in the values of enthalpy calculated from the Van't Hoff plots of a few points could be quite significant. Besides, the linear treatment of the data is based on the assumption that the enthalpy remains constant in the whole temperature range. Therefore, the enthalpies from the Van't Hoff plots represent the “average” values in the temperature range. To determine the enthalpies of protonation of HEDTA at 25°C accurately, calorimetry experiments were performed in this work and the results are discussed in the next section.

Figure 4. Protonation constants of HEDTA at different temperatures. $I = 1.0 \text{ mol}\cdot\text{L}^{-1} \text{ NaClO}_4$ (see uncertainties of $\ln\beta$ in Table 1).

3.2 Enthalpy of Protonation of HEDTA at 25°C

Data of the calorimetric titrations for the protonation of HEDTA are shown in Fig. 5. The observed reaction heat (“partial” or stepwise Q) is a function of a number of parameters, including the concentrations of reactants (C_H , C_L), the protonation constants ($\log\beta_H$) and the enthalpy of protonation of HEDTA (ΔH). Using the stoichiometric concentrations of the reactants and the protonation constants measured by potentiometry in this work, the enthalpies of

protonation of HEDTA at 25°C are calculated from the calorimetric titration data, and are presented in Table 1.

Figure 5. Calorimetric titrations of the protonation of HEDTA. $I = 1.0 \text{ mol}\cdot\text{L}^{-1} \text{ NaClO}_4$, $t = 25^\circ\text{C}$. Upper: a representative thermogram. Lower: a plot of Q_{partial} vs. the volume of titrant. Symbols in the lower figure: ■ - experimental Q , solid line – fitted Q (left y-axis); dashed lines – speciation of the ligand (right y-axis). Initial cup solutions: $V^0 = 0.900 \text{ mL}$, $C_{\text{H}}^0/C_{\text{L}}^0 \text{ (mmol}\cdot\text{L}^{-1}) = 29.88/9.96$. Titrant: $99.83 \text{ mmol}\cdot\text{L}^{-1} \text{ NaOH}$, injection volume: $5.0 \mu\text{L}$.

The stepwise enthalpies of protonation measured by microcalorimetry at 25°C are $-(27.8 \pm 0.4) \text{ kJ}\cdot\text{mol}^{-1}$ (for $\text{H}^+ + \text{L}^{3-} = \text{HL}^{2-}$), $-(21.5 \pm 0.6) \text{ kJ}\cdot\text{mol}^{-1}$ (for $\text{H}^+ + \text{HL}^{2-} = \text{H}_2\text{L}^-$), and $+(2.8 \pm 0.7) \text{ kJ}\cdot\text{mol}^{-1}$ (for $\text{H}^+ + \text{H}_2\text{L}^- = \text{H}_3\text{L}$). Again, the enthalpies of protonation measured by calorimetry indicate that the first two protonation steps are exothermic while the third is slightly endothermic, generally consistent with the enthalpies obtained by the Van't Hoff plots in this work. However, it should be pointed out the exact values of enthalpies of protonation for the second step from the two methods are quite different $(-(12.3 \pm 3.7) \text{ vs. } -(21.5 \pm 0.6) \text{ kJ}\cdot\text{mol}^{-1})$.

We believe that the values from calorimetry are more accurate because these are directly measured at 25°C while those from Van't Hoff are “average” values in the experimental temperature range where the enthalpy of reaction may not be constant.

The trends in the stepwise enthalpy of protonation for HEDTA are very similar to those observed for the protonation of another polyaminocarboxylic acid, ethylenediaminetetraacetic acid (EDTA). The first two stepwise protonation of EDTA are exothermic (-19.8 and -15.2 kJ·mol⁻¹) while the successive steps are endothermic (+7.1 and +1.9 kJ·mol⁻¹) [12]. It is known that polyaminocarboxylic acids exist in aqueous solutions as zwitter ions, where the amine nitrogen is protonated and possess a positive charge, leaving the carboxylate oxygen unprotonated with a negative charge. This similarity between HEDTA and EDTA suggests that, for both HEDTA and EDTA, the HL and H₂L species probably exist as zwitter ions in the solution, where the first two protonation steps occur on the two amine nitrogen atoms. The exothermic enthalpies of the first two protonation steps result from the fact that the amine nitrogen atoms are less hydrated than the carboxylate oxygen atoms so that less dehydration energy is required upon protonation. The ¹H NMR studies described below assist in the confirmation that the first two protonation steps occur on the amine nitrogen atoms of HEDTA.

3.3 ¹H NMR

Before analyzing the ¹H NMR spectra, the peaks in the spectra needed to be assigned. In this work, the assignments were accomplished with the help from the 2D ¹H-¹H COSY data. As shown in Fig. 6, J-J coupling exists between the protons on the neighboring alkyl groups of HEDTA, e.g., between b and b' protons, and between the e and d protons, while the two non-

coupling peaks can be easily assigned to c and a/a' protons. The 2D ^1H - ^1H COSY data are in complete agreement with the assignments of the protons shown on the top of Fig.6.

Figure 6. 2D ^1H - ^1H COSY of HEDTA solution. $[\text{HEDTA}] = 80 \text{ mmol}\cdot\text{L}^{-1}$, $\text{pD} = 1.2$.

^1H NMR spectra of four HEDTA solutions (Solutions I, II, III, and IV) were collected to help identify the protonation sites of HEDTA (Fig. 7). The acidities (expressed as $\text{pD} = -\log[\text{D}^+]$) of the solutions are 12.6, 9.3, 5.5, and 1.3, for solutions I, II, III, and IV, respectively. Using the protonation constants and considering the effect of deuteration on the protonation constants and water dissociation constant [15, 16], the dominant species of HEDTA in these solutions were calculated to be: Solution I: L^{3-} (99%), Solution II: HL^{2-} (69%), Solution III: H_2L^- (70%), and

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4 Solution IV: H₃L (90%). Therefore, the variations in the NMR spectra from Solution I to IV
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6 could be discussed as reflecting the stepwise protonation of HEDTA.
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9 Usually, protonation increases the shielding of the hydrogen atom of the adjacent alkyl
10 groups, resulting in downfield displacements of the chemical shift. The closer to the protonation
11 site an alkyl group is, the larger the downfield displacement of the chemical shift is (i.e., the
12 “proximity effect”). As shown in Fig.7, from Solution I to II, the dominant species changes from
13 L³⁻ to HL²⁻, representing the first protonation step ($H^+ + L^{3-} = HL^{2-}$). The largest downfield
14 displacement of the chemical shift (~ 0.40 ppm) occurs on the hydrogen atoms b and b',
15 therefore suggesting the first protonation occurs on one of the two amine nitrogen atoms.
16 Equation (4) could reasonably be used to describe the first protonation step. It should be noted
17 that, solely based on the changes in the NMR spectra between Solution I and II, it is not
18 conclusive on which nitrogen (the nitrogen with two identical carboxylate groups or the nitrogen
19 with one carboxylate and one hydroxylethyl group) the first protonation occurs. However, the
20 changes in the NMR spectra between Solution II and III, discussed below, seem to support that
21 Equation (4), indicating the first proton goes to the nitrogen with two identical carboxylate
22 groups, probably represents the first protonation step.
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Figure 7. ^1H spectra of four HEDTA solutions. $C_L = 80 \text{ mmol}\cdot\text{L}^{-1}$.

From Solution II to III (Fig.7), the dominant species changes from HL^{2-} to H_2L^- , representing the second protonation step ($\text{H}^+ + \text{HL}^{2-} = \text{H}_2\text{L}^-$). Again, the chemical shifts of

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4 hydrogen atoms b, b', and d show the largest downfield displacement (0.56 ppm for b and b'),
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6 suggesting the second protonation also occurs on one of the two amine nitrogen atoms. In
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8 addition, c, as well as d, shows larger downfield shifts than a, which suggests that the second
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10 protonation occurs on the nitrogen with one carboxylate and one hydroxylethyl group, as
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12 described by Equation (5).
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16 In the HL^{2-} and H_2L^- species where the amine group(s) is protonated, intramolecular
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18 hydrogen bonding could form between the proton(s) on the amine nitrogen and the negatively
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20 charged carboxylate group (deprotonated), stabilizing the HL^{2-} and/or H_2L^- species. The
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22 existence of the intramolecular hydrogen bonding could, in fact, result in changes in the NMR
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24 spectra. Though the NMR data in Figure 7 do not allow a detailed analysis to conclude whether
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26 or not the intramolecular hydrogen bonding actually forms, but the data certainly indicate that
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28 the amine nitrogen atoms are the first two sites where protonation occurs.
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33 From Solution III to IV (Fig.7), the dominant species changes from H_2L^- to H_3L ,
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35 representing the third protonation step ($H^+ + H_2L^- = H_3L$). The largest displacement of the
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37 chemical shift (~ 0.3 ppm) occurs on the hydrogen atom c, clearly indicating that the third
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39 protonation step occurs on the carboxylate groups that shares the same nitrogen with the
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41 hydroxylethyl group (Equation (6)). It is interesting to note that, for solution IV, the peaks of b
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43 and b' separate, this is most likely due to the two halves of HEDTA being different due to
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45 different electronegativity on the two amine nitrogen atoms.
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51 In brief, the ^1H NMR data confirm that the first two steps of protonation of HEDTA
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53 occur on the amine nitrogen atoms and the third step of protonation occurs on a carboxylate
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55 group. These results help to interpret the calorimetric results discussed in Section 3.2. By
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57 calorimetry, the enthalpies of the first two steps of protonation were found to be exothermic
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4 while the third step of protonation slightly endothermic. The slightly endothermic enthalpy of
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6 protonation of the third step is consistent with many carboxylate ligands (e.g., acetate) that are
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8 strongly hydrated so that much energy is needed to dehydrate the carboxylate upon protonation.
9
10 On the contrary, the amine nitrogen atoms are much less hydrated than the carboxylate oxygen
11
12 atoms so that less dehydration energy is required upon protonation, resulting in exothermic
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14 enthalpy of protonation of the amine groups.
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21 **3.4 Effect of Temperature on the Speciation of HEDTA**

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23 With the protonation constants measured at different temperatures, it is possible to
24
25 evaluate the change of speciation of HEDTA in the $-\log[H^+]$ region of 2 to 12. Fig. 8 compares
26
27 the speciation of HEDTA (in the absence of metal ions) at 25°C and 70°C. For the acidity region
28
29 of TALSPEAK ($-\log[H^+] = 3 - 5$), H_2L^- is the major species. When the temperature is increased
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31 from 25°C and 70°C, the percentage of H_2L^- decreases by 5 - 8% while the percentages of H_3L
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33 (at $-\log[H^+] < 4$) and HL^{2-} (at $-\log[H^+] > 4$) increases correspondingly. The effect of the change
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35 in the speciation of HEDTA on the complexation of An^{3+} and Ln^{3+} in the modified TALSPEAK
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37 system can be evaluated when the stability constants of the An^{3+}/Ln^{3+} complexes with HEDTA
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39 at different temperatures are available
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Figure 8. Speciation of HEDTA as a function of acidity ($-\log[\text{H}^+]$) at 25°C and 70°C. $I = 1.0 \text{ mol}\cdot\text{L}^{-1} \text{ NaClO}_4$.

4 SUMMARY

The effect of temperature on the protonation of HEDTA was evaluated by potentiometry and calorimetry. The overall protonation constants decrease by 0.58 – 0.85 orders of magnitude as the temperature is increased from 25 to 70°C. Stepwise, the first two protonation steps occur on the two amine nitrogen atoms and are exothermic, while the third protonation step occurs on a carboxylate oxygen atom and is slightly endothermic. The energetics of the protonation can be well explained by the difference in the degree of hydration between the amine nitrogen and carboxylate oxygen sites. The data from this work, in conjunction with the thermodynamic data on the complexation of $\text{An}^{3+}/\text{Ln}^{3+}$ with HEDTA, will help to evaluate the effect of temperature on the speciation of $\text{An}^{3+}/\text{Ln}^{3+}$ in the modified TALSPEAK process.

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