Effect of Temperature on the Protonation of the TALSPEAK Ligands: Lactic and Diethylenetrinitropentaacetic Acids

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Abstract. The protonation reactions of two ligands that play important roles in the TALSPEAK process for the separation of trivalent actinides from lanthanides, lactic acid and diethylenetrinitropentaacetic acid (DTPA), have been studied at variable temperatures. The protonation constants at 10 – 70°C were determined by titration potentiometry and the protonation enthalpies were determined at 25°C by titration microcalorimetry. The protonation constants remain essentially unchanged (25 – 70°C) within the experimental uncertainties, indicating that the effect of temperature on the protonation of lactate is insignificant. In contrast, the protonation constants of DTPA ($\log\beta_H$'s) generally decrease as the temperature is increased. Results from this study indicate that the effect of temperature on the protonation of DTPA could alter the speciation of metal ions (actinides and lanthanides) in the TALSPEAK system, since lower values of $\log\beta_H$ at higher temperatures suggest that the hydrogen ions would compete less strongly with the metal ions for the complexation of DTPA at higher temperatures.

1 INTRODUCTION

The TALSPEAK process (Trivalent Actinide Lanthanide Separations by Phosphorus-reagent Extraction from Aqueous Komplexes) [1,2] could be a promising option for accomplishing one of the most challenging tasks in the Advanced Fuel Cycle – separation of the trivalent actinides (An(III)) from the trivalent fission product lanthanides (Ln(III)). In practice, effective separations of An(III) from Ln(III) by TALSPEAK have been demonstrated in several pilot-scale operations. However, the fundamental chemistry underlying the separations remains unclear. It has been shown that, in the regions of pC_{H} (i.e., -log[H^+]) above ~3.5, the measured distribution coefficients of An(III) and Ln(III) decrease while those predicted by the model increase as pC_{H} becomes higher [3,4].

To achieve accurate prediction and precise control of the behavior of actinides and lanthanides in the TALSPEAK process, it is necessary to determine the thermodynamic parameters of the reactions in the TALSPEAK system and evaluate the effect of operating conditions (e.g. temperature) on the thermodynamic parameters. For example, the protonation and dissociation of the TALSPEAK ligands, lactic acid and diethylenetrinitropentaacetic acid (DTPA), and their complexation with An(III) and Ln(III) play very important roles in controlling the speciation of actinides and lanthanides and the efficiency of separation. Currently, there are only very limited thermodynamic data for these reactions for temperatures at or near 25^{o}C. The lack of thermodynamic data at different temperatures makes it difficult to predict the behavior of actinides and lanthanides in the TALSPEAK process if the “envelop” of operating conditions change, e.g., at temperatures higher than 25^{o}C. To help with the development of advanced An(III)/Ln(III) separation processes, we have started systematic studies on the thermodynamics of major reactions involved in TALSPEAK, including the protonation of lactate and DTPA and their complexation with actinides and lanthanides. This paper summarizes the results on the protonation constants of lactate and DTPA at different temperatures.

2 EXPERIMENTAL

2.1 Chemicals

All chemicals are ACS reagent grade or higher. All solutions were prepared with water of high purity from a Milli-Q system. Prior to use, the water was boiled and cooled in sealed bottles to reduce the amount of dissolved carbon dioxide. Working solutions of lactic acid and DTPA were prepared by dilution from a stock solution of lactic acid (Sigma-Aldrich) and dissolution of solid DTPA (Sigma-Aldrich) with water, respectively, without further purification. The ionic strength of all working solutions was maintained at 1.0 $\mathrm{mol \cdot dm^{-3}}$ ($NaClO_4$) at $25^{o}C$, equivalent to 1.05 $\mathrm{mol \cdot kg^{-1}}$ ($NaClO_4$) at variable temperatures. In this paper, all the concentrations in molarity are referred to $25^{o}C$.

2.2. Potentiometry

The apparatus for potentiometry consists of a 100 cm^3 cell with a special lid. Both the cell and the lid are water-jacketed and maintained at the desired temperatures by circulating water from a constant-temperature bath. It is important, especially for the titrations at temperatures above the ambient, to maintain the lid at the same temperature as the cell to avoid water condensation underneath the lid. Details of the titration setup have been provided elsewhere [5].

The electrode potential (E, in millivolts) was measured with a Metrohm pH meter (Model 713) equipped with a Ross combination pH electrode (Orion Model 8102). In this work, the original inner solution of the glass electrode (3 $\mathrm{mol \cdot dm^{-3}}$ KCl) was replaced with 1 $\mathrm{mol \cdot dm^{-3}}$ sodium chloride to reduce the electrode junction potential. In acidic and basic regions, E can be expressed by equations (1) and (2), respectively,

$$E = E^0 + RT/F \ln[H^+] + E_{j,H}[H^+] \qquad (1)$$

$$E = E^0 + RT/F \ln K_w - RT/F \ln[OH^-] + E_{j,OH}[OH^-] \qquad (2)$$

where R is the gas constant, F is the Faraday constant and T is the temperature. K_w is the ionic product of water (= $[H^+][OH^-]$). The terms of the electrode junction potentials for the hydrogen and hydroxide ions, $E_{j,H}[H^+]$ and $E_{j,OH}[OH^-]$, are assumed to be proportionate to the concentrations of the hydrogen and hydroxide ions, respectively. Prior to each protonation titration, an acid/base titration with standard $HClO_4$ and NaOH solutions was performed to obtain the electrode parameters of E^0, $E_{j,H}$ and $E_{j,OH}$. These parameters allowed the calculation of hydrogen ion concentrations from the electrode potential in the subsequent titration. In the protonation titrations of lactate, the correction for the junction potential of the hydroxide ion was not necessary because the pK_a of lactic acid is below 4 and the titrations were carried out only in the acidic region.

Multiple titrations were conducted with solutions of different concentrations of the ligands (C_L for lactic acid and C_A for DTPA) and different acidity (C_H for total hydrogen ion). Approximately 50 - 75 data points for the lactate system and 200 – 400 points for the DTPA system were collected in each titration. The protonation constants of lactate and DTPA at different temperatures were calculated using the program Hyperquad 2000 [6].

2.3. Microcalorimetry

Microcalorimetric titrations were carried out using an isothermal microcalorimeter (ITC-4200, Calorimetry Sciences Corp.). The performance of the calorimeter has been tested by measuring the enthalpy of protonation of tris(hydroxymethyl)-aminomethane (THAM). The result was –(47.7 ± 0.2) kJ·mol^{-1} at 25ºC, in excellent agreement with the value in the literature [5,7]. Details of the microcalorimeter are provided elsewhere [8]. Multiple titrations were conducted with solutions of different concentrations of the ligands and different acidity. For each titration, n experimental values of the heat produced in the reaction vessel ($Q_{ex,j}$, j = 1 to n, usually n = 40 -

50) were calculated as a function of the volume of the titrant added. These values were corrected for the heat of dilution of the titrant ($Q_{\mathrm{dil,j}}$), which was determined in separate runs. The net reaction heat at the *j*-th point ($Q_{\mathrm{r,j}}$) was obtained from the difference: $Q_{\mathrm{r,j}} = Q_{\mathrm{ex,j}} - Q_{\mathrm{dil,j}}$. These data, in conjunction with the protonation constants obtained by potentiometry, were used to calculate the enthalpy of protonation with the computer program Letagrop [9].

3 RESULTS and DISCUSSION

3.1 Equilibrium Constants of the Protonation of Lactate and DTPA at 10 – 70°C

Potentiometric titrations show that the titration curves (-log[H+] vs. V_{titrant} or the ratio of $C_{\mathrm{H}}/C_{\mathrm{ligand}}$) at different temperatures are quite similar for the titrations of lactate, but significantly different for the titrations of DTPA, indicating that the effect of temperature is small on the protonation of lactate, but significant on the protonation of DTPA. Figure 1 shows one set of protonation titrations of DTPA at different temperatures. As the temperature was increased from 10°C to 70°C, values of -log[H+] at the same $C_{\mathrm{H}}/C_{\mathrm{A}}$ became lower, a clear indication that the protonation of DTPA became weaker at higher temperatures.

(*insert Figure 1*)

Representative potentiometric titrations at 10°C and 70°C and the fits obtained by using the Hyperquad program are shown in Figure 2 for lactate and Figure 3 for DTPA. The speciation of the ligands in the course of the titrations (species HL and L^- for lactate, H_5A, H_4A^-, H_3A^{2-}, H_4A^- and A^{5-} for DTPA) is also shown in the figures. From multiple titrations at each temperature, the protonation constants of lactate and DTPA at different temperatures were calculated.

(*insert Figures 2 and 3*)

The protonation constants from this work, together with the protonation constants at I = 1.0 mol·dm^{-3} in the literature [10], are shown in Table 1 and Figure 4. To compare the equilibrium constants at different temperatures, the constants in molarity should be converted to the constants in molality using equation (3) described in the literature [11].

$$\log K_{\mathrm{m}} = \log K_{\mathrm{M}} + \Sigma_{\mathrm{r}} \nu_{\mathrm{r}} \log \vartheta \qquad (3)$$

where K_{m} and K_{M} are the equilibrium constants in molality and molarity, respectively. $\Sigma_{\mathrm{r}} \nu_{\mathrm{r}}$ 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$_i$L). ϑ 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 mol·dm^{-3} $NaClO_4$, $\log\vartheta$ is about 0.02 [11]. The converted protonation constants of lactate and DTPA are also shown in Table 1.

The protonation constants of lactate ($\log\beta_{\mathrm{H}}$ = 3.5 – 3.7 at 10 – 70°C) indicate that lactic acid is a slightly stronger acid than simple monocarboxylic acids (e.g., $\log\beta_{\mathrm{H}} \sim 4.6$ for acetic, butanoic and hexanoic acids [10]), but similar to other α-hydroxycarboxylic acids (e.g., $\log\beta_{\mathrm{H}} \sim 3.6$ for 2-hydroxybutanoic and 2-hydroxyhexanoic acids [10]) and isosaccharinic acid ($\log\beta_{\mathrm{H}} \sim$ 3.2 – 3.3 [12]). Such slightly stronger acidity might be attributed to the formation of hydrogen bonding between the carboxylate group and the hydroxyl group, which could stabilize the deprotonated form and result in a lower value for logβ_H. Data from this work also indicate that the protonation constant of lactate remained essentially unchanged (within experimental uncertainties) as the temperature was increased from 25°C to 70°C, suggesting the effect of temperature on the protonation of lactate is minimal. The Van't Hoff plot of logβ_H vs. $1/T$ shows that the enthalpy of protonation for lactate should be near zero (Figure 4, left).

(*insert Table 1, Figure 4*)

In contrast, the protonation constants of DTPA decreased significantly as the temperature was increased (Table 1 and Figure 4), suggesting that the protonation of DTPA is weakened and DTPA becomes a stronger acid at higher temperatures. This observation could have impact on the speciation of An(III)/Ln(III) in the TALSPEAK system, because the hydrogen ions would compete less strongly with An(III)/Ln(III) ions for the complexation with anionic DTPA species at higher temperatures. The Van't Hoff plot of logβ_H vs. $1/T$ (Figure 4, right) indicates that the protonation reactions of DTPA are all exothermic. From the linear fits in Figure 4, the average "overall" enthalpies of protonation of DTPA in the temperature range of 10 – 70°C were calculated to be –(26.6 ± 1.3), –(48.5 ± 1.3), –(53.7 ± 1.8), –(47.9 ± 3.2), and –(54.6 ± 3.1) kJ·mol^{-1} for HA^{4-}, H_2A^{3-}, H_3A^{2-}, H_4A^-, and H_5A(aq), respectively.

3.2 Enthalpy of Protonation of Lactate and DTPA at 25°C

Data of the calorimetric titrations for the protonation of lactate and DTPA are shown in Figures 5 and 6. 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 or C_A), the protonation constants

($\log\beta_H$) and the enthalpy of protonation of the ligand (ΔH). Using the stoichiometric concentrations of the reactants and the protonation constants measured by potentiometry in this work, the enthalpies of protonation for lactate and DTPA at 25°C are calculated from the calorimetric titration data, and listed in Table 1.

(*insert Figures 5, 6*)

The enthalpy of protonation of lactate measured by microcalorimetry is very small, –(0.55 ± 0.22) kJ·mol^{-1}, consistent with the value estimated by the Van't Hoff plot and the observation that the protonation constant of lactate remains nearly constant in the temperature range of 25 – 70°C. Also, it is typical of carboxylic acids that the protonation enthalpy is small, probably because the energy required by the dehydration of H^+ and the carboxylate group ($-C(O)O^-$) is more or less compensated by the energy released by the combination of the two species of opposite charges ($H^+ + -C(O)O^- \rightarrow -C(O)OH$). For DTPA, the "overall" enthalpies of protonation determined directly by microcalorimetry are all negative, consistent with the general trends that all "overall" protonation constants decrease as the temperature is increased. The stepwise enthalpies for the first two protonation steps (HA^{4-} and H_2A^{3-}) measured by microcalorimetry are -26.2 and -26.4 kJ·mol^{-1}, in good agreement with those from the linear fits of the Van't Hoff plots (-26.6 and -21.9 kJ·mol^{-1}). The large negative enthalpies of protonation suggest that the first two protonation steps probably occur on the nitrogen atoms and zwitterions similar to those in the system of EDTA [11] form in the protonated DTPA species. For the three successive protonation steps of DTPA (H_3A^{2-}, H_4A^- and H_5A), the agreement between the values of enthalpies from microcalorimetry and those from Van't Hoff plots is less satisfactory. We believe that the values from microcalorimetry 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.

3.3 Effect of Temperature on the Speciation of Lactate and DTPA

With the protonation constants measured at different temperatures, it is possible to evaluate the change of speciation of lactate and DTPA in the pC_H region of 2 to 5, an acidity region covering the operating envelop of the TALSPEAK process. For lactate, it is obvious that the change of temperature would have little effect on the speciation of the ligand. For DTPA, Figure 7 compares the speciation of the ligand (in the absence of metal ions) at 10°C and 40°C. At both temperatures, the HA^{4-} and A^{5-} species are insignificant in the region of pC_H = 2 – 5. Small but definite differences between the two temperatures can be observed for other species. For example, at the same acidity, there is less H_5A species at 40°C (the highest percentage: 60%) than at 10°C (70%), and there is more H_2A^{3-} species at 40°C (the highest percentage: 85%) than at 10°C (80%). In brief, the protonation of DTPA generally becomes weaker at higher temperatures. Such changes in the speciation of DTPA would certainly affect the speciation of An(III) and Ln(III) in the TALSPEAK system. The significance of the effect will be evaluated when the stability constants of the An(III)/Ln(III) complexes with DTPA at different temperatures are available.

4 SUMMARY

The increase in temperature (up to 70°C) has a negligible effect on the protonation of lactate. Therefore no effect of temperature on the speciation of lactate is expected in this temperature range. In contrast, the overall protonation constants of DTPA decrease by 0.8 – 1.5 orders of magnitude as the temperature is increased from 10 to 70°C. The shift of the protonation equilibrium toward more ionized DTPA species at higher temperatures could alter the speciation of the actinides and lanthanides and, in turn, their extraction behavior in the TALSPEAK system.

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Table 1 Thermodynamic parameters for the protonation of lactate and DTPA, I = 1.05 mol·kg^{-1} NaClO$_4$. HL and H$_5$A stand for lactic acid and DTPA. log$\beta_{\mathrm{H,M}}$ and log$\beta_{\mathrm{H,m}}$ represent the protonation constants in molarity and molality, respectively.

Reaction	t ^{o}C	log$\beta_{\mathrm{H,M}}$	log$\beta_{\mathrm{H,m}}$	ΔH kJ·mol^{-1}	ΔS J·K^{-1}·mol^{-1}
$H^+ + L^- = HL(aq)$	10	3.46 ± 0.04	3.44 ± 0.04		
	25	3.67 ± 0.03	3.65 ± 0.03	-0.55 ± 0.22	68 ± 1
		3.59, 3,62, 3.64 [10]			
	40	3.68 ± 0.04	3.66 ± 0.04		
	55	3.70 ± 0.04	3.68 ± 0.04		
	70	3.72 ± 0.04	3.70 ± 0.04		
$H^+ + A^{5-} = HA^{4-}$	10	9.73 ± 0.02	9.71 ± 0.02		
	20	9.48, 10.46 [10]			
	25	9.43 ± 0.02	9.41 ± 0.02	-26.2 ± 1.4	93 ± 5
		9.98 [10]			
	40	9.29 ± 0.03	9.27 ± 0.03		
	55	9.00 ± 0.04	8.98 ± 0.04		
	70	8.91 ± 0.06	8.89 ± 0.06		
$2H^+ + A^{5-} = H_2A^{3-}$	10	18.23 ± 0.03	18.19 ± 0.03		
	20	17.74, 18.75 [10]			
	25	17.69 ± 0.02	17.65 ± 0.02	-52.6 ± 1.6	162 ± 5
		18.27 [10]			
	40	17.34 ± 0.03	17.30 ± 0.03		
	55	16.97 ± 0.04	16.93 ± 0.04		
	70	16.75 ± 0.07	16.71 ± 0.07		
$3H^+ + A^{5-} = H_3A^{2-}$	10	22.61 ± 0.03	22.55 ± 0.03		
	25	21.92 ± 0.03	21.86 ± 0.03	-64.2 ± 2.0	204 ± 7
		22.42 [10]			
	40	21.54 ± 0.04	21.48 ± 0.04		
	55	21.19 ± 0.05	21.13 ± 0.05		
	70	21.01 ± 0.08	20.95 ± 0.08		
$4H^+ + A^{5-} = H_4A^-$	10	25.14 ± 0.06	25.06 ± 0.06		
	25	24.48 ± 0.04	24.40 ± 0.04	-65.0 ± 4.6	250 ± 16
		25.02 [10]			
	40	24.14 ± 0.06	24.06 ± 0.06		
	55	23.86 ± 0.08	23.78 ± 0.08		
	70	23.68 ± 0.15	23.60 ± 0.15		
$5H^+ + A^{5-} = H_5A(aq)$	10	27.65 ± 0.05	27.55 ± 0.05		
	25	26.85 ± 0.04	26.75 ± 0.04	-63.6 ± 5.7	301 ± 19
		27.12 [10]			
	40	26.46 ± 0.07	26.36 ± 0.07		
	55	26.21 ± 0.09	26.11 ± 0.09		
	70	26.16 ± 0.14	26.06 ± 0.14		

Figure Captions

Figure 1: Potentiometric titrations of DTPA protonation at different temperatures, I = 1.05 mol·kg^{-1} NaClO$_4$. Cup solution:, V^{o} = 20.00 mL, $C_{DTPA}{}^{o}$ = 6.665 mmol·dm^{-3}; $C_{H}{}^{o}$ = 33.34 mmol·dm^{-3} (for 10, 25, 40 and 55°C) and $C_{H}{}^{o}$ = 38.32 mmol·dm^{-3} (for 70°C). Titrant: 100.1 mmol·dm^{-3} NaOH. Negative values of C_H/C_A represent the region where hydroxide is in excess ($-C_H/C_A = C_{OH}/C_A$).

Figure 2: Representative potentiometric titrations of the protonation of lactate at 10°C (left) and 70°C (right), I = 1.05 mol·kg^{-1} NaClO$_4$. Cup solution: V^{o} = 20.00 mL, 0.100 mol·dm^{-3} sodium lactate. Titrant: 0.9994 HClO$_4$. Symbols: ○ - experimental data (-log[H$^+$]), dashed line – fit (-log[H$^+$]); solid lines - percentage of lactate species (right y-axis), L$^-$ (red) and HL(blue), where HL stands for the neutral lactic acid.

Figure 3: Representative potentiometric titrations of the protonation of DTPA at 10°C (left) and 70°C (right), I = 1.05 mol·kg^{-1} NaClO$_4$. Cup solution: for 10°C, V^{o} = 30.00 mL, $C_{DTPA}{}^{o}$ = 6.667 mmol·dm^{-3}; $C_{H}{}^{o}$ = 50.00 mmol·dm^{-3}; for 70°C, V^{o} = 20.00 mL, $C_{DTPA}{}^{o}$ = 6.665 mmol·dm^{-3}; $C_{H}{}^{o}$ = 38.32 mmol·dm^{-3}. Titrant: 100.1 mmol·dm^{-3} NaOH. Symbols: ○ - experimental data (-log[H$^+$]), dashed line – fit (-log[H$^+$]); solid lines - percentage of DTPA species (right y-axis), H_5A (brown), H_4A^- (cyan), H_3A^{2-} (magenta), H_2A^{3-} (green), HA^{4-} (blue) and A^{5-} (red), where H_5A stands for the neutral DTPA acid.

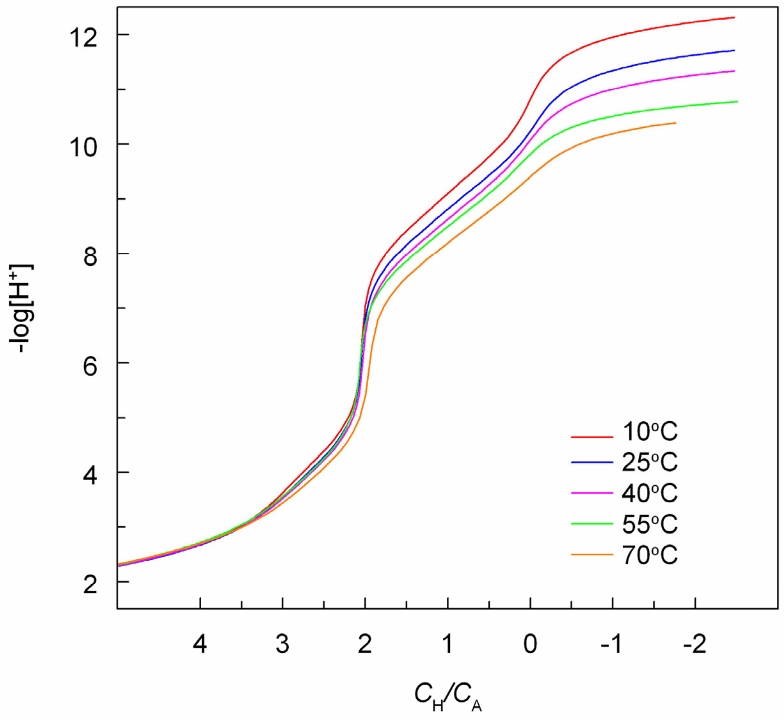
Figure 4: Protonation constants of lactate (left) and DTPA (right) at different temperatures, I = 1.05 mol·kg^{-1} NaClO$_4$. Solid symbols: data from this work; open symbols, data from the literature [10]; lines: linear fits of the data from this work.

Figure 5: Calorimetric titrations of the protonation of lactate, I = 1.05 mol·kg^{-1} NaClO$_4$, t = 25°C. (Top) a representative thermogram. (Bottom) A plot of $Q_{partial}$ vs. the volume of titrant, symbols - experimental Q, lines - fit; initial cup solutions: sodium lactate, $C_{NaL}{}^{o}$ (mmol·dm^{-3}) = 22.22 (I), 19.44 (II) and 16.67 (III); titrant: 99.80 mmol·dm^{-3} HClO$_4$, 5.0 μL/addition.

Figure 6: Calorimetric titrations of the protonation of DTPA, I = 1.05 mol·kg^{-1} NaClO$_4$, t = 25°C. (Top) a representative thermogram. (Bottom) A plot of $Q_{partial}$ vs. the volume of titrant, symbols - experimental Q, lines - fit; initial cup solutions: DTPA, $C_{H}{}^{o}/C_{A}{}^{o}$ (mmol·dm^{-3}) = 22.22/4.440 (I), 20.38/4.076 (II) and 18.50/3.700 (III); titrant: 100.0 mmol·dm^{-3} NaOH, 5.0 μL/addition.

Figure 7: Speciation of DTPA as a function of acidity (-log[H$^+$]) at different temperatures. I = 1.05 mol·kg^{-1} NaClO$_4$, C_{DTPA} = 0.05 mol·dm^{-3}. Lines: percentage of DTPA species, H_5A (cyan), H_4A^- (rose), H_3A^{2-} (green), H_2A^{3-} (magenta). The species of HA^{4-} and A^{5-} are insignificant in the region of -log[H$^+$] = 2 – 5.

Figure 1



294 Figure 2

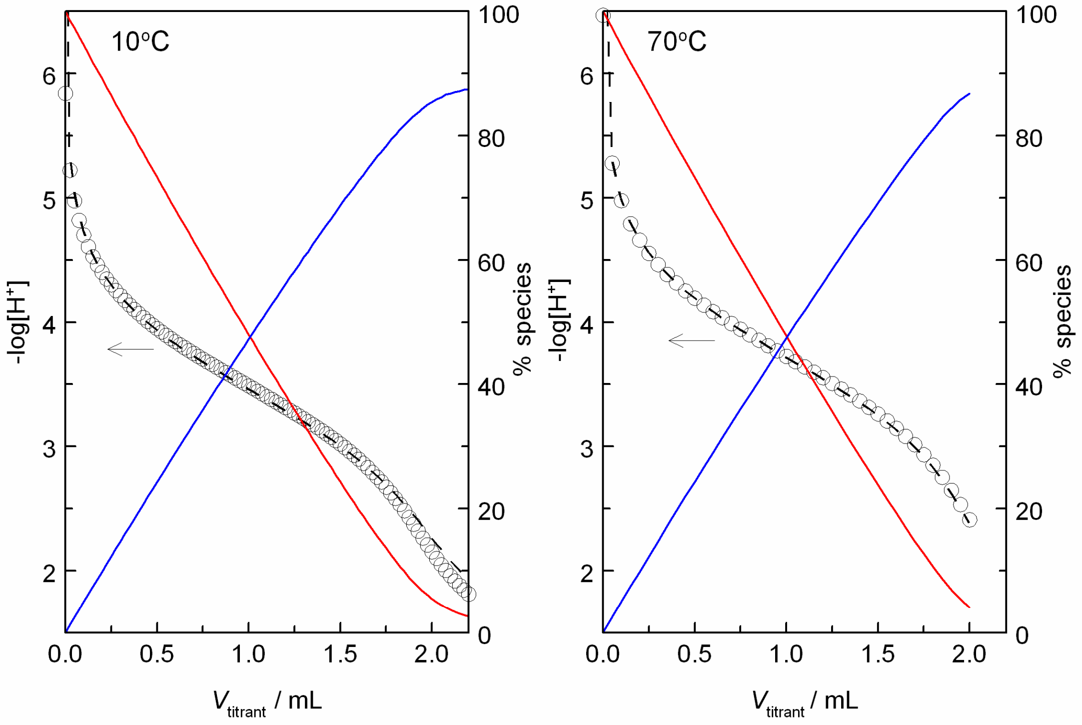


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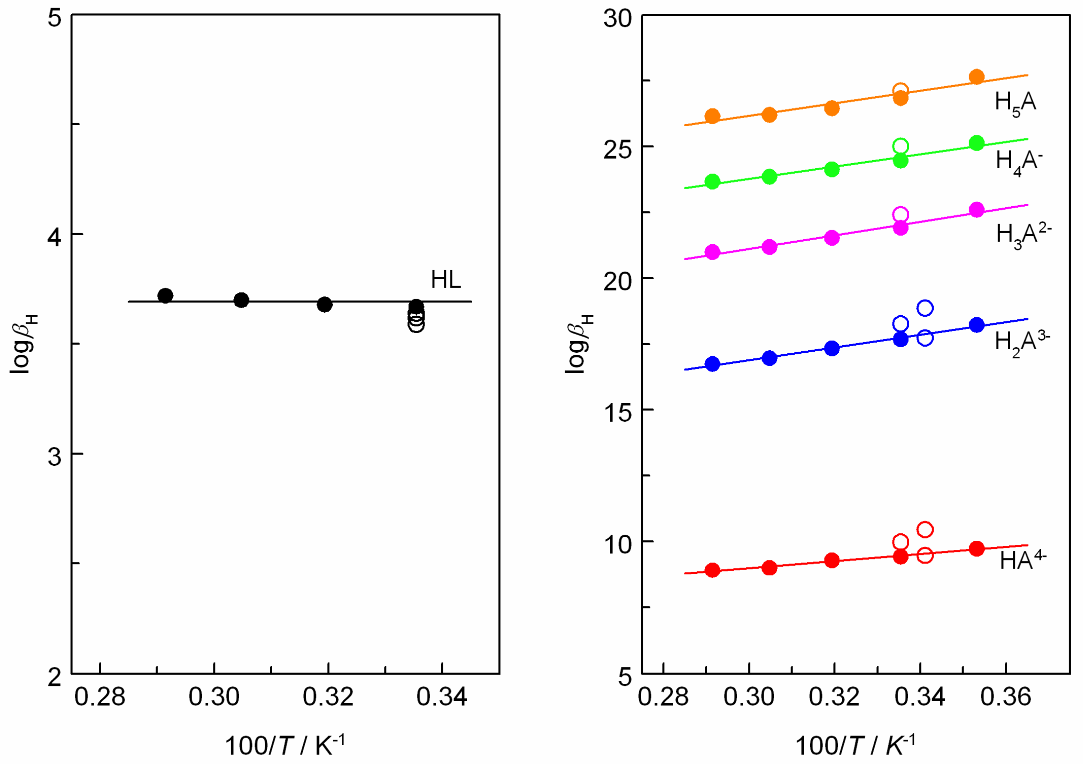
Figure 3

Figure 4



logβ_H
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2
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0.34
100/T / K^{-1}
logβ_H
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20
15
10
5
H$_5$A
H$_4$A$^-$
H$_3$A^{2-}
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HA^{4-}
0.28
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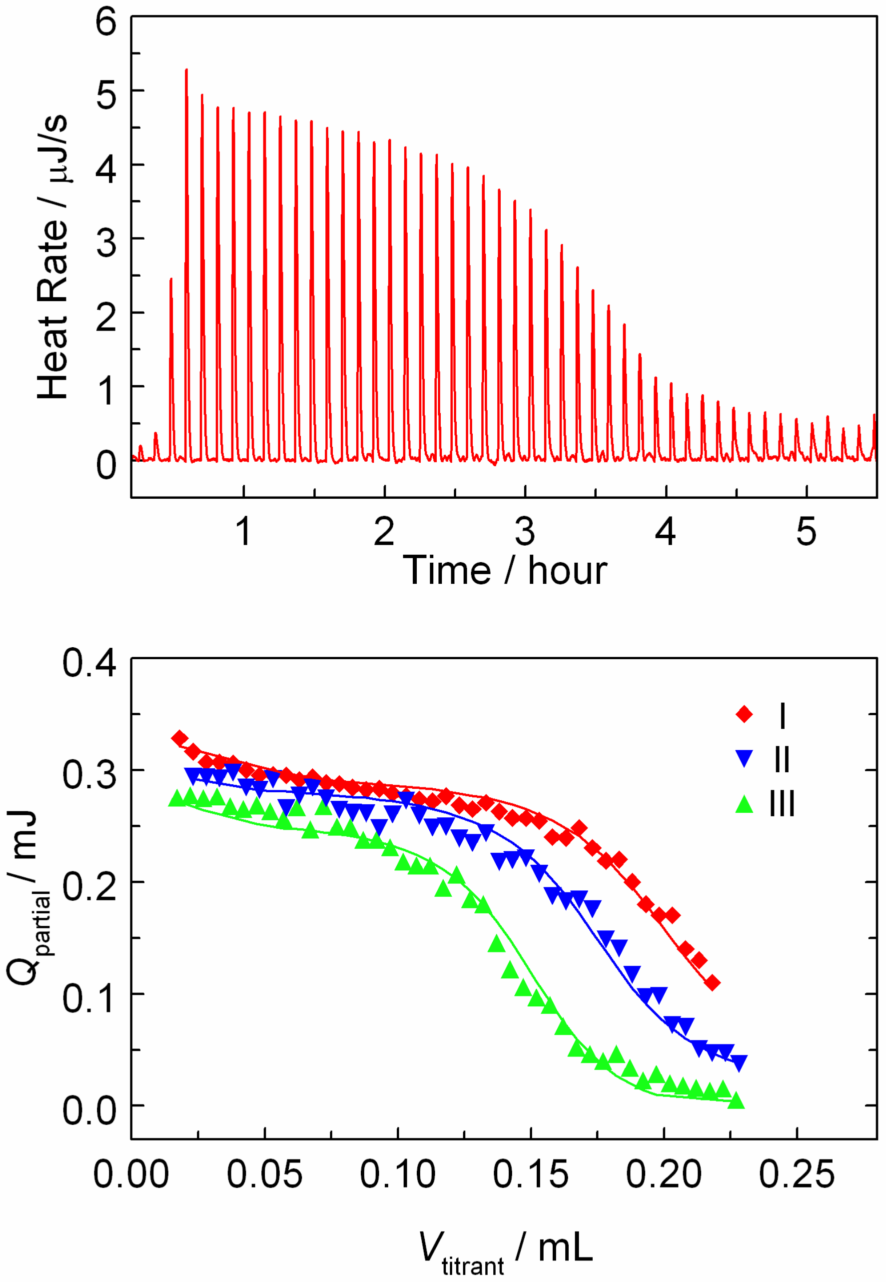
Figure 5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1
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3
4
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6
Time / hour
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$Q_{partial}$ / mJ
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$V_{titrant}$ / mL
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0.05
0.10
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◆ I
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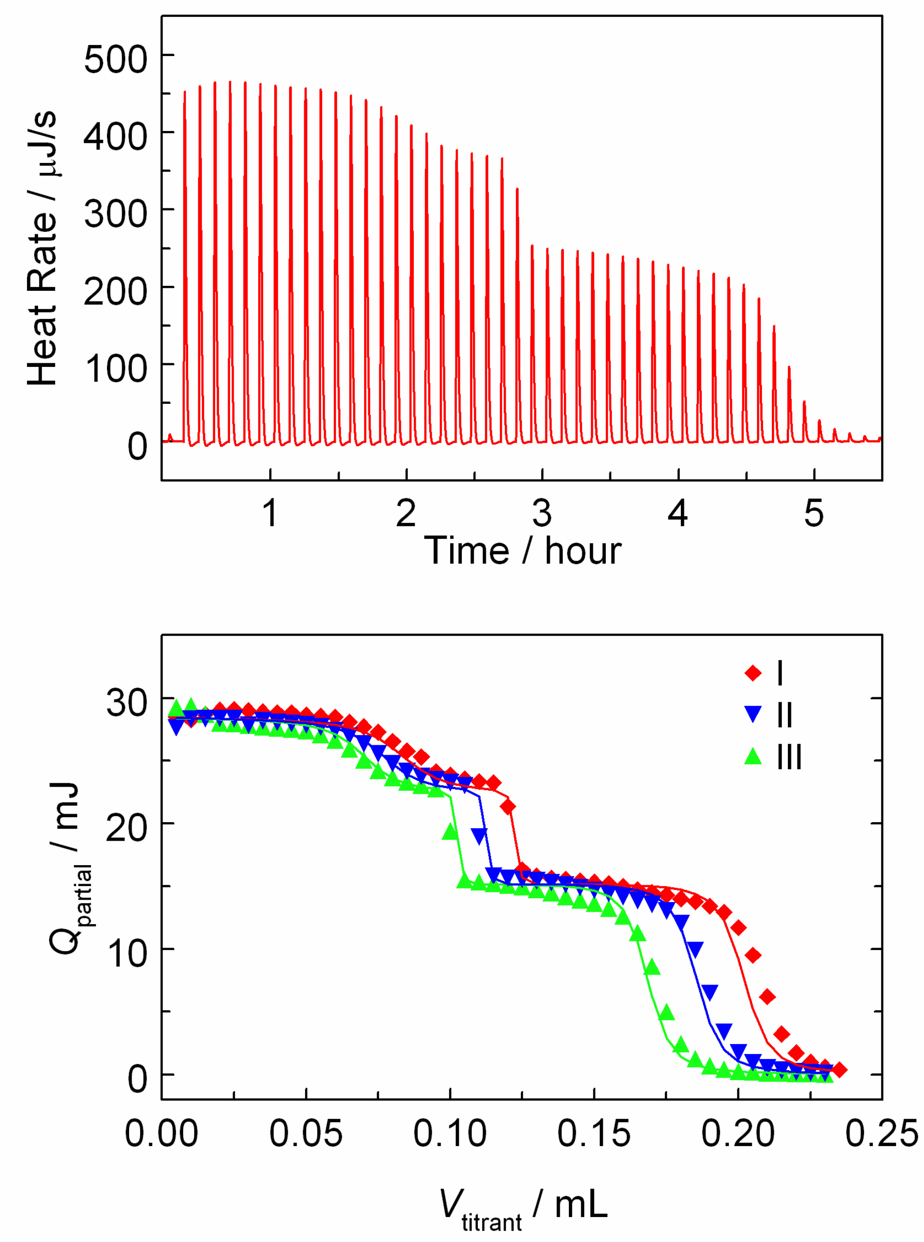
Figure 6



Heat Rate / μJ/s
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Time / hour
Q_partial / mJ
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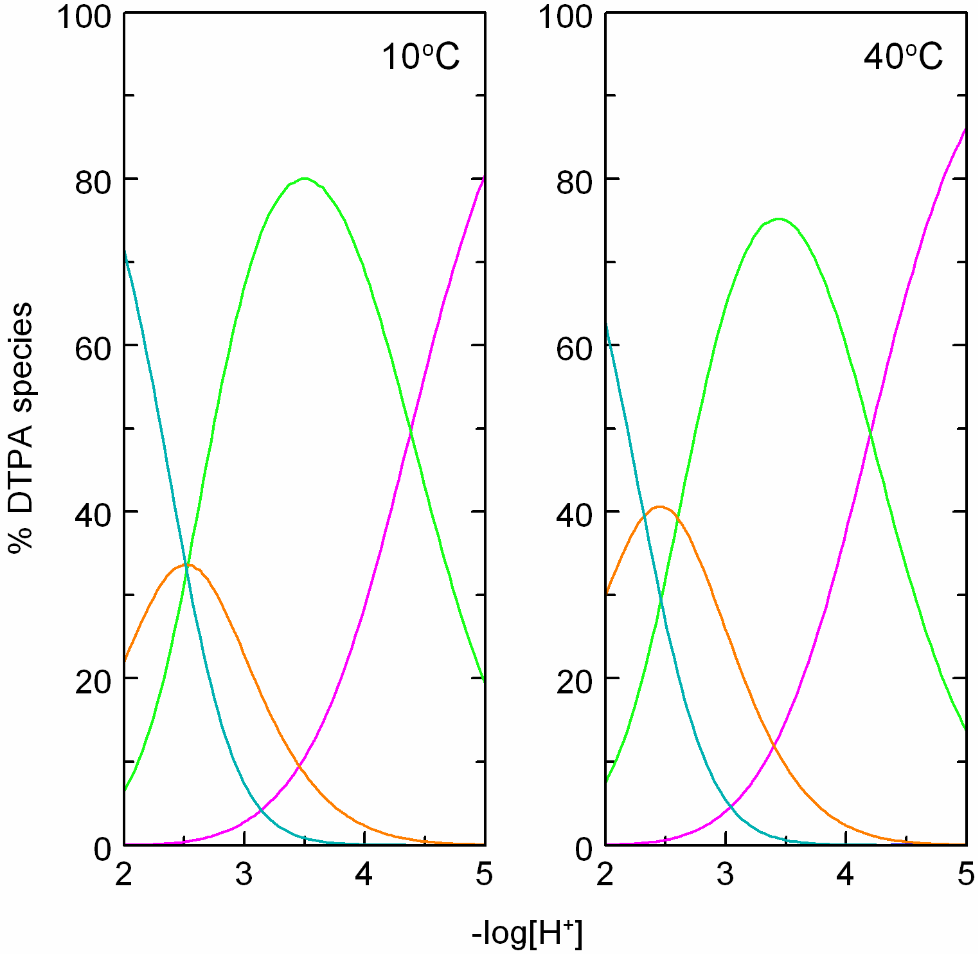
0.20
0.25
V_titrant / mL
I
II
III

304 Figure 7



305