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1 **Effect of Temperature on the Protonation of the TALSPEAK Ligands: Lactic**
2 **and Diethylenetrinitropentaacetic Acids**
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7

8   **Abstract.** The protonation reactions of two ligands that play important roles in the

9 TALSPEAK process for the separation of trivalent actinides from lanthanides, lactic acid and

10 diethylenetrinitropentaacetic acid (DTPA), have been studied at variable temperatures. The

11 protonation constants at $10 - 70^{\circ}$C were determined by titration potentiometry and the

12 protonation enthalpies were determined at 25°C by titration microcalorimetry. The protonation

13 constants remain essentially unchanged $(25 - 70^{\circ}$C$)$ within the experimental uncertainties,

14 indicating that the effect of temperature on the protonation of lactate is insignificant. In contrast,

15 the protonation constants of DTPA $(\log\beta_{H}$'s$)$ generally decrease as the temperature is increased.

16 Results from this study indicate that the effect of temperature on the protonation of DTPA could

17 alter the speciation of metal ions (actinides and lanthanides) in the TALSPEAK system, since

18 lower values of $\log\beta_{H}$ at higher temperatures suggest that the hydrogen ions would compete less

19 strongly with the metal ions for the complexation of DTPA at higher temperatures.

20

21 **1 INTRODUCTION**

22 The TALSPEAK process (Trivalent Actinide Lanthanide Separations by Phosphorus-reagent

23 Extraction from Aqueous Komplexes) [1,2] could be a promising option for accomplishing one

24 of the most challenging tasks in the Advanced Fuel Cycle – separation of the trivalent actinides

25 (An(III)) from the trivalent fission product lanthanides (Ln(III)). In practice, effective

26 separations of An(III) from Ln(III) by TALSPEAK have been demonstrated in several pilot-scale

27   operations. However, the fundamental chemistry underlying the separations remains unclear. It

28   has been shown that, in the regions of pC_H (i.e., $-\log[H^+]$) above ~3.5, the measured distribution

29   coefficients of An(III) and Ln(III) decrease while those predicted by the model increase as pC_H

30   becomes higher [3,4].

31   To achieve accurate prediction and precise control of the behavior of actinides and

32   lanthanides in the TALSPEAK process, it is necessary to determine the thermodynamic

33   parameters of the reactions in the TALSPEAK system and evaluate the effect of operating

34   conditions (e.g. temperature) on the thermodynamic parameters. For example, the protonation

35   and dissociation of the TALSPEAK ligands, lactic acid and diethylenetrinitropentaacetic acid

36   (DTPA), and their complexation with An(III) and Ln(III) play very important roles in controlling

37   the speciation of actinides and lanthanides and the efficiency of separation. Currently, there are

38   only very limited thermodynamic data for these reactions for temperatures at or near 25°C. The

39   lack of thermodynamic data at different temperatures makes it difficult to predict the behavior of

40   actinides and lanthanides in the TALSPEAK process if the "envelop" of operating conditions

41   change, e.g., at temperatures higher than 25°C. To help with the development of advanced

42   An(III)/Ln(III) separation processes, we have started systematic studies on the thermodynamics

43   of major reactions involved in TALSPEAK, including the protonation of lactate and DTPA and

44   their complexation with actinides and lanthanides. This paper summarizes the results on the

45   protonation constants of lactate and DTPA at different temperatures.

46

47   **2 EXPERIMENTAL**

48   **2.1 Chemicals**

49   All chemicals are ACS reagent grade or higher. All solutions were prepared with water of high

50   purity from a Milli-Q system. Prior to use, the water was boiled and cooled in sealed bottles to

51   reduce the amount of dissolved carbon dioxide. Working solutions of lactic acid and DTPA were

52   prepared by dilution from a stock solution of lactic acid (Sigma-Aldrich) and dissolution of solid

53   DTPA (Sigma-Aldrich) with water, respectively, without further purification. The ionic strength

54   of all working solutions was maintained at 1.0 mol·dm^{-3} (NaClO$_4$) at 25°C, equivalent to 1.05

55   mol·kg^{-1} (NaClO$_4$) at variable temperatures. In this paper, all the concentrations in molarity are

56   referred to 25°C.

57   **2.2. Potentiometry**

58   The apparatus for potentiometry consists of a 100 cm^3 cell with a special lid. Both the cell and

59   the lid are water-jacketed and maintained at the desired temperatures by circulating water from a

60   constant-temperature bath. It is important, especially for the titrations at temperatures above the

61   ambient, to maintain the lid at the same temperature as the cell to avoid water condensation

62   underneath the lid. Details of the titration setup have been provided elsewhere [5].

63   The electrode potential (E, in millivolts) was measured with a Metrohm pH meter (Model 713)

64   equipped with a Ross combination pH electrode (Orion Model 8102). In this work, the original inner

65   solution of the glass electrode (3 mol·dm^{-3} KCl) was replaced with 1 mol·dm^{-3} sodium chloride to reduce

66   the electrode junction potential. In acidic and basic regions, E can be expressed by equations (1) and (2),

67   respectively,

68
69    $$E = E^0 + RT/F \ln[\text{H}^+] + E_{j,H}[\text{H}^+] \tag{1}$$

70    $$E = E^0 + RT/F \ln K_w - RT/F \ln[\text{OH}^-] + E_{j,OH}[\text{OH}^-] \tag{2}$$

71

72   where R is the gas constant, F is the Faraday constant and T is the temperature. K_w is the ionic

73   product of water (= $[H^+][OH^-]$). The terms of the electrode junction potentials for the hydrogen

74   and hydroxide ions, $E_{j,H}[H^+]$ and $E_{j,OH}[OH^-]$, are assumed to be proportionate to the

75   concentrations of the hydrogen and hydroxide ions, respectively. Prior to each protonation

76   titration, an acid/base titration with standard $HClO_4$ and NaOH solutions was performed to

77   obtain the electrode parameters of E^0, $E_{j,H}$ and $E_{j,OH}$. These parameters allowed the calculation of

78   hydrogen ion concentrations from the electrode potential in the subsequent titration. In the

79   protonation titrations of lactate, the correction for the junction potential of the hydroxide ion was

80   not necessary because the pK_a of lactic acid is below 4 and the titrations were carried out only in

81   the acidic region.

82   Multiple titrations were conducted with solutions of different concentrations of the ligands

83   (C_L for lactic acid and C_A for DTPA) and different acidity (C_H for total hydrogen ion).

84   Approximately 50 - 75 data points for the lactate system and 200 – 400 points for the DTPA

85   system were collected in each titration. The protonation constants of lactate and DTPA at

86   different temperatures were calculated using the program Hyperquad 2000 [6].

87   **2.3. Microcalorimetry**

88   Microcalorimetric titrations were carried out using an isothermal microcalorimeter (ITC-4200,

89   Calorimetry Sciences Corp.). The performance of the calorimeter has been tested by measuring

90   the enthalpy of protonation of tris(hydroxymethyl)-aminomethane (THAM). The result was –

91   (47.7 ± 0.2) kJ·mol^{-1} at 25ºC, in excellent agreement with the value in the literature [5,7]. Details

92   of the microcalorimeter are provided elsewhere [8]. Multiple titrations were conducted with

93   solutions of different concentrations of the ligands and different acidity. For each titration, n

94   experimental values of the heat produced in the reaction vessel ($Q_{ex,j}$, $j = 1$ to n, usually $n = 40$ -

95   50) were calculated as a function of the volume of the titrant added. These values were corrected

96   for the heat of dilution of the titrant ($Q_{\mathrm{dil,j}}$), which was determined in separate runs. The net

97   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

98   data, in conjunction with the protonation constants obtained by potentiometry, were used to

99   calculate the enthalpy of protonation with the computer program Letagrop [9].

100

101 **3 RESULTS and DISCUSSION**

102 **3.1 Equilibrium Constants of the Protonation of Lactate and DTPA at 10 – 70$^{\mathrm{o}}$C**

103 Potentiometric titrations show that the titration curves (-log[H+] vs. V_{titrant} or the ratio of

104 $C_{\mathrm{H}}/C_{\mathrm{ligand}}$) at different temperatures are quite similar for the titrations of lactate, but significantly

105 different for the titrations of DTPA, indicating that the effect of temperature is small on the

106 protonation of lactate, but significant on the protonation of DTPA. Figure 1 shows one set of

107 protonation titrations of DTPA at different temperatures. As the temperature was increased from

108 10$^{\mathrm{o}}$C to 70$^{\mathrm{o}}$C, values of -log[H+] at the same $C_{\mathrm{H}}/C_{\mathrm{A}}$ became lower, a clear indication that the

109 protonation of DTPA became weaker at higher temperatures.

110

111 (*insert Figure 1*)

112

113   Representative potentiometric titrations at 10$^{\mathrm{o}}$C and 70$^{\mathrm{o}}$C and the fits obtained by using

114 the Hyperquad program are shown in Figure 2 for lactate and Figure 3 for DTPA. The speciation

115 of the ligands in the course of the titrations (species HL and L$^-$ for lactate, H_5A, H_4A^-, H_3A^{2-},

116 H_4A^- and A^{5-} for DTPA) is also shown in the figures. From multiple titrations at each

117   temperature, the protonation constants of lactate and DTPA at different temperatures were

118   calculated.

119

120   (*insert Figures 2 and 3*)

121

122   The protonation constants from this work, together with the protonation constants at $I =$

123   1.0 mol·dm^{-3} in the literature [10], are shown in Table 1 and Figure 4. To compare the

124   equilibrium constants at different temperatures, the constants in molarity should be converted to

125   the constants in molality using equation (3) described in the literature [11].

126

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

128

129   where K_{m} and K_{M} are the equilibrium constants in molality and molarity, respectively. $\Sigma_{\mathrm{r}} \nu_{\mathrm{r}}$ is the

130   stoichiometric coefficient of the reaction (ν_{r} is positive for products and negative for reactants)

131   and is equal to $-i$ for the protonation reactions ($i\mathrm{H} + \mathrm{L} = \mathrm{H}_i\mathrm{L}$). ϑ is the ratio of the values of

132   molality to molarity for the specific ionic medium and varies for different media and

133   concentrations. For 1.0 mol·dm^{-3} NaClO$_4$, $\log \vartheta$ is about 0.02 [11]. The converted protonation

134   constants of lactate and DTPA are also shown in Table 1.

135   The protonation constants of lactate ($\log \beta_{\mathrm{H}} = 3.5 - 3.7$ at $10 - 70^{\circ}$C) indicate that lactic

136   acid is a slightly stronger acid than simple monocarboxylic acids (e.g., $\log \beta_{\mathrm{H}} \sim 4.6$ for acetic,

137   butanoic and hexanoic acids [10]), but similar to other α-hydroxycarboxylic acids (e.g., $\log \beta_{\mathrm{H}} \sim$

138   3.6 for 2-hydroxybutanoic and 2-hydroxyhexanoic acids [10]) and isosaccharinic acid ($\log \beta_{\mathrm{H}} \sim$

139   3.2 – 3.3 [12]). Such slightly stronger acidity might be attributed to the formation of hydrogen

6

140   bonding between the carboxylate group and the hydroxyl group, which could stabilize the

141   deprotonated form and result in a lower value for $\log\beta_H$. Data from this work also indicate that

142   the protonation constant of lactate remained essentially unchanged (within experimental

143   uncertainties) as the temperature was increased from 25^oC to 70^oC, suggesting the effect of

144   temperature on the protonation of lactate is minimal. The Van't Hoff plot of $\log\beta_H$ vs. $1/T$ shows

145   that the enthalpy of protonation for lactate should be near zero (Figure 4, left).

146

147   (*insert Table 1, Figure 4*)

148

149   In contrast, the protonation constants of DTPA decreased significantly as the temperature

150   was increased (Table 1 and Figure 4), suggesting that the protonation of DTPA is weakened and

151   DTPA becomes a stronger acid at higher temperatures. This observation could have impact on

152   the speciation of An(III)/Ln(III) in the TALSPEAK system, because the hydrogen ions would

153   compete less strongly with An(III)/Ln(III) ions for the complexation with anionic DTPA species

154   at higher temperatures. The Van't Hoff plot of $\log\beta_H$ vs. $1/T$ (Figure 4, right) indicates that the

155   protonation reactions of DTPA are all exothermic. From the linear fits in Figure 4, the average

156   "overall" enthalpies of protonation of DTPA in the temperature range of $10 - 70^oC$ were

157   calculated to be $-(26.6 \pm 1.3)$, $-(48.5 \pm 1.3)$, $-(53.7 \pm 1.8)$, $-(47.9 \pm 3.2)$, and $-(54.6 \pm 3.1)$

158    $kJ \cdot mol^{-1}$ for HA^{4-}, H_2A^{3-}, H_3A^{2-}, H_4A^-, and $H_5A(aq)$, respectively.

159   **3.2 Enthalpy of Protonation of Lactate and DTPA at 25^oC**

160   Data of the calorimetric titrations for the protonation of lactate and DTPA are shown in Figures 5

161   and 6. The observed reaction heat ("partial" or stepwise Q) is a function of a number of

162   parameters, including the concentrations of reactants (C_H, C_L or C_A), the protonation constants

163   ($\log\beta_H$) and the enthalpy of protonation of the ligand (ΔH). Using the stoichiometric

164   concentrations of the reactants and the protonation constants measured by potentiometry in this

165   work, the enthalpies of protonation for lactate and DTPA at 25°C are calculated from the

166   calorimetric titration data, and listed in Table 1.

167

168   (*insert Figures 5, 6*)

169

170   The enthalpy of protonation of lactate measured by microcalorimetry is very small, –

171   (0.55 ± 0.22) kJ·mol^{-1}, consistent with the value estimated by the Van't Hoff plot and the

172   observation that the protonation constant of lactate remains nearly constant in the temperature

173   range of 25 – 70°C. Also, it is typical of carboxylic acids that the protonation enthalpy is small,

174   probably because the energy required by the dehydration of H$^+$ and the carboxylate group (-

175   C(O)O$^-$) is more or less compensated by the energy released by the combination of the two

176   species of opposite charges (H$^+$ + -C(O)O$^-$ → -C(O)OH). For DTPA, the "overall" enthalpies of

177   protonation determined directly by microcalorimetry are all negative, consistent with the general

178   trends that all "overall" protonation constants decrease as the temperature is increased. The

179   stepwise enthalpies for the first two protonation steps (HA^{4-} and H$_2$A^{3-}) measured by

180   microcalorimetry are -26.2 and -26.4 kJ·mol^{-1}, in good agreement with those from the linear fits

181   of the Van't Hoff plots (-26.6 and -21.9 kJ·mol^{-1}). The large negative enthalpies of protonation

182   suggest that the first two protonation steps probably occur on the nitrogen atoms and zwitterions

183   similar to those in the system of EDTA [11] form in the protonated DTPA species. For the three

184   successive protonation steps of DTPA (H$_3$A^{2-}, H$_4$A$^-$ and H$_5$A), the agreement between the values

185   of enthalpies from microcalorimetry and those from Van't Hoff plots is less satisfactory. We

186 believe that the values from microcalorimetry are more accurate because these are directly

187 measured at 25°C while those from Van't Hoff are "average" values in the experimental

188 temperature range.

189 **3.3 Effect of Temperature on the Speciation of Lactate and DTPA**

190 With the protonation constants measured at different temperatures, it is possible to evaluate the

191 change of speciation of lactate and DTPA in the pC_H region of 2 to 5, an acidity region covering

192 the operating envelop of the TALSPEAK process. For lactate, it is obvious that the change of

193 temperature would have little effect on the speciation of the ligand. For DTPA, Figure 7

194 compares the speciation of the ligand (in the absence of metal ions) at 10°C and 40°C. At both

195 temperatures, the HA^{4-} and A^{5-} species are insignificant in the region of pC_H = 2 − 5. Small but

196 definite differences between the two temperatures can be observed for other species. For

197 example, at the same acidity, there is less H$_5$A species at 40°C (the highest percentage: 60%)

198 than at 10°C (70%), and there is more H$_2$A^{3-} species at 40°C (the highest percentage: 85%) than

199 at 10°C (80%). In brief, the protonation of DTPA generally becomes weaker at higher

200 temperatures. Such changes in the speciation of DTPA would certainly affect the speciation of

201 An(III) and Ln(III) in the TALSPEAK system. The significance of the effect will be evaluated

202 when the stability constants of the An(III)/Ln(III) complexes with DTPA at different

203 temperatures are available.

204

205 **4 SUMMARY**

206 The increase in temperature (up to 70°C) has a negligible effect on the protonation of lactate.

207 Therefore no effect of temperature on the speciation of lactate is expected in this temperature

208 range. In contrast, the overall protonation constants of DTPA decrease by 0.8 − 1.5 orders of

209 magnitude as the temperature is increased from 10 to 70°C. The shift of the protonation

210 equilibrium toward more ionized DTPA species at higher temperatures could alter the speciation

211 of the actinides and lanthanides and, in turn, their extraction behavior in the TALSPEAK system.

212

216

217 **References**

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219 americium and curium from the lanthanides by extraction from an aqueous solution of an

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248 **Table 1** Thermodynamic parameters for the protonation of lactate and DTPA, $I = 1.05$ mol·kg^{-1}

249 NaClO$_4$. HL and H$_5$A stand for lactic acid and DTPA. $\log\beta_{H,M}$ and $\log\beta_{H,m}$ represent the

250 protonation constants in molarity and molality, respectively.

Reaction	t °C	$\log\beta_{H,M}$	$\log\beta_{H,m}$	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		

251

Figure Captions

253

254 Figure 1: Potentiometric titrations of DTPA protonation at different temperatures, $I = 1.05$ mol·kg^{-1}
255 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
256 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.
257 Negative values of C_H/C_A represent the region where hydroxide is in excess ($-C_H/C_A = C_{OH}/C_A$).

258

259 Figure 2: Representative potentiometric titrations of the protonation of lactate at 10°C (left) and
260 70°C (right), $I = 1.05$ mol·kg^{-1} NaClO$_4$. Cup solution: $V^o = 20.00$ mL, 0.100 mol·dm^{-3} sodium
261 lactate. Titrant: 0.9994 HClO$_4$. Symbols: O - experimental data ($-\log[H^+]$), dashed line – fit ($-$
262 $\log[H^+]$); solid lines - percentage of lactate species (right y-axis), L$^-$ (red) and HL(blue), where
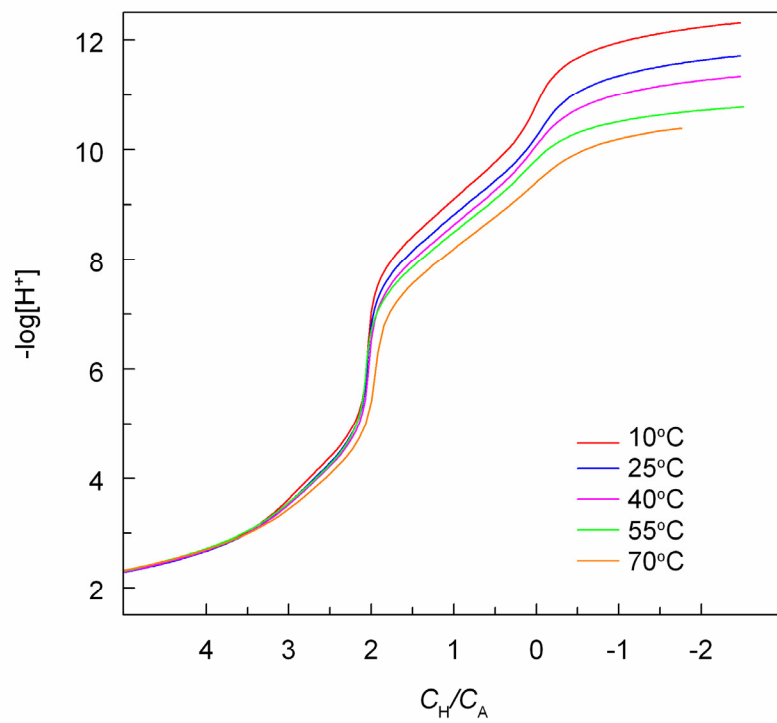263 HL stands for the neutral lactic acid.

264

265 Figure 3: Representative potentiometric titrations of the protonation of DTPA at 10°C (left) and
266 70°C (right), $I = 1.05$ mol·kg^{-1} NaClO$_4$. Cup solution: for 10°C, $V^o = 30.00$ mL, $C_{DTPA}^o = 6.667$
267 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}; $C_H^o =$
268 38.32 mmol·dm^{-3}. Titrant: 100.1 mmol·dm^{-3} NaOH. Symbols: O - experimental data ($-\log[H^+]$),
269 dashed line – fit ($-\log[H^+]$); solid lines - percentage of DTPA species (right y-axis), H$_5$A
270 (brown), H$_4$A$^-$ (cyan), H$_3$A^{2-} (magenta), H$_2$A^{3-} (green), HA^{4-} (blue) and A^{5-} (red), where H$_5$A
271 stands for the neutral DTPA acid.

272

273 Figure 4: Protonation constants of lactate (left) and DTPA (right) at different temperatures, $I =$
274 1.05 mol·kg^{-1} NaClO$_4$. Solid symbols: data from this work; open symbols, data from the literature
275 [10]; lines: linear fits of the data from this work.

276

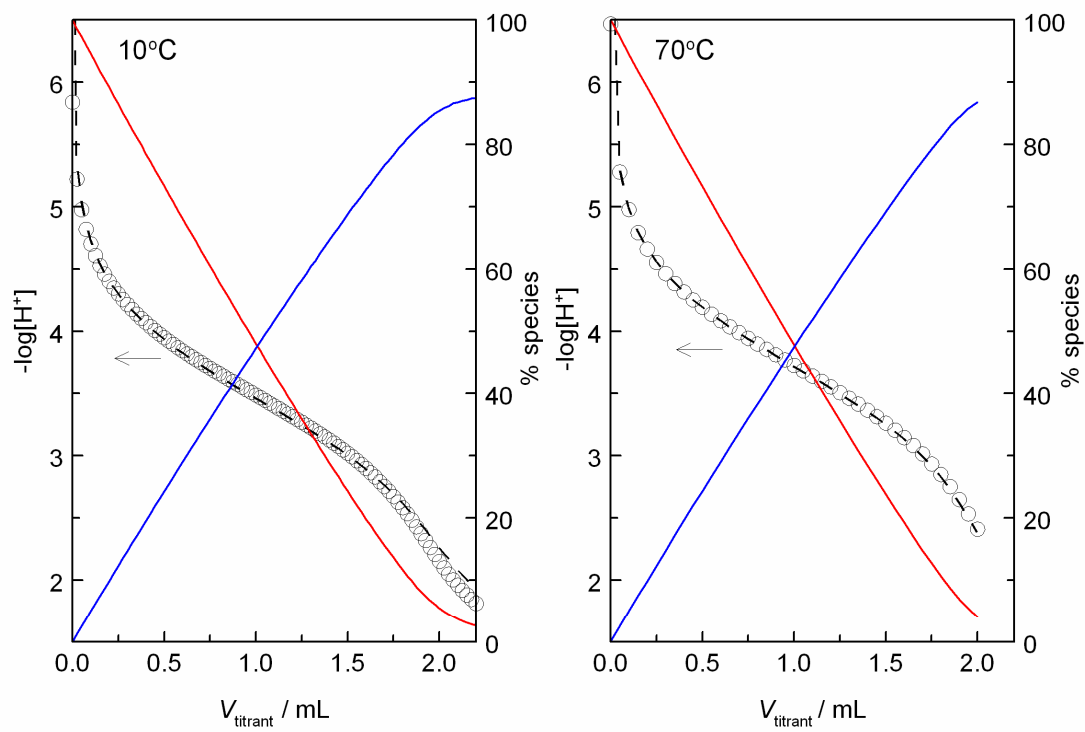277 Figure 5: Calorimetric titrations of the protonation of lactate, $I = 1.05$ mol·kg^{-1} NaClO$_4$, $t = 25$^{o}C. (Top)
278 a representative thermogram. (Bottom) A plot of $Q_{partial}$ vs. the volume of titrant, symbols - experimental
279 Q, lines - fit; initial cup solutions: sodium lactate, C_{NaL}^o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

281

282 Figure 6: Calorimetric titrations of the protonation of DTPA, $I = 1.05$ mol·kg^{-1} NaClO$_4$, $t = 25$^{o}C. (Top)
283 a representative thermogram. (Bottom) A plot of $Q_{partial}$ vs. the volume of titrant, symbols - experimental
284 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
285 18.50/3.700 (III); titrant: 100.0 mmol·dm^{-3} NaOH, 5.0 µL/addition.

286

287 Figure 7: Speciation of DTPA as a function of acidity ($-\log[H^+]$) at different temperatures. $I =$
288 1.05 mol·kg^{-1} NaClO$_4$, $C_{DTPA} = 0.05$ mol·dm^{-3}. Lines: percentage of DTPA species, H$_5$A (cyan),
289 H$_4$A$^-$ (rose), H$_3$A^{2-} (green), H$_2$A^{3-} (magenta). The species of HA^{4-} and A^{5-} are insignificant in the
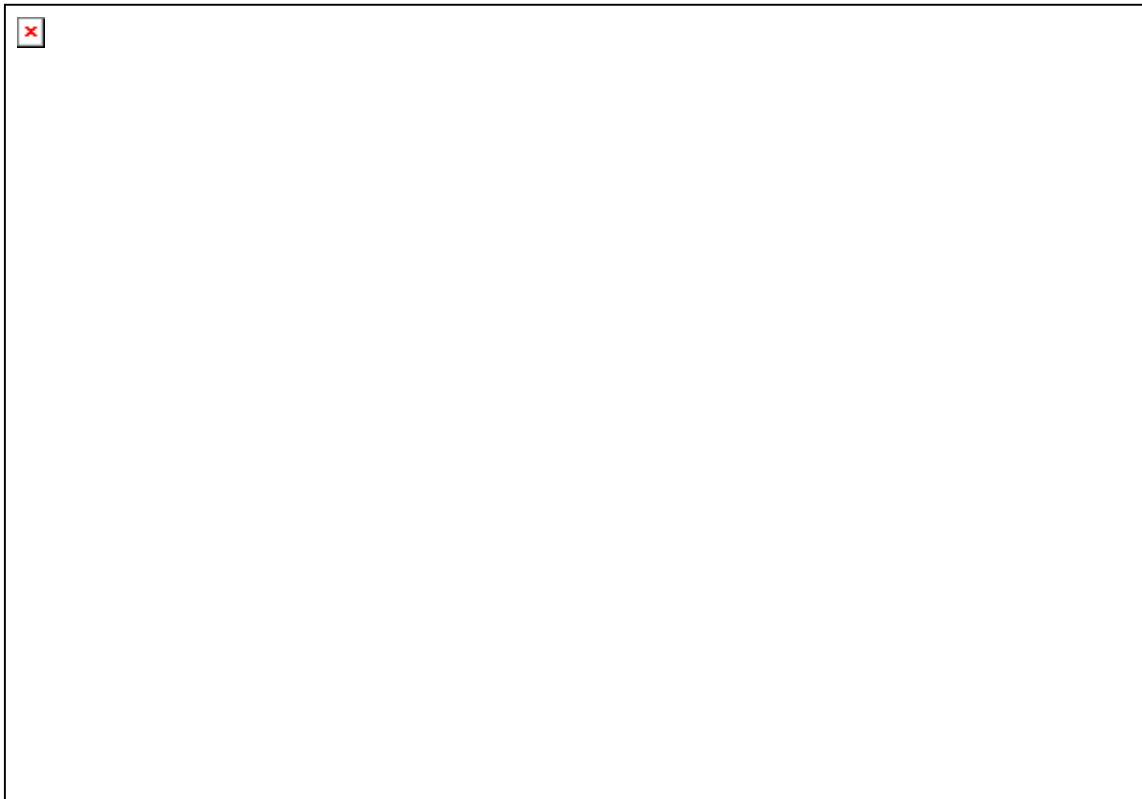290 region of $-\log[H^+] = 2 – 5$.

291

292   Figure 1

293

294   Figure 2

295

296   Figure 3

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298   Figure 4

299

300   Figure 5

301

302   Figure 6

303

304   Figure 7

305