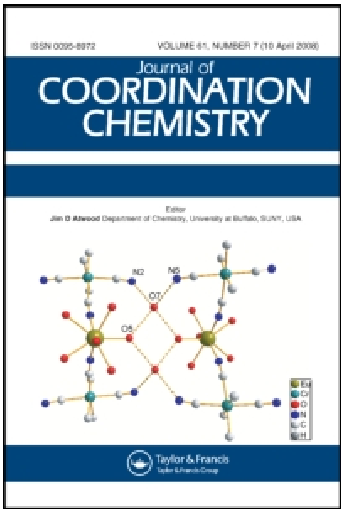

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

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To cite this Article Choi, Ki-Young and Choppin, Gregory R.(1991) 'Dissociation Kinetics of TMDTA and TMEDTA Complexes of Lanthanides', Journal of Coordination Chemistry, 24: 1, 19 — 28

To link to this Article: DOI: 10.1080/00958979109409732

URL: http://dx.doi.org/10.1080/00958979109409732

J. Coord. Chem. 1991, Vol. 24, pp. 19–28
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DISSOCIATION KINETICS OF TMDTA AND TMEDTA COMPLEXES OF LANTHANIDES

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(Received July 2, 1990)

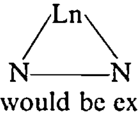
The dissociation kinetics of TMDTA (trimethylenedinitrilotetraacetic acid) and TMEDTA (tetramethylenedinitrilotetraacetic acid) complexes of Ce(III), Eu(III), and Yb(III) ions have been studied in aqueous solution using Cu(II) ions as the scavenger in acetate buffer (I = 0.1 M) at 25°C. All the complexes exhibit acid-dependent and acid-independent pathways in a manner similar to $LnDCTA^-$ complexes. The buffer concentration dependence of the rate of dissociation has also been investigated. The rates of dissociation of $LnTMDTA^-$ and $LnTMEDTA^-$ complexes are much faster than those of $LnEDTA^-$ complexes. The chelate ring size effect is discussed by comparing the rate constants to those of analogous EDTA and DCTA systems.

Keywords: Lanthanides, polydentates, complexes, dissociation, kinetics

INTRODUCTION

The kinetics of exchange and dissociation of lanthanide polyaminocarboxylate chelates have been studied for a variety of ligands.[2–6] In general, these studies have shown that exchange of the metal cation occurs by both $[H^+]$-dependent and $[H^+]$-independent mechanisms. The $[H^+]$-catalyzed dissociation has been described as involving a LnYH intermediate. The $[H^+]$-independent pathway has been interpreted as proceeding *via* a binuclear intermediate LnYM although we find no rate dependence on [M] in this study where $M = Cu^{2+}$.

The metal exchange reaction between $EuEDTA^-$ and Am(III),[2] Cu(II) exchange with $LnDCTA^-$ [3] and with $LnK22DA^{2-}$,[4] as well as with LnMEDTA[5] all had rate laws with acid-dependent and acid-independent terms.

To further understand the factors involved in lanthanide chelation kinetics, we have studied the dissociation of Ce(III), Eu(III), and Yb(III) complexes of TMDTA (trimethylenedinitrilotetraacetic acid) and Yb(III) complexes of TMEDTA (tetramethylenedinitrilotetraacetic acid). $LnTMDTA^-$ and $LnTMEDTA^-$ complexes have, respectively, one and two additional carbon atoms in the  ring than does the $LnEDTA^-$ complex. An increase in chelate ring size would be expected to reduce the stability of the chelate. The dissociation rates of the $LnTMDTA^-$ and $LnTMEDTA^-$ complexes were in fact much faster than those of other polyaminocarboxylate complexes, requiring that the study be performed on a stopped-flow spectrophotometer.

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EXPERIMENTAL

Reagents and Solutions

Lanthanide stock solutions were prepared by dissolving the metal oxide (99.9%, Aldrich Co.) in a minimum amount of concentrated perchloric acid. The solutions were evaporated to remove excess acid and diluted to volume with water. The lanthanide concentrations were determined by titration with EDTA (Aldrich Co.) using xylenol orange as an indicator in acetate buffer. TMDTA (trimethylenedinitrilototraacetic acid) and TMEDTA (tetramethylenedinitrilotetraacetic acid) were synthesized by the method of Tanaka *et al.*[7,8] The compounds were recrystallized twice from 25% ethanol. Stock solutions of the disodium salt of TMDTA and TMEDTA were prepared by dissolving the required amount of the acid in two equivalents of sodium hydroxide. The concentration of the ligands was determined by a complexometric titration with copper chloride using murexide indicator and ammonia buffer at pH 8.

Stock solutions of $LnTMDTA^-$ (Ln = Ce, Eu, Yb) and $YbTMEDTA^-$ were prepared by mixing equimolar amounts of $Ln(ClO_4)_3$ and ligand stock solutions. Solutions of copper(II) perchlorate, acetate buffer and sodium perchlorate were prepared from commercially available analytical grade reagents. Distilled water, deionized by passage through a mixed-bed ion exchange-resin cartridge (Barnstead Ultra pure), was used for all solutions.

Measurements

Ionic strength was adjusted to 0.1 M with $NaClO_4$. pH measurements were made with a Fisher Accunment 925 pH meter. The hydrogen ion concentration, pcH, was calculated from the measured pH using the relation $pcH = pH - 0.11$.

The kinetics were followed with a Durrum-Gibson D-109 stopped-flow spectrophotometer. For single wavelength measurements, monochromatic light is carried to the observation cell (path length, 2 cm) and the transmitted light conducted to a Hamamatsu Model R 136 photomultiplier tube with Oriel liquid light guides. The current from the phototube is amplified and converted to a voltage signal that is transmitted to an IBM-XT computer using a Data Translation Model 2801, an A/D converter, and stored on a floppy diskette. Graphical display of the data, the conversion of transmittance to absorbance, and subsequent quantitative analysis was accomplished with standard programs. More than 200 data points were used in each rate constant determination. Each reported rate constant is the average of a minimum of five runs.

The lanthanide complexes do not show appreciable absorption in the near-ultraviolet or visible region. Copper(II) was used as the scavenger of free ligand and the reaction monitored at 286 nm for the formation of $CuY(Ac)_n^{(2+n)-}$.

RESULTS AND DISCUSSION

The stability constants of $LnTMDTA^-$ [9] ($\log \beta_{101} = 11.74 - 15.95$) and $YbTMEDTA^-$ [10] ($\log \beta_{101} = 11.35$) complexes are much smaller than those of the corresponding copper complexes[9] (log $\beta_{101} = 18.80$, and 17.25, respectively, for CuTMDTA and CuTMEDTA formation). Therefore, the exchange reaction is complete in the presence of a tenfold excess of Cu(II) ions, *i.e.*;

$$LnY^- + Cu^{2+} \longrightarrow CuY^{2-} + Ln^{3+} \tag{1}$$

The experimental data corresponded well with pseudo-first-order reaction rates. The data in Table I show that the observed rate constants remained constant over a threefold range of Cu^{2+} concentration. The dissociation kinetics of $LnDCTA^-$,[3] LnMEDTA,[5] and $LnENDPDA^-$ [11] complexes were also reported to be independent of $[Cu^{2+}]$. The observed first-order rate constants for reaction (*1*) at various hydrogen ion concentrations for each metal complex are listed in the Appendix. The error limits represent one standard deviation.

TABLE I
Effect on the dissociation rates of LnY^- of Cu^{2+}; $I = 0.10$ M ($NaClO_4$); $C_{Buffer} = 0.01$ M (acetate) T = 298 K; $[LnY^-]_T = 0.10$ mM.

Metal	Ligand	$[Cu(Ac)_i^{2-i}]$	pH	$k_{obs} \times 10^{-1}$
Ce	TMDTA	1.00	5.841	3.13 ± 0.50
		2.00	5.837	3.15 ± 0.96
		3.00	5.845	3.03 ± 1.53
Yb	TMEDTA	1.00	5.833	3.68 ± 0.50
		2.00	5.835	3.78 ± 0.50
		3.00	5.830	3.73 ± 0.85

The dependence of the observed rate constants on the hydrogen ion concentration at various buffer concentrations is shown in Figures 1 and 2 for the Yb-TMDTA and Yb-TMEDTA systems. For all systems, a linear least-squares fit to these plots had a non-zero intercept which is consistent with the exchange reaction proceeding *via* both an acid-independent and an acid-dependent pathway. The observed rate constants for the lanthanide complexes can be written as in (*2*).

$$k_{obs} = k_d + k_H[H^+] \tag{2}$$

Figure 3 shows that K_d and K_H are directly proportional to the total acetate buffer concentration after correction for the formation of copper acetate complexes. The enhancement in the dissociation rates of these complexes by the acetate buffer can be attributed to acetate ion complexation. Thus, the overall rate of reaction can be expressed as in (*3*).

$$\text{Rate} = k_1[LnY^-] + k_2[LnY^-][Ac^-] + k_3[LnY^-][H^+] + k_4[LnY^-][H^+][Ac^-] \tag{3}$$

Values of specific rate constants, k_n (n = 1–4), calculated from a weighted least-squares program, are listed in Table II. The consistent decrease in the acid-independent rate constant of the $LnTMDTA^-$ complexes from Ce^{3+} to Yb^{3+} parallels the thermodynamic stability of these complexes.

Values of acid-independent rate constants compared to the rate constants for water exchange or for complex formation indicate that self dissociation of the

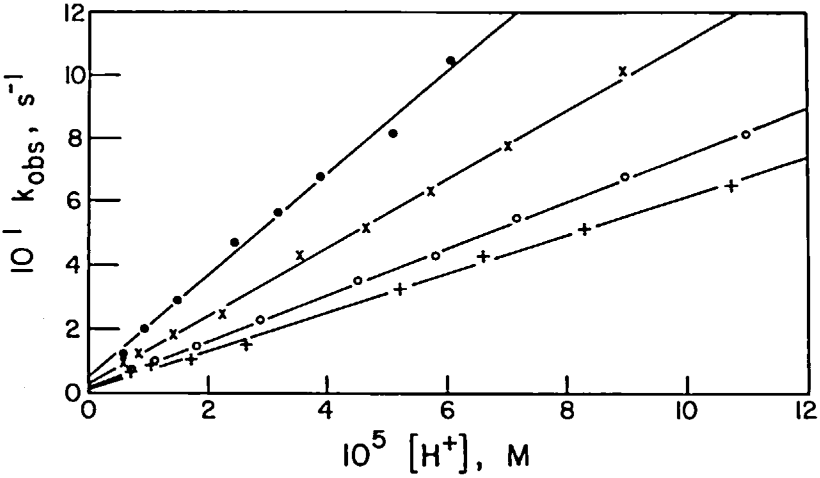

FIGURE 1 Plots of k_{obs} *vs* [H^{+}] for Yb(TMDTA)$^{-}$ with Cu(II) at different buffer concentrations. The concentrations of acetate are 5.0 mM (□); 10.0 mM (◆); 25.0 mM (■); 50.0 mM (◇).

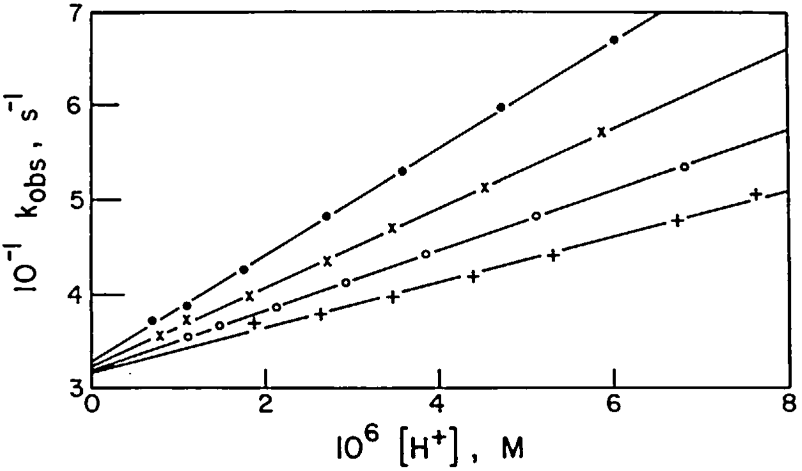

FIGURE 2 Plots of k_{obs} *vs* [H^{+}] for Yb(TMEDTA)$^{-}$ with Cu(II) at different buffer concentrations. The concentrations of acetate are 5.0 mM (□); 10.0 mM (◆); 25.0 mM (■); 50.0 mM (◇).

complex does not occur in one step. It must involve a rate determining distortion of the complex, yielding an intermediate that is rapidly scavenged by copper or hydrogen ion to give the final products. The reaction sequence for the acid-independent mechanism may be expressed as in (*4*) and (*5*).

$$\mathrm{LnY^{-}} \underset{k_f^{\mathrm{LnY}}}{\overset{k_d^{\mathrm{LnY}}}{\rightleftharpoons}} \mathrm{(LnY^{-})^{*}} \qquad (4)$$

$$\mathrm{(LnY^{-})^{*}} \underset{\text{fast}}{\overset{\mathrm{Cu^{2+}/H}}{\rightleftharpoons}} \text{products} \qquad (5)$$

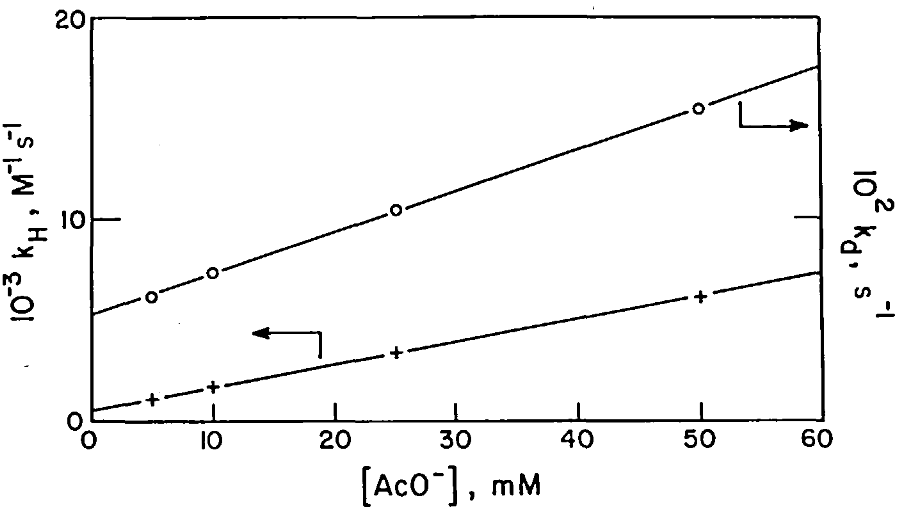

FIGURE 3 Plots of k_H and K_d *vs* acetate buffer concentrations for Yb(TMDTA)$^-$ with Cu(II).

TABLE II
Rate constants for the exchange LnY^-/Cu^{2+}; I = 0.10 M ($NaClO_4$); T = 298 K.

Exchange Reaction	$k_1\ [LnY^-]$ (s^{-1})	$k_2\ [LnY^-][Ac^-]$ $(M^{-1}s^{-1})$	$k_3\ [LnY^-][H^-]$ $(M^{-1}s^{-1})$	$k_4\ [LnY^-][Ac^-][H^+]$ $(M^{-1}s^{-1})$
CeTMDTA$^-$	$2.25 \pm 0.30 \times 10^1$	$5.89 \pm 0.79 \times 10^1$	$3.99 \pm 0.54 \times 10^6$	$1.28 \pm 0.17 \times 10^8$
EuTMDTA$^-$	1.85 ± 0.60	9.96 ± 0.30	$2.32 \pm 0.73 \times 10^5$	$1.38 \pm 0.43 \times 10^7$
YbTMDTA$^-$	$6.90 \pm 0.74 \times 10^{-3}$	1.02 ± 0.11	$5.16 \pm 0.55 \times 10^3$	$2.09 \pm 0.22 \times 10^5$
YbTMEDTA$^-$	$3.22 \pm 0.57 \times 10^1$	8.80 ± 0.16	$2.09 \pm 0.37 \times 10^6$	$7.49 \pm 0.12 \times 10^7$

Water exchange rate constants[12] for Ce^{3+} and Yb^{3+} are roughly 1.0×10^8 to 1.0×10^7 sec^{-1}. If this value is accepted for the rate constant for the formation of LnY^- from $(LnY^-)^*$, the equilibrium constants ($K = k_d^{LnY}/k_f^{LnY}$) for CeTMDTA$^-$ and YbTMEDTA$^-$ with respect to reaction (*4*) are calculated to be 2.3×10^{-7} and 3.2×10^{-6}. The stability constants for CeTMDTA$^-$ [9] and YbTMEDTA$^-$ [10] are log $\beta_{101} = 11.74$ and 11.34 respectively. These values imply that the equilibrium constant K′ for reaction (*6*)

$$Ln^{3+} + Y^{4-} \underset{}{\overset{K'}{\rightleftharpoons}} (LnY^-)^* \qquad (6)$$

should be at least 1.3×10^5 and 7.0×10^5 M^{-1}, values which are close to those of the LaDCTA$^-$ complex.[3] The dissociation mechanism can be written as in (*7*).

$$\begin{array}{l} LnY^- \underset{}{\overset{H^+}{\rightleftharpoons}} LnHY \underset{slow}{\longrightarrow} [LnHY]^* \underset{fast}{\longrightarrow} Ln^{3+} + HY^{3-} \\ \downarrow\uparrow \\ [LnY^-]^* \underset{fast}{\overset{Cu^{2+}}{\longrightarrow}} CuY^{2-} + Ln^{3+} \end{array} \tag{7}$$

The acid-dependent rate constants for LnTMDTA$^-$ complexes decrease with lanthanide atomic number (*i.e.*, from Ce^{3+} to Yb^{3+}), corresponding to a gradual increase in stability with increase in atomic number. If values for the acid-dependent dissociation rate constants (Table II), stability constants (β_{101}), and the acid dissociation constants (K_{4a}) of HY^{3-} are known from (*8*),

$$LnY^- + H^+ \underset{k_F^{HY}}{\overset{k_D^{LnY^-}}{\rightleftharpoons}} Ln^{3+} + HY^{3-} \underset{fast}{\overset{Cu^{2+}}{\longrightarrow}} \text{products} \tag{8}$$

it is possible to calculate the overall formation rate constant, k_F^{HY} of LnY^- for equation (*9*).

$$k_F^{HY} = k_D^{LnY} \cdot \beta_{101} \cdot K_{4a} \tag{9}$$

These data are given in Table III. Analogous values for EDTA and DCTA kinetics are also included in Table III for comparison.

TABLE III

Rate constants* for the reaction $Ln + HY \underset{K_D}{\overset{K_F}{\rightleftharpoons}} + LnY + H$; T = 298 K; I = 0.10 M($NaClO_4$).

	TMEDTA (p.w.)		TMDTA (p.w.)		EDTA (2, 13)		DCTA (3)	
Metal	k_F	k_D	k_F	k_D	k_F	k_D	k_F	k_D
Ce			8.93×10^7	3.99×10^6	7.08×10^8	1.38×10^3	1.09×10^7	6.00×10^1
Eu			3.94×10^8	2.32×10^5	2.62×10^9	2.28×10^2	3.41×10^7	2.20
Yb	2.69×10^7	2.09×10^6	1.96×10^9	5.16×10^3	1.45×10^9	7.60×10^{-1}	1.10×10^8	2.32×10^{-2}

*$M^{-1}s^{-1}$.

The data reflect the effects of ligand structure. The dissociation rate constant of the TMEDTA complex was found to be much faster than those of the TMDTA, EDTA, and DCTA complexes. This can be attributed to the lower stability of the complexes as the size of the N–Ln–N ring increases from 5 to 7 atoms. However, the slower rate of dissociation of the DCTA chelate may be attributed to stereochemical rigidity imposed by the cyclohexyl ring. The relative formation rate constants may also be explained by these factors. Since the dissociation rate constant of YbEDTA$^-$ is expected to be greater than the value in Table III obtained by Ryhl[13] and Betts,[14] we tried to measure the rate of dissociation of the Cu^{2+} and YbEDTA$^-$ complex by stopped-flow spectrometry under the same conditions. However, no reaction was observed, because YbEDTA$^-$ complex forms a stronger complex than CuEDTA^{2+} (log β_{YbEDTA} = 19.51, log β_{CuEDTA} = 18.78).[9] We also failed to observe dissociation of YbEDTA$^-$ through ligand exchange with Arsenazo(III) and DTPA, and metal exchange with Fe^{3+}.

ACKNOWLEDGEMENTS

Ki-Young Choi thanks the Korea Science and Engineering Foundation for a Fellowship. We also acknowledge support of this research by a Grant from the U.S.D.O.E.-O.B.E.S. Division of Chemical Sciences.

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Appendix

Pseudo-first-order rate constants, k_{obs}, for the dissociation reaction of LnY$^-$ at different [H$^+$]; I = 0.10 M (NaClO$_4$); [Cu(Ac)$_i^{2-i}$] = 1.00 mM; [LnY$^-$] = 0.10 mM; T = 298 K

	C_{Buffer} (mM)	10^6[H$^+$] (M)	10^{-1} k_{obs} (s^{-1})
Ce-TMDTA	5	5.234	48.5 ± 1.3
		5.334	43.3 ± 1.7
		5.407	40.5 ± 0.6
		5.487	36.8 ± 1.0
		5.640	32.3 ± 1.5
		5.785	30.3 ± 0.6
		5.914	28.3 ± 1.0
	10	5.237	55.3 ± 0.6
		5.345	48.3 ± 0.5
		5.423	43.8 ± 1.0
		5.514	39.8 ± 0.5
		5.703	34.0 ± 1.0
		5.842	31.3 ± 0.5

Appendix (*continued*)

	C_{Buffer} (mM)	$10^6[H^+]$ (M)	$10^{-1} k_{obs}$ (s^{-1})
		5.959	29.0 ± 1.0
	25	5.331	57.5 ± 0.6
		5.431	50.8 ± 0.5
		5.526	45.5 ± 1.3
		5.714	38.0 ± 1.4
		5.900	32.5 ± 0.7
		6.066	30.5 ± 1.3
		6.208	28.5 ± 0.6
	50	5.355	70.7 ± 0.6
		5.453	61.7 ± 1.5
		5.558	54.5 ± 2.1
		5.752	44.3 ± 3.3
		5.955	37.3 ± 0.6
		6.131	32.7 ± 0.5
		6.301	30.3 ± 0.6
Eu-TMDTA	5	4.976	5.06 ± 0.15
		5.086	4.53 ± 0.09
		5.174	4.03 ± 0.02
		5.270	3.65 ± 0.06
		5.361	3.30 ± 0.07
		5.466	3.08 ± 0.09
		5.595	2.55 ± 0.07
		5.757	2.35 ± 0.06
	10	4.983	5.90 ± 0.10
		5.076	4.93 ± 0.15
		5.178	4.35 ± 0.13
		5.287	3.80 ± 0.14
		5.363	3.65 ± 0.13
		5.458	3.25 ± 0.05
		5.636	2.90 ± 0.07
		5.799	2.50 ± 0.08
	25	5.003	7.63 ± 0.06
		5.096	6.37 ± 0.23
		5.203	5.63 ± 0.25
		5.300	4.93 ± 0.21
		5.407	4.27 ± 0.06
		5.498	3.90 ± 0.08
		5.686	3.13 ± 0.06
		5.873	2.78 ± 0.09
	50	5.003	11.00 ± 0.02
		5.118	10.00 ± 0.01
		5.218	8.15 ± 0.07
		5.317	7.05 ± 0.25
		5.416	6.13 ± 0.06

Appendix (*continued*)

	C_{Buffer} (mM)	$10^6[H^+]$ (M)	$10^{-1} k_{\text{obs}}$ (s^{-1})
		5.519	5.20 ± 0.08
		5.712	3.83 ± 0.10
		5.914	3.28 ± 0.05
Yb-TMDTA	5	3.969	0.650 ± 0.019
		4.082	0.513 ± 0.006
		4.181	0.430 ± 0.001
		4.282	0.325 ± 0.010
		4.578	0.153 ± 0.005
		4.764	0.106 ± 0.002
		4.971	0.087 ± 0.002
		5.143	0.065 ± 0.001
	10	3.959	0.809 ± 0.006
		4.047	0.673 ± 0.008
		4.147	0.547 ± 0.006
		4.236	0.430 ± 0.017
		4.347	0.353 ± 0.012
		4.541	0.227 ± 0.006
		4.742	0.143 ± 0.012
		4.951	0.103 ± 0.005
		5.131	0.071 ± 0.001
	25	4.048	1.011 ± 0.024
		4.155	0.768 ± 0.010
		4.242	0.630 ± 0.008
		4.334	0.513 ± 0.009
		4.451	0.427 ± 0.006
		4.650	0.243 ± 0.006
		4.854	0.185 ± 0.006
		5.071	0.125 ± 0.005
		5.244	0.096 ± 0.004
	50	4.219	1.041 ± 0.007
		4.291	0.815 ± 0.030
		4.411	0.678 ± 0.013
		4.499	0.565 ± 0.031
		4.611	0.473 ± 0.017
		4.827	0.290 ± 0.008
		5.022	0.203 ± 0.005
		5.229	0.125 ± 0.010
Yb-TMEDTA	5	5.118	50.5 ± 2.9
		5.172	47.8 ± 1.0
		5.276	44.0 ± 0.8
		5.358	41.8 ± 0.7
		5.461	39.8 ± 0.7
		5.578	37.8 ± 0.5
		5.730	36.8 ± 1.1

Appendix (*continued*)

C_{Buffer} (mM)	$10^6[H^+]$ (M)	$10^{-1} k_{obs}$ (s^{-1})
10	5.167	53.5 ± 3.1
	5.291	48.3 ± 0.5
	5.416	44.2 ± 3.8
	5.533	41.3 ± 0.6
	5.672	38.5 ± 1.3
	5.833	36.8 ± 0.5
	5.959	35.3 ± 0.6
25	5.232	57.0 ± 1.2
	5.346	51.3 ± 0.5
	5.462	47.0 ± 1.6
	5.567	43.5 ± 0.6
	5.740	39.8 ± 0.5
	5.955	37.3 ± 0.5
	6.108	35.5 ± 0.6
50	5.221	67.0 ± 1.0
	5.328	59.8 ± 2.3
	5.447	53.0 ± 3.5
	5.567	48.3 ± 3.5
	5.757	42.5 ± 0.9
	5.959	38.8 ± 0.5
	6.149	37.3 ± 0.5