

# The Complex Formation Equilibria of Ethylenediaminetetrapropionic Acid (EDTP) with Some Divalent Transition Metal Ions in Aqueous NaClO<sub>4</sub> Solutions

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The complex equilibria between ethylenediaminetetrapropionic acid (EDTP) and Co(II), Ni(II), Cu(II), Zn(II) or Cd(II) ions have been studied as a series of emf titrations in 0.1 and 0.5 M NaClO<sub>4</sub> solutions at 25 °C. Computer analysis of the potentiometric data showed the formation of the MHL<sup>-</sup> and ML<sup>2-</sup> complexes in each system studied. In the case of copper, the MH<sub>2</sub>L species was also found to be formed. The stabilities of these complexes are considerably lower than those of the corresponding EDTA complexes. The <sup>13</sup>C NMR measurements suggest that in the ZnL complex, six-membered chelate rings are formed through the nitrogen and oxygen atoms of the amino and propionate groups, respectively.

A number of papers have been published concerning the complexation of aminocarboxylate ligands with different metal ions.<sup>1</sup> However, little quantitative information has been reported on the effect of chelate ring enlargement on the metal complex formation of ethylenediaminepolycarboxylic acids.<sup>2,3</sup> In this paper we report the results of studies of the complexation of Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) ions by ethylenediaminetetrapropionic acid, EDTP. This compound is structurally related to ethylenediaminetetraacetic acid, EDTA, and differs only in that the acetic acid groups are replaced by propionic acid. EDTA is capable of forming stable five-membered chelate rings with metal ions through the amino and acetate groups, while the present ligand can form six-membered rings through the amino and propionate groups.

This study was conducted as a series of potentiometric titrations and <sup>13</sup>C NMR measurements.

## Experimental

**Reagents.** Stock solutions of NaClO<sub>4</sub> and metal nitrates were prepared and analyzed as described previously.<sup>4</sup>

EDTP was prepared by mixing ethylenediamine, 3-chloropropionic acid and NaOH.<sup>5</sup> The final product was recrystallized from hot water.

**Potentiometric measurements.** A Radiometer PHM 64 potentiometer equipped with a Beckman N 90495 glass electrode was used for the emf measurements. The calibration of the electrode system was carried out as described in detail earlier.<sup>6</sup>

The present investigation was carried out at 25 °C using a constant ionic medium of 0.1 and 0.5 M NaClO<sub>4</sub> as a series

of potentiometric titrations. The total concentrations of metal, C<sub>M</sub>, and ligand, C<sub>L</sub>, were kept constant. The free hydrogen ion concentration, [H<sup>+</sup>], was decreased by adding CO<sub>2</sub>-free NaOH solution. A total of from seven to ten different titrations with 30 to 40 potential readings were carried out for each metal-EDTP equilibrium system within the limits 2.5 ≤ -log[H<sup>+</sup>] ≤ 4.5–6.5 (depending on the metal-EDTP system), 0.0007 ≤ C<sub>L</sub> ≤ 0.02 M, and 0.16 ≤ C<sub>L</sub> : C<sub>M</sub> ≤ 6.

**<sup>13</sup>C NMR measurements.** The proton decoupled <sup>13</sup>C NMR spectra were recorded on a JNM-GX400 FT spectrometer using 10 mm sample tubes and a tunable probe. The field was locked on the <sup>2</sup>H signal of D<sub>2</sub>O, the amount of which was ca. 20 % of the total water content in the sample. Dioxane was used as an internal chemical shift reference. The shift scale was chosen to be positive to higher frequency. The number of accumulated scans varied from 2000 to 5000. In order to improve the signal-to-noise ratio of the spectra, the FID signal was multiplied by an exponential window function resulting in the line broadening of 3 Hz.

C<sub>L</sub> and C<sub>L</sub> : C<sub>M</sub> in the test solutions were 0.02 M and 0.5, respectively. The ionic strength of the solutions was adjusted to be 1.0 (NaClO<sub>4</sub>). The pH values of the solutions were evaluated using the relation: pD = pH + 0.4.

**Data treatment.** The stability constants were calculated with an improved version of the programs SCOGS and SCOGS-2,<sup>7,8</sup> written by K. Pieniniemi in this laboratory.<sup>9</sup> In this new version the input data is read by the free format, and the program contains new sub-routines for the statistical calculations and for plotting the distribution dia-

Table 1. The protonation constants for EDTP at 25 °C.<sup>a</sup>

Medium	log β <sub>011</sub>	log β <sub>021</sub>	log β <sub>031</sub>	log β <sub>041</sub>	log β <sub>051</sub>	log β <sub>061</sub>
0.1(NaClO <sub>4</sub> )	9.74	15.99	20.28	23.58	26.56	28.06
0.5(NaClO <sub>4</sub> )	9.10	14.59	19.02	22.18	25.19	26.79

<sup>a</sup>Ref. 11.

grams. The statistical analysis is based on the residuals of titre(calcd.)-titre(exptl.). The calculations give the  $\chi^2$  statistics and an agreement index  $R$  as calculated by the program MINQUAD.<sup>10</sup>  $\chi^2$  is a measure of the normality of the distribution of residuals of titre(calcd.)-titre(exptl.). The acceptable value of  $\chi^2$  at the 95 % confidence level for 6 degrees of freedom should be less than the value 12.6. The agreement index  $R$  is defined as

$$R = [\sum_i \{ \text{titre}_i(\text{exptl.}) - \text{titre}_i(\text{calcd.}) \}^2 / \sum_i \{ \text{titre}_i(\text{exptl.}) \}^2]^{1/2}.$$

The smaller the value of  $R$ , the better the set of constants. Statistically, there is a significant difference between two models 1 and 2, if the ratio  $R_1 : R_2$  is greater than 1.5.

In the calculations of the stability constants, the values given in Table 1 were used for the protonation constants of EDTP at  $I = 0.1$  and  $0.5$  M NaClO<sub>4</sub>.<sup>11</sup>

## Results and discussion

**Potentiometry.** The treatment of the potentiometric data was initiated by making Bjerrum plots of  $\bar{n}(-\log[L])$ . One of these for the copper-EDTP system is presented in Fig. 1. This plot shows that the system cannot be described solely by the stepwise formation of ML<sub>*y*</sub> complexes, and the formation of protonated and/or polynuclear species must be taken into account. Further, the plot shows that complexes with a ligand-to-metal ratio higher than 1 are hardly formed because of the low values of  $\bar{n}$  under the conditions studied.

The proposed stability constants are given in Table 2.

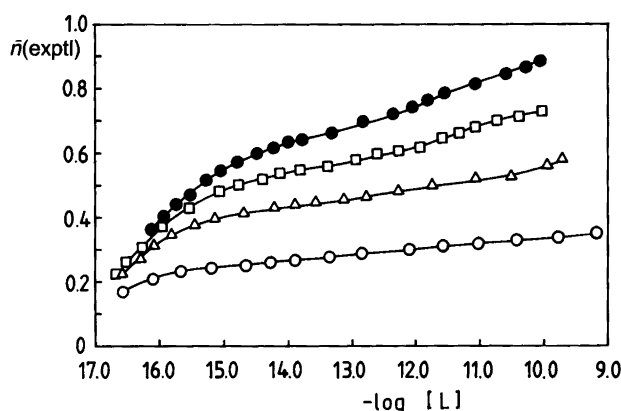


Fig. 1. A part of the potentiometric data plotted as curves  $\bar{n}(-\log[L])$  for the copper(II)-EDTP system at  $I = 0.10$  M NaClO<sub>4</sub>. In each titration  $C_M = 0.002$  M;  $\circ$ :  $C_L = 0.00075$  M;  $\triangle$ :  $C_L = 0.00119$  M;  $\square$ :  $C_L = 0.00149$  M;  $\bullet$ :  $C_L = 0.00179$  M.

These are the “best sets of constants” for each metal-ligand equilibrium system, viz. the results of the models which gave the lowest standard deviations of the constants, and the lowest  $\chi^2$  and  $R$  values in the statistical analysis of the residuals. Simultaneous calculations on 4 to 7 different titrations using 150 to 200 data points gave values of 3.9 to 11.6, and 0.005 to 0.01 for the  $\chi^2$  and  $R$  values, respectively. The inclusion of the MHL complexes in the model originally including only the ML complexes considerably decreased the standard deviations and  $\chi^2$  values in each system. Statistically, the difference between models including

 Table 2. The proposed stability constants for the Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) complexes with EDTP.<sup>a</sup>

Metal ion	Medium	log β <sub>121</sub>	log β <sub>111</sub>	log β <sub>101</sub>
Co(II)	0.1(NaClO <sub>4</sub> )	—	13.61(0.04)	8.68(0.02)
	0.5(NaClO <sub>4</sub> )	—	—	7.27(0.02)
Ni(II)	0.1(NaClO <sub>4</sub> )	—	14.58(0.04)	10.38(0.02)
	0.5(NaClO <sub>4</sub> )	—	12.99(0.15)	8.95(0.02)
Cu(II)	0.1(NaClO <sub>4</sub> )	21.45(0.02)	18.804(0.004)	14.85(0.02)
	0.5(NaClO <sub>4</sub> )	19.83(0.03)	16.87(0.002)	12.26(0.03)
Zn(II)	0.1(NaClO <sub>4</sub> )	—	13.71(0.03)	9.31(0.01)
	0.5(NaClO <sub>4</sub> )	—	12.17(0.09)	7.94(0.02)
Cd(II)	0.1(NaClO <sub>4</sub> )	—	12.6(0.1)	7.25(0.04)
	0.5(NaClO <sub>4</sub> )	—	—	5.48(0.06)

<sup>a</sup>Values in parentheses are standard deviations.

Table 3. Computer analysis of the potentiometric data for the Zn-EDTP and Cu-EDTP equilibrium systems at  $I = 0.1$  ( $\text{NaClO}_4$ ) and  $t = 25^\circ\text{C}$ .<sup>a</sup>

$\log \beta_{121}$	$\log \beta_{111}$	$\log \beta_{101}$	$\log \beta_{201}$	$\chi^2$	$R$
<b>Zn-EDTP</b>					
—	—	9.328 (0.028)	—	15.3	0.0067
—	13.709 (0.029)	9.310 (0.007)	—	8.4	0.0038
<sup>b</sup>	13.788 (0.035)	9.240 (0.019)	—	39.8	0.225
—	—	9.28 (0.072)	11.95 (0.068)	72.0	0.432
<b>Cu-EDTP</b>					
—	—	15.348 (0.087)	—	29.6	0.235
—	18.757 (0.017)	14.667 (0.032)	—	17.1	0.101
—	—	15.03 (0.08)	19.84 (0.15)	16.7	0.450
—	18.59 (0.05)	14.61 (0.15)	19.00 (0.15)	19.2	0.320
21.46 (0.04)	18.80 (0.03)	14.87 (0.15)	17.1 (1.6)	52.0	0.048
21.451 (0.017)	18.804 (0.004)	14.853 (0.009)	—	8.8	0.0035

<sup>a</sup>Number of titrations/points: Zn-EDTP, 5/190; Cu-EDTP, 7/200. Values in parentheses are standard deviations. <sup>b</sup>Calculations were unsuccessful, and no value was obtained.

only one ( $\text{ML}^{2-}$ ), two ( $\text{ML}^{2-}$  and  $\text{MHL}^-$ ) and three ( $\text{CuL}^{2-}$ ,  $\text{CuHL}^-$  and  $\text{CuH}_2\text{L}$ ) species was most significant in the case of copper and smallest in the case of zinc (Table 3).

Courtney<sup>3</sup> *et al.* have reported the protonation and stability constants for EDTP with some divalent metal ions at  $I = 0.1$  and  $t = 30^\circ\text{C}$ . The relative stabilities of the  $\text{ML}^{2-}$  complexes determined by them are in agreement with those

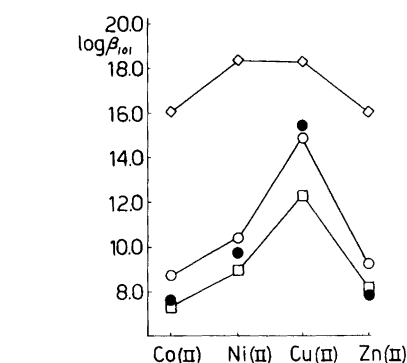
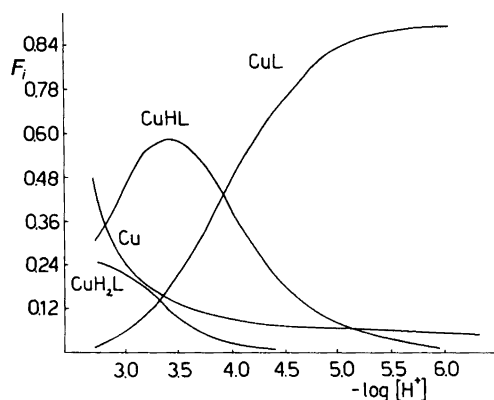


Fig. 2. Stability constants for the ML complexes of EDTP and EDTA as a function of metal ion atomic number. EDTP:  $I = 0.1$  ( $\circ$ ) and  $I = 0.5$  ( $\square$ ); EDTA by Courtney *et al.*<sup>3</sup> ( $\bullet$ ); EDTA by Schwarzenbach and Freitag<sup>12</sup> ( $\diamond$ ).

obtained in this study, and with those usually found for other chelating agents:  $\text{Cu(II)} \gg \text{Ni(II)} > \text{Co(II)}$ ,  $\text{Zn(II)} > \text{Cd(II)}$  (Fig. 2). Small differences between the corresponding values reported by them and by us are due to the difference in the protonation constants used in the calculations and to their assumption that only  $\text{ML}^{2-}$  complexes are formed.

The stabilities of metal(II) EDTP complexes are significant lower than those of the corresponding EDTA complexes. Schwarzenbach and Freitag<sup>12</sup> have reported the values 18.3, 18.4, 16.1, 16.1 and 16.4 for the Cu(II), Ni(II), Co(II), Zn(II) and Cd(II) EDTA complexes ( $\text{ML}^{2-}$ ), respectively, at  $I = 0.1$  and  $t = 30^\circ\text{C}$ . The replacement of the acetate groups in EDTA by propionate groups (EDTP) results in a decrease of from 4 (Cu) to 10 (Cd) log units in stability. This can be explained by the greater size of the chelate rings formed by EDTP.

Comparison of the stability constants at two different ionic strengths (0.1 and 0.5), shows that these are in qualitative agreement, for each metal ion system, with the prediction of the extended Debye-Hückel theory.

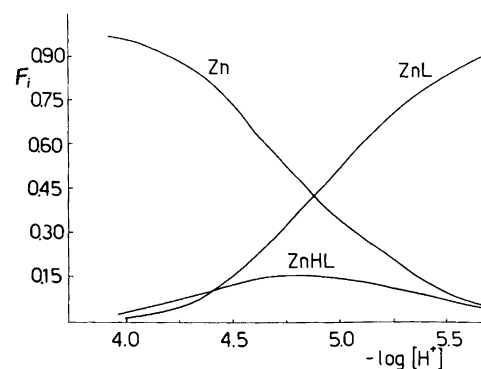


Fig. 3. Distribution diagrams  $F_i(-\log[\text{H}^+])$ .  $F_i$  is defined as the ratio between copper(II) or zinc(II) in a species and total copper or zinc. Left: the copper(II)-EDTP system,  $C_L = 0.002$  M and  $C_M = 0.002$  M; right: the zinc(II)-EDTP system,  $C_L = 0.002$  M and  $C_M = 0.002$  M.  $I = 0.1$  ( $\text{NaClO}_4$ ) and  $t = 25^\circ\text{C}$ .

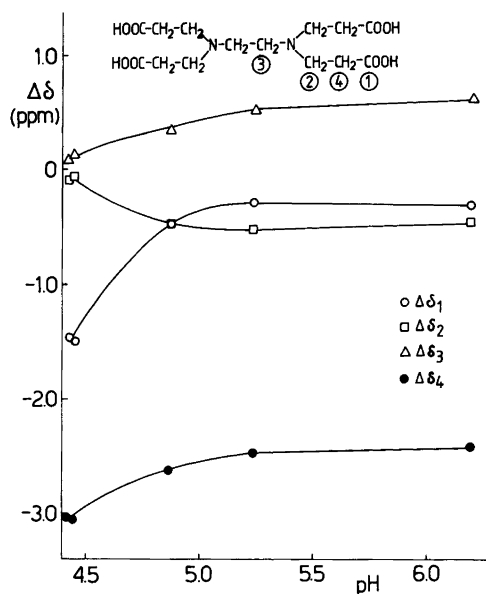


Fig. 4.  $^{13}\text{C}$  chemical shift differences (in ppm) between the Zn-EDTP system and deprotonated EDTP anion ( $\text{L}^{4-}$ ) as a function of pH. The chemical shift difference is defined as  $\delta_i = \delta_i(\text{Zn-EDTP}) - \delta_i^{\text{pH}=11}(\text{EDTP})$ .

In order to visualize the relative amounts of the different metal species as a function of pH, two distribution diagrams for individual copper and zinc systems are presented in Fig. 3.

$^{13}\text{C}$  NMR spectrometry. Table 4 gives the  $^{13}\text{C}$  chemical shifts for the  $\text{H}^+$ -EDTP and  $\text{Zn}^{2+}$ -EDTP equilibrium systems at various pH values. Fig. 4 illustrates in turn the variation of the  $^{13}\text{C}$  chemical shifts as a function of pH. From these data one can draw the following conclusions: First, the largest change is observed for the carbon C-1 chemical shift when compared to the  $\delta_i^{\text{pH}=11}$  value in EDTP. Second, all the other changes,  $\Delta\delta_i$ , except  $\Delta\delta_3$ , are negative, indicating upfield shifts in the resonances. Third, increasing pH in the  $\text{Zn}^{2+}$ -EDTP system causes the C-1, C-3 and C-4 resonances to shift to higher frequency (lower field) while the C-2 resonance behaves in the opposite manner. Fourth, above a pH value of approximately 5.3 to 6.2 the chemical shifts remain constant within experimental uncertainty. Above pH 6.2, measurements were not possible owing to precipitation.

According to these findings, the  $\text{ZnL}^{2-}$  species is formed completely under the conditions employed at  $5.3 < \text{pH} < 6.2$ . Thus, the  $^{13}\text{C}$  chemical shifts at pH 6.2 represent the

Table 4.  $^{13}\text{C}$  chemical shift dependence on pH for the H-EDTP and Zn-EDTP systems. All the shifts are given in ppm with respect to the internal dioxane reference. Estimated error for each  $\delta$  value is  $\pm 0.02$  ppm unless otherwise indicated.

pH	$\delta_1$	$\delta_2$	$\delta_3$	$\delta_4$
<b>H-EDTP</b>				
4.37	110.48	-15.73	-19.05	-36.43
4.95	110.93	-15.60	-19.19	-36.14
5.31	111.12	-15.65	-19.16	-35.95
6.00	111.68	-16.08	-18.77	-35.28
7.00	112.56	-16.82	-18.21	-34.36
11.00	114.38	-16.68	-16.82	-32.57
<b>Zn-EDTP</b>				
4.43	112.91 <sup>b</sup>	-16.74 <sup>a</sup>	-16.74 <sup>a</sup>	-35.61
4.45	112.87 <sup>c</sup>	-16.69 <sup>a</sup>	-16.69 <sup>a</sup>	-35.63
4.87	113.87	-17.12	-16.49	-35.20
5.24	114.08	-17.14	-16.29	-35.06
6.20	114.07	-17.06	-16.18	-34.99

<sup>a</sup>Overlapping signals. <sup>b</sup>Error  $\pm 1$  ppm. <sup>c</sup>Error  $\pm 0.8$  ppm.

chemical shifts of the  $\text{ZnL}^{2-}$  complex. The shift of the C-3 resonance to lower field as a function of the formation of the  $\text{ZnL}^{2-}$  complex is an indication that the nitrogen atoms take part in the bonding, and that six-membered chelate rings are formed through the nitrogen and oxygen atoms of the amino and propionate groups, respectively.

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