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Complexation of *N*-tris[(1,2-dicarboxyethoxy)ethyl]amine with Ca(II), Mn(II), Cu(II) and Zn(II) in aqueous solution

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In a search for environmentally friendly metal chelating ligands for industrial applications, the protonation and complex formation equilibria of *N*-tris[(1,2-dicarboxyethoxy)ethyl]amine (TCA6) with Ca(II), Mn(II), Cu(II) and Zn(II) ions in aqueous 0.1 M NaCl solution were studied at 25°C by potentiometric titration. A model for complexation and stability constants of the complexes were determined. With all of the metals, complex formation was dominated by ML^{4-} . Comparison of TCA6 and six other chelating agents showed TCA6 to be suitable for applications where strong calcium binding is essential.

Keywords: *N*-tris[(1,2-dicarboxyethoxy)ethyl]amine; Complexes; Equilibria; Stability constants; Chelating agents

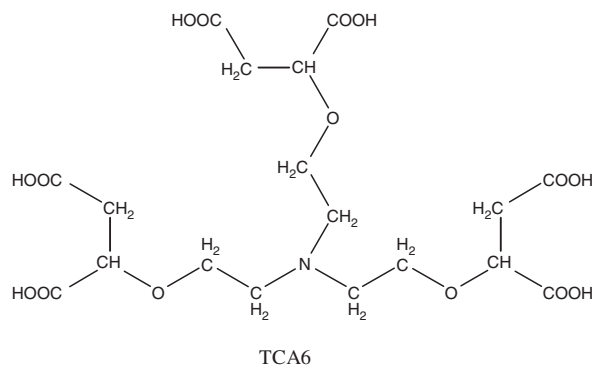
1. Introduction

The ability of aminopolycarboxylates and aminopolyphosphonates to form stable metal complexes has been widely used in analytical chemistry and industry. Aminopolycarboxylates such as ethylenediaminetetraacetic acid (EDTA), nitrilotriacetic acid (NTA) and diethyleneaminepentaacetic acid (DTPA) have been used for decades as effective chelating agents in a variety of large-scale industrial applications, from detergents to agrochemicals. During the past few years, the non-biodegradability of most of these ligands and their accumulation in the environment have been a cause for concern [1]. There is another environmental aspect to take into account. As the chelating agents are a source of nitrogen in wastewater, the nitrogen content of the ligands should be as low as possible. More environmentally friendly chelating agents, with complex forming properties comparable to those of EDTA, NTA and DTPA, are desirable.

For pulp bleaching applications, where EDTA and DTPA are commonly used, possible alternative ligands are ethylenedisuccinic acid (EDDS) and iminodisuccinic

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acid (ISA). Their suitability for pulp bleaching has been proven [2] and their complexation with Fe(III), Cu(II), Zn(II) and Mn(II) ions has been described [3, 4]. In continuation of our studies of environmentally friendly chelating agents, we report here the aqueous complexation of a new, low-nitrogen ligand, *N*-tris[(1,2-dicarboxyethoxy)ethyl]amine (TCA6) with Ca(II), Mn(II), Cu(II) and Zn(II).



2. Experimental

2.1. Preparation of TCA6 and stock solutions of metal ions

TCA6 was synthesized by a lanthanide-catalysed Michael addition of triethanolamine to maleic acid [5–7]. The purity of the preparations was checked by ^{13}C NMR and ^1H NMR and potentiometric titration. Aqueous Cu(II), Mn(II), Zn(II) and Ca(II) chloride solutions were prepared by dissolving CuCl_2 and MnCl_2 hydrates in distilled water and ZnO and CaO in aqueous hydrochloric acid. Metal contents of stock solutions were standardized by EDTA titration. The Cu(II) concentration was also determined electrogravimetrically. Acid contents of metal solutions were determined by titration with 0.1 M NaOH solution after liberation of H^+ ions by cation exchange.

2.2. Potentiometric measurements

Protonation and complex formation equilibria were studied in aqueous 0.1 M NaCl at 25.0°C through a series of potentiometric EMF titrations carried out with a Schott–Geräte GmbH TPC2000 titrator using TR600 version 5.00 titration software. The cell arrangement for the measurement of the hydrogen ion concentration, $[\text{H}^+]$, was as in equation (1):



where GE denotes the glass electrode (Schott N2680) and RE is $\text{Hg}, \text{Hg}_2\text{Cl}_2 \mid \mid 0.1 \text{ M NaCl}$.

Assuming activity coefficients to be constant, expression (2) is valid,

$$E = E_0 + 59.157 \log[\text{H}^+] + j_{\text{H}}[\text{H}^+] + j_{\text{OH}}[\text{OH}^-] \quad (2)$$

The cell parameter, E_0 , and the liquid junction coefficient, j_H , valid in acidic solutions, were determined for each titration by addition of a known amount of HCl to the background electrolyte. The value of the liquid junction coefficient, j_{OH} , valid in basic solutions, was determined periodically. Only stable emf readings (0.2 mV/2–3 min) were used in the calculations.

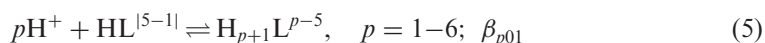
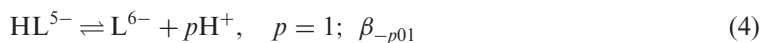
During measurements of the metal complex equilibria, aqueous NaOH or HCl was added to the solution. The ratio of the total concentrations of metal, C_M , to ligand, C_L , was usually held constant. Initial concentrations were varied within the limits $0.0007 \text{ M} \leq C_M \leq 0.0065 \text{ M}$ and $0.0013 \text{ M} \leq C_L \leq 0.0020 \text{ M}$, covering the metal-to-ligand ratios 3:1 to 1:2. In some runs aqueous metal chloride was used as the titrant; 3–5 independent titrations were carried out for each system. The number of data points used in the calculation of the stability constants varied between 240 and 367 in the pH ($= -\log[H^+]$) ranges 5.1–10.8 Ca(II), 4.0–10.6 Mn(II), 2.6–10.2 Cu(II) and 3.2–10.3 Zn(II). In some titrations the upper pH values were limited by the appearance of a precipitate or very slow attainment of equilibrium. Reproducibility and reversibility of the equilibria were tested by performing forward (increasing pH) and backward (decreasing pH) titrations.

2.3. Data treatment

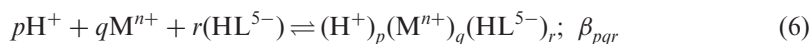
Protonation/deprotonation of the ligand was controlled with HCl/NaOH additions. Curves of Z_H versus pH were drawn to visualize the experimental data sets. Z_H describes the average number of H^+ ions added or liberated per mol of ligand and is given by equation (3):

$$Z_H = (C_H - [H^+] + k_w[H^+]^{-1})/C_L \quad (3)$$

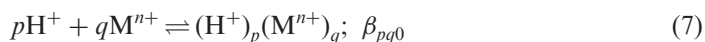
where C_H denotes the total concentration of protons calculated over the zero level HL^{5-} , H_2O and M^{n+} . In evaluating the equilibrium constants the two-component equilibria (4) and (5) were considered,



Metal complex formation can be characterized by the general three-component equilibrium (6),



and hydrolysis of metal ions can be written as in equation (7):



Protonation constants of the ligand and hydrolysis constants of the metal ions [8] were considered as known parameters in the evaluation of the three-component system (6).

Mathematical analysis of the systems involves a search for complex models (*pqr*-triplets) and equilibrium constants of complexes that best fit the experimental data. Calculations were carried out with the computer program SUPERQUAD [9]. Sample standard deviation, *s*, and the χ^2 statistics used as criteria in selection of complex models were those given by the program.

2.4. Chelation of calcium: TCA6 compared with EDTA, DTPA, MGDA, NTA, EDDS and ISA

The chelating effectiveness for calcium was also tested for comparison of TCA6 with six other ligands, ethylenediaminetetraacetic acid (EDTA), diethylenetriaminepentaacetic acid (DTPA), methylglycinediacetic acid (MGDA), nitrilotriacetic acid (NTA), ethylenedisuccinic acid (EDDS) and iminodisuccinic acid (ISA). Chelating agents were tested in $\text{NH}_4\text{Cl-NH}_3$ buffer at pH 9.5 at a hardness level of 1000 ppm (calculated as CaCO_3). Each chelating agent was added to buffered calcium solution until the mol ratio Ca:ligand was 1:1. At the same time free calcium concentration was measured by using an ion selective electrode.

3. Results and discussion

3.1. Protolytic properties of TCA6

Neutralization titrations showed the stepwise deprotonation of H_7L^+ to HL^{5-} to occur in the pH range from 2 to neutral (Z_{H} from 6 to 0). HL^{5-} is the major species in the pH range 6–9 when $Z_{\text{H}}=0$. Negative Z_{H} values, reached in the pH range from neutral to 11, showed that one proton (from amino nitrogen, HL^{5-} to L^{6-}) can leave the ligand in alkaline solution (figure 1, the curve for free ligand). Equilibrium constants for reactions (4) and (5) obtained in the final refinements are listed in table 1

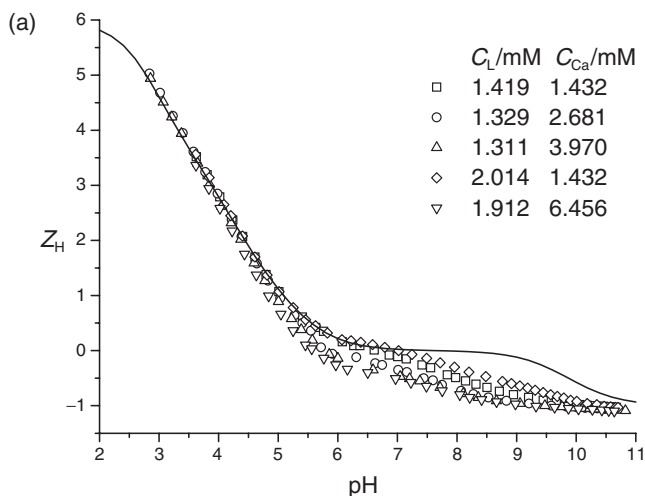


Figure 1. Z_{H} vs. pH for complexation of (a) Ca(II), (b) Mn(II), (c) Cu(II) and (d) Zn(II) with TCA6 (solid line: Z_{H} vs. pH for TCA6).

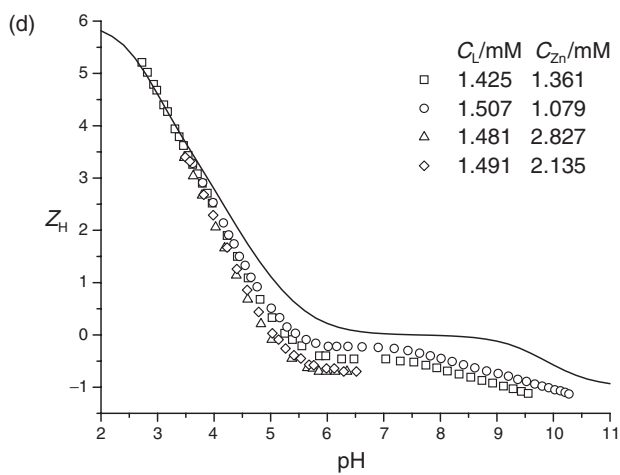
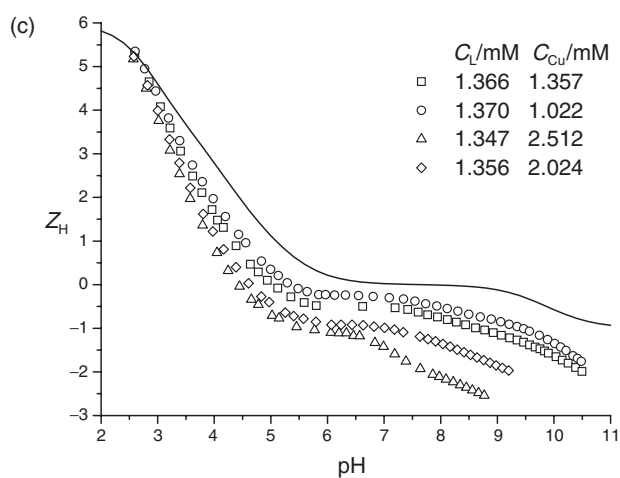
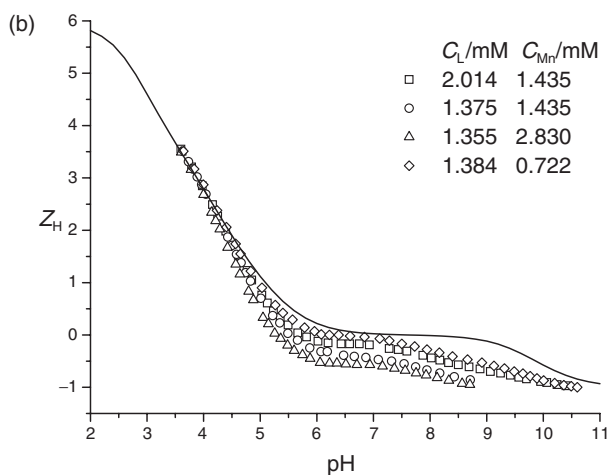


Figure 1. Continued.

Table 1. Protonation and complex formation data for TCA6 with Ca(II), Mn(II), Cu(II) and Zn(II) in aqueous 0.1 M NaCl at 25°C.

pqr	$\log(\beta_{pqr} \pm 3\sigma)$	Formula
H⁺		
-1 0 1	-9.87 ± 0.05	L ⁶⁻
1 0 1	5.40 ± 0.03	H ₂ L ⁴⁻
2 0 1	10.08 ± 0.02	H ₃ L ³⁻
3 0 1	14.25 ± 0.03	H ₄ L ²⁻
4 0 1	17.87 ± 0.03	H ₅ L ⁻
5 0 1	20.81 ± 0.05	H ₆ L
6 0 1	23.56 ± 0.05	H ₇ L ⁺
χ^2/s	148.81/0.46	
Points/Titrations	364/3	
Ca²⁺		
-2 1 1	-15.27 ± 0.17	Ca(OH)L ⁵⁻
-1 1 1	-3.72 ± 0.05	CaL ⁴⁻
0 1 1	2.02 ± 0.49	CaHL ³⁻
1 1 1	7.58 ± 0.30	CaH ₂ L ²⁻
-1 2 1	-0.97 ± 0.13	Ca ₂ L ²⁻
0 2 1	4.81 ± 0.17	Ca ₂ HL ⁻
-1 3 1	1.65 ± 0.19	Ca ₃ L
χ^2/s	10.22/0.58	
Points/Titrations	240/5	
Mn²⁺		
-2 1 1	-13.74 ± 0.28	Mn(OH)L ⁵⁻
-1 1 1	-2.40 ± 0.03	MnL ⁴⁻
0 1 1	2.99 ± 0.07	MnHL ³⁻
-1 2 1	0.51 ± 0.06	Mn ₂ L ²⁻
0 2 1	5.76 ± 0.11	Mn ₂ HL ⁻
χ^2/s	19.37/0.87	
Points/Titrations	263/4	
Cu²⁺		
-2 1 1	-9.44 ± 0.10	Cu(OH)L ⁵⁻
-1 1 1	0.39 ± 0.05	CuL ⁴⁻
0 1 1	5.68 ± 0.06	CuHL ³⁻
1 1 1	10.08 ± 0.10	CuH ₂ L ²⁻
2 1 1	14.22 ± 0.05	CuH ₃ L ⁻
3 1 1	17.36 ± 0.10	CuH ₄ L
-3 2 1	-10.53 ± 0.24	Cu ₂ (OH) ₂ L ⁴⁻
-2 2 1	-2.30 ± 0.31	Cu ₂ (OH)L ³⁻
-1 2 1	5.02 ± 0.07	Cu ₂ L ²⁻
0 2 1	9.40 ± 0.12	Cu ₂ HL ⁻
χ^2/s	48.38/1.60	
Points/Titrations	367/4	
Zn²⁺		
-2 1 1	-11.70 ± 0.25	Zn(OH)L ⁵⁻
-1 1 1	-1.15 ± 0.02	ZnL ⁴⁻
0 1 1	4.19 ± 0.02	ZnHL ³⁻
1 1 1	8.68 ± 0.05	ZnH ₂ L ²⁻
2 1 1	12.81 ± 0.03	ZnH ₃ L ⁻
3 1 1	15.94 ± 0.39	ZnH ₄ L
-2 2 1	-4.97 ± 0.46	Zn ₂ (OH)L ³⁻
-1 2 1	1.79 ± 0.07	Zn ₂ L ²⁻
χ^2/s	28.80/0.56	
Points/Titrations	342/4	

Table 2. Protonation and complex formation constants for TCA6 compared to EDTA, DTPA, NTA, MGDA, EDDS and ISA (25°C, $\mu=0.1$; ^a20°C, ^b $\mu=1.0$).

Reaction	TCA6 H ₆ L	EDTA H ₄ L [10]	DTPA H ₅ L [10]	NTA H ₃ L [10]	MGDA H ₃ L [10]	EDDS H ₄ L [3]	ISA H ₄ L [4]
L + H \rightleftharpoons HL	9.87	9.52–10.37	9.90–10.79	9.46–9.84	(9.85)	10.1	10.52
HL + H \rightleftharpoons H ₂ L	5.40	6.13	8.40–8.60	2.52	(2.58)	6.94	4.55
H ₂ L + H \rightleftharpoons H ₃ L	4.68	2.69	4.28	(1.81)	(1.5) ^a	3.85	3.53
H ₃ L + H \rightleftharpoons H ₄ L	4.17	2.00	2.70	(1.0)		3.08	2.43
H ₄ L + H \rightleftharpoons H ₅ L	3.62	(1.5)	2.0			1.6	1.52
H ₅ L + H \rightleftharpoons H ₆ L	2.94	(0.0)	(1.6)			1.6	
H ₆ L + H \rightleftharpoons H ₇ L	2.75		(0.7)				
H ₇ L + H \rightleftharpoons H ₈ L			(–0.1)				
Ca(II)							
M(OH)L + H \rightleftharpoons ML	11.55						
M + L \rightleftharpoons ML	6.15	10.65	10.75	6.3–6.64	6.97 ^a	4.58 [10]	4.3 [10]
ML + H \rightleftharpoons MHL	5.74	3.1	6.11			6.8 [10]	
MHL + H \rightleftharpoons MH ₂ L	5.56						
ML + M \rightleftharpoons M ₂ L	2.75		1.6				
M ₂ L + H \rightleftharpoons M ₂ HL	5.78						
M ₂ L + M \rightleftharpoons M ₃ L	2.62						
M + 2L \rightleftharpoons ML ₂				8.81–9.27			
Mn(II)							
M(OH)L + H \rightleftharpoons ML	11.34						11.26
M + L \rightleftharpoons ML	7.47	13.89	15.2	7.27–7.46		8.69	7.26
ML + H \rightleftharpoons MHL	5.39	3.1	4.45			5.0	
ML + M \rightleftharpoons M ₂ L	2.91		2.09 ^a				
M ₂ L + H \rightleftharpoons M ₂ HL	5.25						
M + 2L \rightleftharpoons ML ₂				10.44–10.94			
MHL + HL \rightleftharpoons M(HL) ₂						4.0	
Cu(II)							
M(OH)L + H \rightleftharpoons ML	9.83	(11.4)		9.2		11.0	10.40
M + L \rightleftharpoons ML	10.26	18.78	21.2	12.7–13.3	13.88 ^a	18.3	12.88
ML + H \rightleftharpoons MHL	5.29	3.1	4.80	1.6		3.8	4.39
MHL + H \rightleftharpoons MH ₂ L	4.40	2.0	2.96			2.5	3.13
MH ₂ L + H \rightleftharpoons MH ₃ L	4.14						
MH ₃ L + H \rightleftharpoons MH ₄ L	3.14						
M ₂ (OH) ₂ L + H \rightleftharpoons M ₂ (OH)L	8.23						

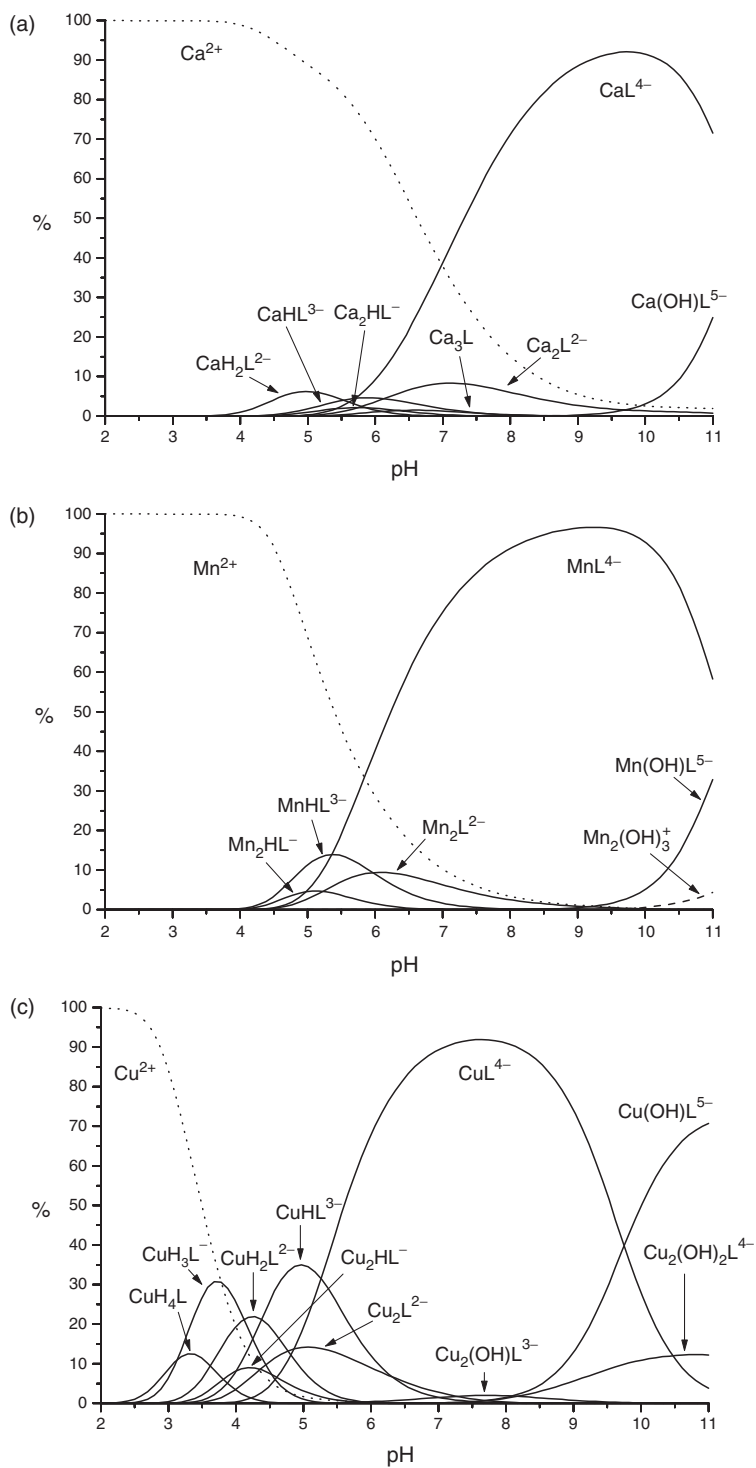


Figure 2. Percentage distribution of the different (a) Ca(II), (b) Mn(II), (c) Cu(II) and (d) Zn(II) complexes of TCA6 as a function of pH ($C_M = C_L = 1$ mM).

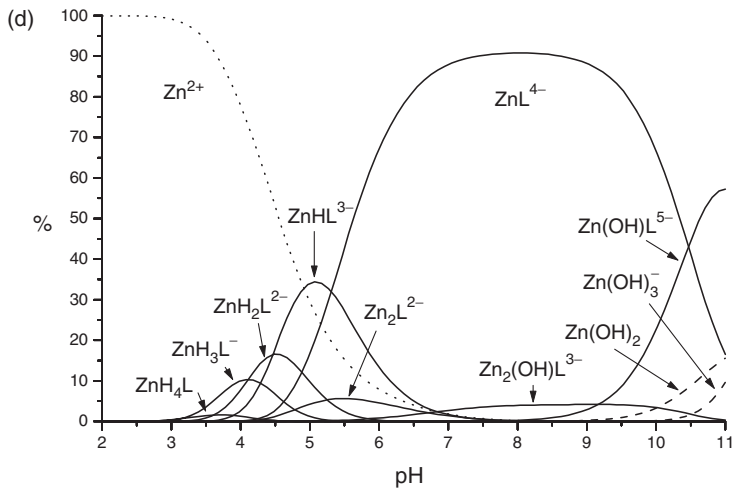


Figure 2. Continued.

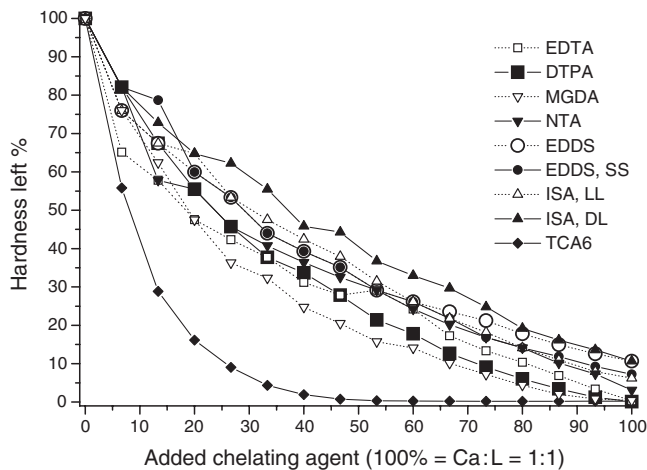


Figure 3. Chelation of Ca(II) at a hardness level of 1000 ppm.

(pH range 2.6–10.9). For comparison with conventionally used ligands EDTA, DTPA, NTA and MGDA [10] and alternative ligands EDDS and ISA [3, 4], the protonation of TCA6 is rewritten in the form given in table 2.

3.2. Complexation with Ca(II), Mn(II), Cu(II) and Zn(II)

Analysis of the data was started by drawing curves of Z_H versus pH (figure 1). In all systems Z_H attains the value -1 with increasing pH, indicating the coordination of TCA6 to metal in the form of L^{6-} . The formation of species ML^{4-} is dominant in all systems. A Z_H value lower than -1 was obtained, indicating the presence of hydroxo complex species for all metal ions. The formation of acidic species MHL^{3-} was found

in all systems and MH_2L^{2-} was found for all metal ions except Mn(II). In addition, the species MH_3L^- and MH_4L were found for Cu(II) and Zn(II). Aqueous complexation of the polydentate ligand can be characterized mainly by the formation of stable, mononuclear, 1:1 metal-to-ligand complexes as the major species. For all metal ions the complexation model was complemented by binuclear species M_2L^{2-} , for all other metal ions except Zn(II) by M_2HL^- , for Zn(II) by $\text{M}_2(\text{OH})\text{L}^{3-}$ and for Cu(II) by $\text{M}_2(\text{OH})\text{L}^{3-}$ and $\text{M}_2(\text{OH})_2\text{L}^{4-}$. For Ca(II), M_3L was also found. The proposed formulas of the species, with corresponding formation constants from equation (6) found in the equilibrium analysis of the different $\text{H}^+-\text{M}^{n+}-\text{HL}^{5-}$ systems, are shown in table 1. Comparison with the findings of earlier studies carried out with EDTA, DTPA, NTA, MGDA, EDDS and ISA [3, 4, 10] was facilitated by rewriting the complexation of TCA6 with Ca(II), Mn(II), Cu(II) and Zn(II) in the form given in table 2. TCA6 formed moderately strong ML^{4-} complexes with all the metal ions studied here. The stability of the complexes follows the Irving–Williams order: $\log K_{\text{MnL}} (7.47) < \log K_{\text{CuL}} (10.26) > \log K_{\text{ZnL}} (8.72)$.

Figure 2 shows the percentage distribution of the metals among the different complex species as a function of pH in the millimolar concentration area ($C_{\text{M}} = C_{\text{L}} = 1 \text{ mM}$). It can be concluded that, in dilute solution, TCA6 is an effective chelating agent (over 80% of metal is bound to complexes) over the pH ranges 8–12 for Ca(II), 7–11 for Mn(II), 5–11 for Cu(II) and 6–11 for Zn(II). In the micromolar concentration area, dilution of the solution increases the lower pH limit of the effective chelation region to more basic values.

Figure 3 shows TCA6 to be more effective as a chelating agent for calcium compared with the widely used ligands EDTA, DTPA, MGDA and NTA and biodegradable alternatives EDDS and ISA. Thus TCA6 seems to be a suitable, easily prepared ligand for calcium binding applications, such as in detergent formulations. Although the biodegradability of TCA6 [11] is not much better than EDTA, for example, its nitrogen content is substantially lower than in EDTA, DTPA, MGDA, NTA, EDDS and ISA. Its ability to chelate calcium is also much better than the more biodegradable ligands EDDS and ISA. The stabilities of the chelates of the new ligand, TCA6, appear to be high enough for practical applications. Use of this low-nitrogen ligand is also recommended from an environmental perspective.

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