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Volume Changes and Equilibrium Constants for Protonation of $[\mathrm{M(edta)}]^{2-}$

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The volume changes and the equilibrium constants for the first protonation of $[\mathrm{Co(edta)}]^{2-}$, $[\mathrm{Ni(edta)}]^{2-}$, and $[\mathrm{Cu(edta)}]^{2-}$ (H_4edta=ethylenediaminetetraacetic acid) have been determined from density and pH measurements at 25 °C. In the case of $[\mathrm{Cu(edta)}]^{2-}$, a second protonation is assumed to successively occur. The volume change and the equilibrium constant for the second protonation have been estimated. The volume changes for the first protonation of Co(II)-, Ni(II)-, and Cu(II)-edta chelates were small and positive (3.5, 3.3, and 4.8 $\mathrm{cm^3\,mol^{-1}}$, respectively) and that for the second protonation of a Cu(II)-edta chelate was larger than the first one (8 $\mathrm{cm^3\,mol^{-1}}$).

Although the structures of a number of metal-edta chelates in the solid state have been established by X-ray studies,[1] their structures in aqueous solutions are still not so clear. Much attention has been given to determining their structures using a variety of experimental techniques.[2–5] Recently, the partial molal volumes and volume changes for the complex formation of $[\mathrm{M(edta)}]^{2-}$ have been determined and useful information about solution structures of the edta-chelates has been obtained.[6]

In this study, the volume changes and the equilibrium constants for the protonation of $[\mathrm{M(edta)}]^{2-}$ (M= Co(II), Ni(II), and Cu(II)) are determined and discussed in relation to their structures in neutral and acidic solutions.

Experimental

The edta-chelates, $\mathrm{Na_2[Co(edta)]\cdot 3.5H_2O}$, $\mathrm{Na_2[Ni(edta)]\cdot 3H_2O}$, and $\mathrm{Na_2[Cu(edta)]\cdot 3H_2O}$, were as previously used.[6] The metal chelates were dried *in vacuo* for one week at 110 °C before use. The concentrations of the metal chelate electrolytes were determined by weight. $\mathrm{HClO_4}$ was obtained from Nakarai Chemicals, Ltd. and was used as received. All the solutions were prepared with distilled and deionized water. The specific conductivity was less than $2\times10^{-7}\ \Omega^{-1}\,\mathrm{cm^{-1}}$. The densities were measured with a digital density meter (Shibayama Scientific Co., Ltd. Model SSD-200). Details of the measurements have been described elsewhere.[7] The pH values of the solutions were determined with a digital pH meter (TOA Electronics Ltd. Model HM-15A), which was calibrated by using standard buffer solutions (Merck). The temperature of the water bath was controlled to 25.00±0.002 °C.

Results and Discussion

The aqueous solutions of edta-chelates (*ca.* 0.02 $\mathrm{mol\,dm^{-3}}$) were mixed with the $\mathrm{HClO_4}$ solutions (*ca.* 0.02 $\mathrm{mol\,dm^{-3}}$). The volume changes on the first protonation, ΔV_1, for eqilibrium, $\mathrm{MY^{2-}+H^+=MHY^-}$, have been determined from the equation:

$$\Delta V_{\mathrm{mix}} = \frac{1000d}{w_1+w_2}\left(\frac{w_1+w_2}{d}-\frac{w_1}{d_1}-\frac{w_2}{d_2}\right) = \alpha[\mathrm{M}]\Delta V_1, \qquad (1)$$

where ΔV_{mix} is the volume change of mixing per 1 $\mathrm{dm^3}$ of the mixed solution, w_1, w_2 and d_1, d_2 are the weights and densities of the edta-chelates and the $\mathrm{HClO_4}$ solutions before mixing, d is the density of the mixed solution, [M] is the total molar concentration of the edta-chelates in the mixed solution, $[\mathrm{M}]=[\mathrm{MY^{2-}}]+[\mathrm{MHY^-}]$, and α is the degree of the protonation, ($\alpha=[\mathrm{MHY^-}]/([\mathrm{MY^{2-}}]+[\mathrm{MHY^-}])$), respectively. No correction for the volume change of the dilution was made, which was assumed to be within the experimental error. The α value can be calculated from the pH value of the mixed solution by a successive iteration as follows. First, the activity coefficients of the ions are assumed to be unity and an approximate α value is obtained from the equation:

$$\alpha = ([\mathrm{A}]-[\mathrm{H^+}])/[\mathrm{M}], \qquad (2)$$

where [A] is the total molar concentration of $\mathrm{H^+}$ and $\mathrm{MHY^-}$ in the mixed solution, $[\mathrm{A}]=[\mathrm{H^+}]+[\mathrm{MHY^-}]$, and can be calculated from the initial concentration of the $\mathrm{HClO_4}$ solution. By using this estimated α value, the ionic strength and the activity coefficients of the ions according to the Davies' equation[8] are obtained. A more accurate α can then be obtained from the pH value, the activity coefficient of $\mathrm{H^+}$ and Eq. 2. The iteration process is repeated until the consistent α value is obtained. The thermodynamic equilibrium constant for the first protonation of $\mathrm{MY^{2-}}$ can be calculated from the obtained consistent α value and activity coefficients:

$$K_1{}^\circ = \frac{\alpha[\mathrm{M}]y_1}{[\mathrm{H^+}]y_1(1-\alpha)[\mathrm{M}]y_2}, \qquad (3)$$

where y_1 and y_2 are the molar activity coefficients of the monovalent and divalent ions, respectively. In Table 1, the total concentrations, [M] and [A], pH, $\log K_1{}^\circ$ and ΔV_1 are listed. In these mixed solutions, the metal chelate ions are considered to be stably present from their stability constants[9] and the pH values of the mixed solutions. The constant $\log K_1{}^\circ$ and ΔV_1 values are obtained for $[\mathrm{Co(edta)}]^{2-}$ ($\log K_1{}^\circ=3.55\pm0.01\ \mathrm{mol^{-1}\,dm^3}$, $\Delta V_1=3.5\pm0.2\ \mathrm{cm^3\,mol^{-1}}$) and for $[\mathrm{Ni(edta)}]^{2-}$ ($\log K_1{}^\circ=3.53\pm0.01\ \mathrm{mol^{-1}\,dm^3}$, $\Delta V_1=3.3\pm0.3\ \mathrm{cm^3\,mol^{-1}}$). However, the $\log K_1{}^\circ$ values for $[\mathrm{Cu(edta)}]^{2-}$ increase with decreasing the pH values of the mixed solutions.

Table 1. The values of the equilibrium constants and the volume changes for the first protonation of $[M(edta)]^{2-}$

[M] mol dm^{-3}	[A] mol dm^{-3}	pH	log K_1°	ΔV_1 cm^3 mol^{-1}
		$[Co(edta)]^{2-}$		
0.01426	0.005849	3.513	3.55	3.6
0.01330	0.006837	3.363	3.55	3.5
0.01246	0.008795	3.224	3.55	3.5
0.01226	0.007901	3.193	3.56	3.7
0.01196	0.008208	3.138	3.56	3.1
0.01139	0.008795	3.033	3.56	3.7
		$[Ni(edta)]^{2-}$		
0.01397	0.006833	3.382	3.54	3.4
0.01396	0.006837	3.379	3.53	3.2
0.01309	0.007690	3.243	3.53	3.0
0.01258	0.008190	3.158	3.53	3.5
0.01226	0.008507	3.105	3.53	2.9
0.01196	0.008793	3.049	3.53	3.4
0.01164	0.009109	2.993	3.53	3.2
0.01117	0.009573	2.902	3.53	3.8
		$[Cu(edta)]^{2-}$		
0.01532	0.005133	3.618	3.53	
0.01460	0.005854	3.520	3.54	
0.01362	0.006832	3.385	3.56	
0.01226	0.008199	3.202	3.61	
0.01167	0.008791	3.120	3.65	
0.01136	0.009097	3.078	3.68	
0.01114	0.009318	3.074	3.71	
0.01022	0.010245	2.908	3.90	
0.009359	0.01117	2.766		
0.009147	0.01138	2.735		
0.009080	0.01139	2.735		
0.008230	0.01229	2.592		
0.007917	0.01261	2.544		

This indicates that the second protonation occurs successively. Therefore, the first and second protonations for $[Cu(edta)]^{2-}$ in these mixed solutions are considered:

$$MY^{2-} + H^+ = MHY^-,\qquad K_1^\circ = [MHY^-]/[MY^{2-}][H^+]y_2, \tag{4}$$

$$MHY^- + H^+ = MH_2Y,\qquad K_2^\circ = [MH_2Y]/[MHY^-][H^+]y_1^2. \tag{5}$$

The total molar concentrations are defined by:

$$[M] = [MY^{2-}] + [MHY^-] + [MH_2Y], \tag{6}$$

$$[A] = [H^+] + [MHY^-] + 2[MH_2Y]. \tag{7}$$

Combining Eqs. 4—7 gives:

$$\frac{[A]-[H^+]}{\{2[M]-([A]-[H^+])\}[H^+]^2y_1^2y_2} = \frac{[M]-([A]-[H^+])}{\{2[M]-([A]-[H^+])\}[H^+]y_1^2}K_1^\circ + K_1^\circ K_2^\circ. \tag{8}$$

A plot of the values of the left-hand side of Eq. 8 against the corresponding values for the coefficients of K_1° enables both K_1° and K_2° to be obtained. The required values of $[H^+]$, y_1 and y_2 are obtained by similar successive iterations as before. The best fitted plot of Eq. 8 is obtained by four iterations and is shown in Fig. 1. Thus, K_1° and K_2° values for the first and second protonations are evaluated from Fig. 1 by a least squares-method (log K_1°=3.49±0.01 mol^{-1} dm^3 and log K_2°=2.26±0.01 mol^{-1} dm^3, respectively). The volume changes for the first and the second protonation for $[Cu(edta)]^{2-}$, ΔV_1 and ΔV_2, are calculated using the equation:

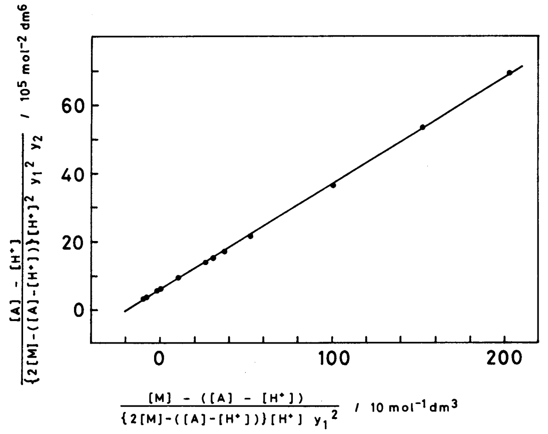

Fig. 1. The best fitted plot of Eq. 8.

$$\Delta V_{mix} = [M]\{\alpha_1\Delta V_1 + \alpha_2(\Delta V_1 + \Delta V_2)\}, \tag{9}$$

where α_1 and α_2 are the fractions of $CuHY^-$ and CuH_2Y, respectively, and can be estimated from the obtained values for K_1° and K_2°. The values of ΔV_1 and ΔV_2 are 4.8±0.2 cm^3 mol^{-1} and 8±1 cm^3 mol^{-1}, respectively.

The estimated values for log K ($K=[MHY^-]/[MY^{2-}][H^+]$) of $[Co(edta)]^{2-}$, $[Ni(edta)]^{2-}$, $[Cu(edta)]^{2-}$ at the 0.1 mol dm^{-3} ionic strength (3.10, 3.08, and 3.04 mol^{-1} dm^3, respectively) are in good agreement with the literature values (3.0, 3.2, and 3.0 mol^{-1} dm^3, respectively).[9]

It is well known that the first and second protonations to a free $edta^{4-}$ ion take place at the nitrogen atoms.[10,11] However, spectrophotometric studies indicate that the first protonation to stable edta-chelate ions takes place at the oxygen atom in the carboxylate group of the ligand.[12,13] Then, the monoprotonated edta-chelate, in which edta acts as a pentadentate ligand, one carboxyl group is free and the water molecule occupies the sixth coordination site, is expressed as $[M(edtaH)(H_2O)]^-$. The volume changes for the first protonation, ΔV_1, of the edta-chelates of Co(II), Ni(II), and Cu(II) (3.5, 3.3, and 4.8 cm^3 mol^{-1}, respectively) are considerably smaller than that for the protonation of the simple acetate ion, which is reported to be 11.3 cm^3 mol^{-1}.[14] The same has been found for the entropy changes for the protonation of these edta-chelates:[15] They are considerably smaller than that for the protonation of H_2edta^{2-}, which relates to the protonation of the carboxylate group in the free ligand.[15] This may be explained by the fact that the first protonation reaction of the edta-chelate involves the substitution reaction of the coordinated carboxylate group by a water molecule prior to actual protonation. The protonation of the free carboxylate group of the edta chelate is accompanied by a positive volume change. However, the substitution reaction may be considered to be accompained by a negative volume change due to the electrostriction of the coordinated water molecule and due to the localized charge of the free carboxylate group.

It has been proposed that, in neutral solutions of these edta chelates, there are dynamic equilibria between the dominant sexidentate form and the quinquedentate form, the latter having a water molecule and a free carboxylate group.[3–5] The amount of the dominant sexidentate form has been estimated by a NMR study as 81, 67, and 62% for Co(II)-, Ni(II)-, and Cu(II)-edta chelate, respectively.[5] The volume change from the sexidentate form to the quinquedentate form for the Co(II)-edta chelate has been estimated to be −4.9 $cm^3 mol^{-1}$ from an ultrasonic study.[4] If this value is assumed to be independent of the central metal cation, the volume changes due to the protonation of the free carboxylate group of the edta chelate are calculated to be 7.5, 6.6, and 7.8 $cm^3 mol^{-1}$ for Co(II)-, Ni(II)-, and Cu(II)-edta chelates, respectively. These values are smaller than that of the volume change for the protonation of the acetate anion (11.3 $cm^3 mol^{-1}$). However, they are comparable in magnitude with that of the formate anion (8.5 $cm^3 mol^{-1}$).[4] Taking into account the difference that one is a simple carboxylate anion and the other is a complex ion, the ΔV_1 values seem to be reasonable.

For simple dibasic carboxylate anions, such as the malonate and the oxalate ions, the volume changes for the first and second protonation, ΔV_1 and ΔV_2, are in the order, $\Delta V_1 > \Delta V_2$,[16] which is expected from simple electrostatic theory such as the Drude-Nernst formulation.[17] The differences between ΔV_1 and ΔV_2 diminish when the two charged centers are sufficiently separeted.[16] However, the ΔV_1 and ΔV_2 obtained for the Cu(II)-edta chelate are in a reverse order. If the second protonation of the Cu(II)-edta chelate takes place at the free carboxylate group in the same manner as the first one, the ΔV_2 should be smaller than that of the ΔV_1, or at least the same magnitude. In the solid state, the diprotonated Cu(II)-edta has a tetragonally distorted structure with a free carboxyl arm and a water molecule occupying the sixth coordination site and two elongated bonds of metal–nitrogen and metal–oxygen of the carboxylate.[18] The second protonation has been assummed to take place at the uncoordinated oxygen atom in the longer bonded carboxylate group.[18] If the diprotonated Cu(II)-edta in the solution has a similar structure to that in the the solid state, the smaller ΔV_1 compared to ΔV_2 for the Cu(II)-edta may be understandable.

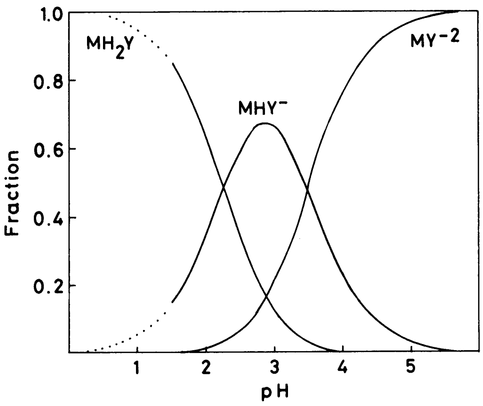

Fig. 2. Distribution of the Cu(II)–edta chelate species as a function of pH.

Although the equilibrium constants for the first protonation of the stable edta-chelate ions have been determined by spectrophotometric studies[3,19] or the byproduct of the determination of the stability constants of the edta-chelates, a study of the second protonation is thought to be difficult because of the low solubility of the diprotonated edta-chelate. In this study, the concentrations of the Cu(II)-edta chelate in the mixed solutions were sufficiently low (0.015—0.008 mol dm^{-3}) and precise pH measurements have enabled us to determine the equilibrium constants for the second protonation of Cu(II)-edta chelate. In Fig. 2, the fractions of three species of the Cu(II)-edta chelate at the acidic medium are shown. The monoprotonated Cu(II)-edta chelate starts to form at around pH 5, and the maximum in the fraction is attained at around pH 3 with a fraction of 0.6. The diprotonated Cu(II)-edta chelate begins to form at around pH 4 and the monoprotonated and diprotonated species are present in an equimolar condition around at pH 2.3.

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References

1) R. H. Nuttall and D. M. Stalker, *Talanta,* **24**, 355 (1977).

2) A. A. McConnell, R. H. Nuttall, and D. M. Stalker, *Talanta,* **25**, 425 (1978).

3) W. C. E. Higginson and B. Samuel, *J. Chem. Soc. (A),* **1970**, 1579.

4) S. Harada, Y. Funaki, and T. Yasunaga, *J. Am. Chem. Soc.,* **102**, 136 (1980); Y. Funaki, S. Harada, K. Okumiya, and T. Yasunaga, *ibid,* **104**, 5325 (1982).

5) J. Oakes and E. G. Smith, *J. Chem. Soc., Faraday Trans. 2,* **77**, 299 (1981); J. Oakes and E. G. Smith, *J. Chem. Soc., Faraday Trans. 1,* **79**, 543 (1983).

6) K. Yoshitani, *Bull. Chem. Soc. Jpn.,* **58**, 1646 (1985).

7) K. Yoshitani, M. Yamamoto, and Y. Yamamoto, *Bull. Chem. Soc. Jpn.,* **56**, 1978 (1983).

8) C. W. Davies, *J. Chem. Soc.,* **1938**, 2093.

9) A. E. Martell and R. M. Smith, "Critical Stability Constants," Plenum Press, New York (1974), Vol. 1, pp. 206—207.

10) K. Nakamoto, Y. Morimoto, and A. E. Martell, *J. Am. Chem. Soc.*, **85**, 309 (1963).

11) D. Chapman, D. R. Lloyd, and R. H. Prince, *J. Chem. Soc.*, **1963**, 3645.

12) D. T. Sawyer and J. T. Tackett, *J. Am. Chem. Soc.*, **85**, 2390 (1963).

13) K. Krishnan and R. H. Plane, *J. Am. Chem. Soc.*, **90**, 3195 (1968).

14) H. Hoiland, *J. Chem. Soc., Faraday Trans. 1*, **70**, 1180 (1974).

15) A. P. Brunetti, G. H. Nancollas, and P. N. Smith, *J. Am. Chem. Soc.*, **91**, 4680 (1969).

16) H. Hoiland, *J. Chem. Soc., Faraday Trans. 1*, **71**, 797 (1975).

17) P. Drude and W. Nernst, *Z. Physik. Chem.* (*Frankfurt*), **15**, 79 (1894).

18) F. S. Stephens, *J. Chem. Soc.* (*A*), **1969**, 1723.

19) T. R. Bhat and M. Krishnamurthy, *J. Inorg. Nucl. Chem.*, **25**, 1147 (1963).