Thermodynamic Studies on the Complexation of Alkaline-Earth Metal Ions with *o*-Phenylenediamine-*N,N,N′,N′*-tetraacetate in Aqueous Solutions

Noriyuki NAKASUKA,*,† Mihoko SAWARAGI (née KUNIMATSU),
Kazunori MATSUMURA, and Motoharu TANAKA
School of Science, Nagoya University, Chikusa, Nagoya 464-01

(Received September 9, 1991)

Synopsis. Potentiometric and calorimetric studies were carried out for the complexation of *o*-phenylenediamine-*N,N,N′,N′*-tetraacetate (PhDTA, L^{4-}) with alkaline-earth metal ions (M^{2+}) in aqueous solutions at 25.0 °C and 1.0 M ($NaClO_4$). The formation constants ($\log K_{ML}$) obtained are 6.48 (Be), 6.481 (Mg), 8.27 (Ca), 5.47 (Sr), and 3.99 (Ba), respectively. The changes in enthalpy (ΔH°_{ML}/kJ mol^{-1}) are 45.5 (Be), 34.3 (Mg), −14.0 (Ca), 2.7 (Sr), and 2.5 (Ba), respectively.

Since the successful determination of calcium ions with EDTA (ethylenediamine-*N,N,N′,N′*-tetraacetic acid),[1] great efforts have been devoted to the development of the chelatometric titration and of the solution chemistry of amino polycarboxylates.[2] The complexation of this type of ligand with metal ions is driven by a large change in entropy rather than enthalpy, and we have revealed that this is especially the case with *o*-phenylenediamine-*N,N,N′,N′*-tetraacetate (PhDTA),[3] in which carbon atoms of the N-C-C-N moiety are part of the phenylene group. In general, the stability constant of complexation of PhDTA is smaller than that of EDTA for a given metal ion, primarily due to more endothermic reaction of the former ligand. Beryllium ions, however, can be titrated successfully with PhDTA,[4] while they ave very little tendency to complex EDTA.[2] These results prompted us to measure thermodynamic quantities for the complexation of PhDTA with alkaline-earth metal ions including the beryllium ion.

Experimental

Reagents. PhDTA (H_4L) and sodium perchlorate were prepared as described previously.[5] Alkaline-earth metal perchlorates were prepared by dissolving the respective reagent grade metal (Be),[4] metal oxide (Mg), or metal carbonates (Ca, Sr, Ba) in aqueous solutions of reagent-grade perchloric acid, followed by recrystallization from water. The concentrations of the hydrogen ion and the metal ions were determined by the Gran method[6] and by complexometry,[2] respectively.

Titration Procedures. Potentiometric titrations were carried out as described previously[5] at 25.0±0.2 °C and at an ionic strength of 1.0 M[7] ($NaClO_4$). A couple of Corning glass-Corning calomel electrodes was used for pH measurements with a Corning 130 pH-meter to a precision of 0.1 mV. In the pH titrations, the initial concentration of PhDTA, C_L was ca. 1×10^{-2} M, while that of a metal ion, C_M, was changed at a ratio of $C_M/C_L=1—5$. Potentiometric data were processed by use of a Fortran program ACREF[8] on a FACOM 382 computer at the Computation Center, Nagoya University. Calorimetric measurements were carried out as described previously with a Resca CM-502 (for metal ions other than Be^{2+}),[3] and with a Tokyo-Riko Model MP-111 (for Be^{2+})[9] twin-type conduction calorimeters. In the calorimetric titrations, a concentrated solution of a metal ion (C_M=0.2—0.3 M) was added to a ligand solution ($C_L=(1—2)\times10^{-2}$ M).

Results and Discussion

Reaction Equilibria of PhDTA Complexes. An alkaline-earth metal (II) ion, M^{2+}, reacts with PhDTA to give rise to a complex, ML^{2-} according to the following reaction

$$M^{2+}+L^{4-}\rightleftarrows ML^{2-}, \qquad (1)$$

to which corresponds a formation constant, K_{ML}. Protonation may occur on a metal complex and its equilibrium constant, K_{MHL}, is relevant to the following reaction:

$$ML^{2-}+H^+\rightleftarrows MHL^-. \qquad (2)$$

The formation constants thus obtained are summarized in Table 1, together with some values in the literature for comparison. Although the formation constants reported by Grimes et al. (30 °C, 0.1 M in KCl)[10] are least accurate among them, allowance should be made for unavailability of a computer and lower accuracy of the potentiometric data to 0.02 pH units that they had to experience at that time. Setting it aside, their constants are comparable with those obtained by Mederos et al. (25 °C 0.1 M in KCl).[11] Our constants are considerably less than those of Mederos' group, except for Be^{2+}. The difference, however, may primarily be explained by the difference in medium salts, namely by the weak interaction of the ligand with the sodium ion added as a supporting electrolyte. Its formation constant has been determined as $\log K_{NaL}=0.73$ at 0.1 M in $(C_2H_5)_4NClO_4$ and 25 °C.[9] The formation constant so far discussed should be taken as a conditional constant in the sense that a certain quantity of the ligand anion, L^{4-}, is not free but bound to the Na^+ ion:

$$\begin{aligned}K_{ML}&=[ML][M]^{-1}[L']^{-1}=[ML][M]^{-1}([L]+[NaL])^{-1}\\&=K^\circ_{ML}(1+K_{NaL}[Na])^{-1},\end{aligned} \qquad (3)$$

where $[L']$ represents the total concentration of the free ligand not bound to metal ions M in question. K°_{ML} is the true constant corrected for the effect of the sodium ion on complexation. Difference in K_{ML} may be estimated from Eq. 3, where the aforementioned value of K_{NaL} may be used as a rough approximation, and the potassium ion is assumed not to complex. Calculation leads to a difference of ΔK_{ML}=0.81, which accounts for the differences at least for Sr^{2+} and Ba^{2+}. The difference in medium salt, however, may affect little on the

---

† Present address: Faculty of General Education, Gifu University, Yanagido, Gifu 501-11.

Table 1. The Formation Constant (log K_{ML}) and the Corresponding Thermodynamic Quantities, and the Protonation Constant (log K_{MHL}) for the Complexes of PhDTA, EDTA, and CyDTA with the Alkaline-Earth Metal Ions

Ion	PhDTA[a]				PhDTA[c,d]				
	log K_{ML}	ΔH°_{ML}	ΔS°_{ML}	log K_{MHL}	log K_{ML}[c]	log K_{MHL}[c]	log K_{MH_2L}	log K_{ML}[d]	log K_{MHL}[d]
Be	6.48(2)[b]	45.5(7)	277(3)	3.48(3)[b]				6.51	3.82
Mg	6.481(5)	34.3(49)	239(17)	2.7(2)	7.1	—	2.6	6.84	2.80
Ca	8.27(2)	−14.0(8)	112(2)	3.0(2)	9.	—	—	8.60	2.95
Sr	5.47(3)	2.7(4)	115(4)	3.2(2)	6.2	3.0	1.3	6.22	3.30
Ba	3.99(4)	2.5(4)	86(3)	4.4(1)	4.8	2.3	1.6	4.85	4.05

Ion	EDTA[e]				CyDTA[e]		
	log K_{ML}	ΔH°_{ML}	ΔS°_{ML}	log K_{MHL}[f]	log K_{ML}	ΔH°_{ML}	ΔS°_{ML}
Mg	8.69	14.6	213	3.85	10.97	15.9	264
Ca	10.70	−27.4	111	3.07	13.15	−15.5	199
Sr	8.63	−17.1	107	3.93	10.54	−3.1	191
Ba	7.76	−20.6	78	4.57	8.64	1.4	171

a) This work (25 °C and 1.0 M ($NaClO_4$)). Experimental errors at the least significant digits shown in parentheses (2σ). Units: ΔH°_{ML} in kJ mol^{-1} and ΔS°_{ML} in J K^{-1} mol^{-1}. b) Ref. 4. c) Ref. 10 (30 °C and 0.1 M (KCl)). d) Ref. 11 (25 °C and 0.1 M (KCl)). e) Ref. 19 (20 °C and 0.1 M (KNO_3), except for log K_{MHL}). f) Ref. 12 and Ref. 13.

protonation constant of a complex, since the sodium ion will be bound to a metal complex and to its protonated complex only to a negligible extent. Accordingly, the protonation constants should be similar each other for a given metal ion, regardless of electrolyte, as can be seen from Table 1.

The formation constant of PhDTA complexes is largest for Ca(II), as is usually the case with amino polycarboxylates. The formation constants of the three ligands change in a parallel fashion, but PhDTA gives the least stability constant for a given metal ion. Nevertheless, Be^{2+} can be titrated with PhDTA,[4] while titration of Be^{2+} with EDTA has not been feasible.[2] This failure may be explained in terms of ready protonation of EDTA, which leads to lowering of the side-reaction coefficient.[4]

On the other hand, the protonation constants show a monotonic increase with the ionic radius, except for Be(II). These values may be compared with the log K_{MHL} value of the PhDTA complex with a divalent transition metal ion (e.g. 2.29 for Mn and 2.95 for Zn), and those (usually ca. 3) of the corresponding complexes of EDTA and CyDTA (cyclohexanediamine- *N*,*N*,*N'*,*N'*-tetraacetate).[12,13] Fe(III)-PhDTA[14] and La(III)-PhDTA,[15] however, have very low values of 1.05 and 1.81, respectively. In these cases, protonation occurs probably at an oxygen atom of the carboxylate group complexed directly by the iron(III) or lanthanum(III) ion, and may be schematized as M–O–CR–OH (R denotes the residual part of the ligand), judging from the crystal structure of the protonated La(III)-EDTA complex, $[La(HA)(H_2O)_4]\cdot 3H_2O$ (A^{4-} denotes the EDTA anion).[16] The protonation constant of the Ba–PhDTA complex, however, is considerably larger than the ligand protonation constants (log K_3=3.53 and log K_4=3.00),[5] and then it can no longer be explained on the basis of protonation at a carboxylate oxygen. Since Ba^{2+} is large in size, the PhDTA anion may not wrap up the whole central ion with donor atoms. Insufficient wrapping and the rigidness of PhDTA[5,17] will lead to partial dissociation of a nitrogen atom, as is substantiated by the very low stability (log K_{BaL}=3.99). The partial dissociation will allow protonation at the nitrogen atom, leading to a higher value of K_{MHL}. Similar phenomena have been observed for the protonation of the alkaline-earth metal complexes of nitrilotris(methylenephosphonate), and the dissociation of the nitrogen atom has been supported by good evidence from ^{31}P NMR spectroscopy and protonation constnts.[18]

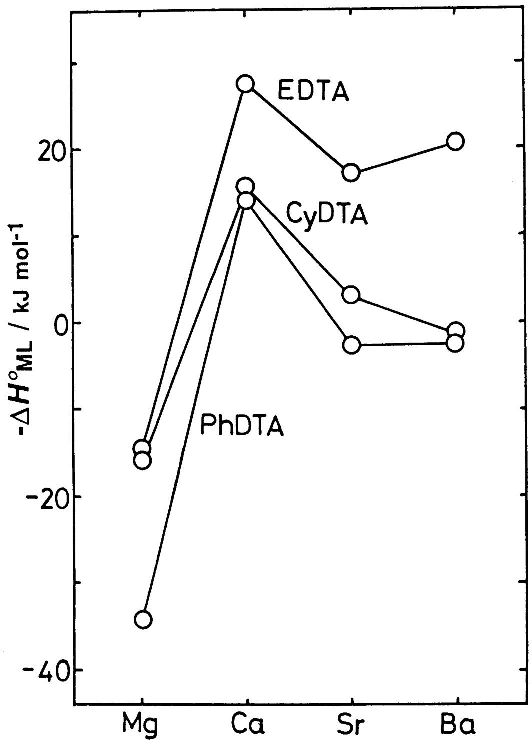

Fig. 1. Comparison of the ΔH°_{ML} values for the complex formation of alkaline-earth metal ions with PhDTA, EDTA and CyDTA.[19]

The Be–PhDTA complex has also a higher protonation constant, despite the smallest size. This may be accounted for by the tendency of Be^{2+} to take a tetrahedral geometry, which will also lead to partial dissociation of a ligand. This explanation is supported by the fact the Mg(II)–PhDTA complex has a relatively low value of protonation, in spite of the fact that Mg^{2+} is only slightly larger than Be^{2+} in size. The Mg(II)–PhDTA complex has a sevencoordinate structure in the solid state, with a water molecule being coordinated.[17]

Thermodynamic Quantities of Complexation. The changes in enthalpy (ΔH°_{ML}) and in entropy (ΔS°_{ML}) of complexation of PhDTA are compared with those of EDTA and CyDTA[19] in Table 1. The van't Hoff method was applied to the Mg(II) system alone, because of less reproducibility in calorimetry. Potentiometry gave formation constants at three temperatures of 15, 25, and 35 °C. Good linearity was observed between $\log K_{ML}$ and T^{-1}, resulting in the following parameters with 2σ:

$$\Delta H^\circ_{MgL} = 27.4 \pm 1.0 \text{ kJ mol}^{-1};$$
$$\Delta S^\circ_{MgL} = 216 \pm 3 \text{ J K}^{-1} \text{mol}^{-1}.$$

The ΔH°_{ML} value of PhDTA complexes changes in parallel with that of EDTA complexes (Fig. 1), as is also the case for transition metal complexes. The Ca–PhDTA complex shows almost the same value of ΔH°_{ML} as Ca–CyDTA, but this may be regarded as a mere coincidence judging from the parallelism mentioned above. The PhDTA complex has the most positive (endothermic) value for any metal ion in general, but the ΔS° value of a PhDTA complex is nearly equal to that of the corresponding EDTA complex, as already been noted fo the transition metal complexes.[3] The beryllium ion shows the most endothermicity in the reaction with the PhDTA anion among the metal ions studied here. Complexation of PhDTA with the alkaline-earth metal ions is endothermic except for Ca–PhDTA, but the reaction is driven by the change in entropy.[3]

References

1) G. Schwarzenbach, *Helv. Chim. Acta,* **29**, 1338 (1946).

2) R. Přibil, "Analytical Applications of EDTA and Related Compounds," Pergamon, Braunschweig (1972).

3) K. Matsumura, N. Nakasuka, and M. Tanaka, *Inorg. Chem.,* **26**, 1419 (1987).

4) N. Nakasuka, K. Takahashi, and M. Tanaka, *Anal. Chim. Acta,* **207**, 361 (1988).

5) N. Nakasuka, M. Kunimatsu, K. Matsumura, and M. Tanaka, *Inorg. Chem.,* **24**, 10 (1985).

6) G. Gran, *Analyst,* **77**, 661 (1952).

7) Non-SI unit: 1 M=1 mol dm^{-3}.

8) M. Cromer-Morin, J. P. Scharff, and R. -P. Martin, *Analusis,* **10**, 92 (1982).

9) N. Nakasuka, Y. Natsume, and M. Tanaka, *Inorg. Chem.,* **29**, 147 (1990).

10) J. H. Grimes, A. J. Huggard, and S. P. Wilford, *J. Inorg. Nucl. Chem.,* **25**, 1225 (1963).

11) A. Mederos, J. V. Herrera, and. M. Felipe, *Anales. Quimica.,* **83**, 22 (1987).

12) G. Schwarzenbach and H. Ackermann, *Helv. Chim. Acta,* **31**, 1029 (1948).

13) G. Schwarzenbach, R. Gut, and G Anderegg, *Helv. Chim. Acta,* **37**, 937 (1954).

14) M. Mizuno, S. Funahashi, N. Nakasuka, and M. Tanaka, *Inorg. Chem.,* **30**, 1550 (1991).

15) M. Yamamoto, N. Nakasuka, and M. Tanaka, *Bull. Chem. Soc. Jpn.,* **65**, 1566 (1992)..

16) M. D. Lind, B. Lee, and J. L. Hoard, *J. Am. Chem. Soc.,* **87**, 1611 (1965).

17) N. Nakasuka and M. Shiro, *Acta Crystallogr., Sect. C,* **45**, 1487 (1989).

18) K. Sawada, T. Araki, and T. Suzuki, *Inorg. Chem.,* **26**, 1199 (1987).

19) G. Anderegg, *Helv. Chim. Acta,* **46**, 1833 (1963).