

Complexation Equilibria of Cadmium Ions with Xylenol Orange as Studied by Cadmium Ion Selective Electrode

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The complexation equilibria of cadmium ion(M) with Xylenol Orange(H₆L) were studied by potentiometry with a cadmium ion selective electrode. The stability constants for MH₃L, MH₂L, MHL, ML, M₂HL and M₂L were obtained. These constants were consistent with the results of potentiometry with only a glass electrode and with those of spectrophotometry. The structure of each species is discussed.

Keywords Xylenol Orange, cadmium ion selective electrode, stability constant, metal buffer

Xylenol Orange(3,3'-bis[*N,N*-bis(carboxymethyl)aminomethyl]-*o*-cresolsulphonphthalein, XO, H₆L) forms colored complexes with various metal ions, and has been widely used as a metallochromic indicator or a spectrophotometric reagent.¹ In general, knowledge about the reaction equilibria of a reagent with hydrogen and metal ions is essential for its effective use. Although there have been many papers dealing with this aspect on Xylenol Orange, the results are still unreliable. In earlier studies XO used was not pure enough as has already been pointed out and fully discussed.^{2,3} Moreover, analysis of the equilibria only by spectrophotometry is not suitable for such a complicated system. Taking these two points into account, potentiometry with a glass electrode has recently been examined by use of "pure" XO.⁴⁻⁸ Important results were obtained in systems containing some metal ions such as alkaline earth metals.⁴ For the other metals, however, there are large discrepancies between the formation constants reported by different authors. For example, log K_{ML} is 13.41 and 15.41 for zinc, and 13.68 and 15.24 for lead.^{6,8} In the cases of these complexes, this method is not suitable because their stabilities are high and thus they are stable even in acidic medium.

We have shown that ion selective electrodes are useful for the determination of the stability constants of metal complexes.⁹⁻¹³ In this paper, we study the equilibria between cadmium ions and Xylenol Orange in detail with Cd ion selective electrode.

Experimental

Reagents

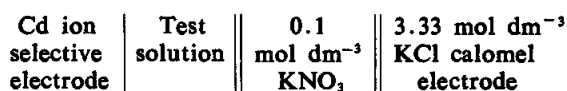
A 10⁻² mol dm⁻³ cadmium solution was prepared

from the nitrate tetrahydrate recrystallized twice, and was standardized against a Na₂H₂edta solution with Eriochrome Black T as an indicator. Potassium nitrate was recrystallized twice. Carbonate-free potassium hydroxide solution was prepared as described previously.¹⁴

Xylenol Orange was prepared and purified as described previously.^{2,3} No colored impurity was found by paper chromatography and liquid chromatography with a silica-ODS column. The purity was determined to be more than 99% as H₆L·2H₂O by potentiometry with a glass electrode.

Measurements

All solutions for measurements were placed in an air bath thermostated at 25±0.1°C. The ionic strength was maintained at 0.10 mol dm⁻³ with potassium nitrate. The cell arrangement for measuring the cadmium ion concentration was:



The cadmium ion selective electrode(Denki Kagaku Keiki Co., DKK type 7120) was conditioned as described elsewhere.⁹⁻¹³ The e.m.f. was read with a DKK ion-meter IOC-10 accurate to 0.1 mV. Hydrogen ion concentration was determined with a Radiometer PHM-64 pH meter equipped with a Radiometer glass electrode(G 202C) and a calomel electrode(K 401). A 1.00×10⁻² mol dm⁻³ nitric acid solution and a 1.00×10⁻³ mol dm⁻³ cadmium ion solution of ionic strength 0.1 mol dm⁻³ (KNO₃) were used as the standards for hydrogen and cadmium ion concentrations, and the change in liquid-junction potential was taken as a

linear function of hydrogen ion concentration, $-410[\text{H}^+]$.¹⁵ The test solution was stirred at a constant speed. Nitrogen was bubbled through the test solution during the measurement. Cadmium ion concentration was monitored as a function of hydrogen ion concentration by titrating the test solution with a potassium hydroxide solution.

Visible spectra were recorded on a Union High-Sens spectrophotometer SM-401 with a thermostated cell compartment.

Results

Protonation constants

The solutions containing 2–3 mmol dm⁻³ of H₆L were titrated with a potassium hydroxide solution. The formation function, \bar{n} , was calculated by

$$\bar{n}_{\text{obsd}} = \frac{6C_L - C_{\text{OH}} - [\text{H}^+] + [\text{OH}^-]}{C_L}$$

where C_L and C_{OH} are the analytical concentrations of Xylenol Orange and hydroxide ion. One of several series of data are shown as a function of $-\log[\text{H}^+]$ by the open circles in Fig. 1. Irrespective of the total concentration of H₆L, all the experimental points of every series lay on a single curve, which has an inflection point at $-\log[\text{H}^+]$ around 4.5.

Below $-\log[\text{H}^+]$ 4.5, only H₃L, H₄L, H₅L and H₆L (charges are omitted) are in the solution, and \bar{n} is given by

$$\bar{n}_{\text{calcd}} = \frac{3[\text{H}_3\text{L}] + 4[\text{H}_4\text{L}] + 5[\text{H}_5\text{L}] + 6[\text{H}_6\text{L}]}{C_L}$$

The stepwise protonation constants K_4 , K_5 and K_6 were refined to give the minimum error square sum, $U = \sum(\bar{n}_{\text{obsd}} - \bar{n}_{\text{calcd}})^2$.

The value of K_3 was obtained by a similar calculation, using the data between $-\log[\text{H}^+]$ 4.5 and 8.0, and also by spectrophotometric measurement. All the constants are summarized in Table 1 together with literature values.

Potential response of Cd ion selective electrode

The solutions containing cadmium ions and H₆L, as shown in Table 2, were titrated with a potassium hydroxide solution. Potential response of the ion

selective electrode was rapid, and the potential became constant within 3 min for $-\log[\text{H}^+] < 8$. In Fig. 2, $-\log[\text{Cd}^{2+}]$ was plotted against $-\log[\text{H}^+]$.

Detection limit in the metal buffer was also determined with a solution containing only H₆L (open circles in Fig. 2). When ion selective electrodes are used for the determination of stability constants of metal complexes, this limit is important as described previously.^{9–13} Since the potentials in the metal buffers came close to this limit at $-\log[\text{H}^+]$ around 8, the ion selective electrode potentials would not correctly reflect

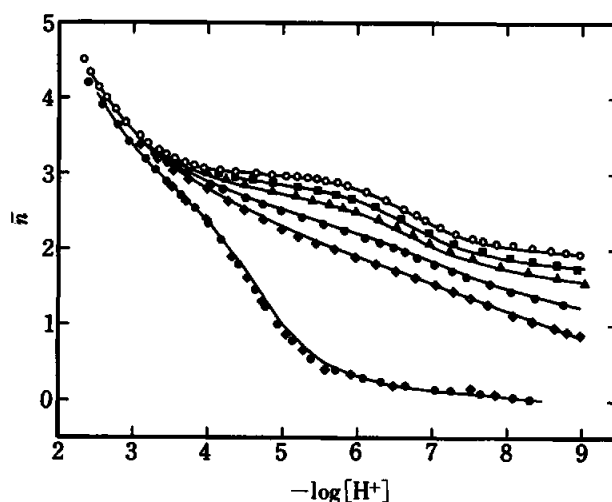


Fig. 1 \bar{n} vs. $-\log[\text{H}^+]$. See Table 2 for experimental conditions. The solid lines are calculated with constants in Table 3.

Table 2 Experimental conditions for potentiometry of complexation equilibria between cadmium ion and Xylenol Orange (25°C; 0.1 mol dm⁻³ KNO₃)

Symbol	C_{Cd} mmol dm ⁻³	C_L mmol dm ⁻³
○	none	3.141
□	0.2028	1.889
△	0.4060	1.971
—	0.6083	2.179
⊙	0.8119	2.263
◇	1.218	2.221
●	4.153	2.207
◆	4.274	2.303

Table 1 Logarithmic protonation constants of Xylenol Orange (25°C; 0.1 mol dm⁻³ KNO₃)

log K_1	log K_2	log K_3	log K_4	log K_5	log K_6	Method ^a	Reference
—	—	6.67 ± 0.01	2.90 ± 0.02	2.30 ± 0.03	1.85 ± 0.1	G	this work
12.23	10.56	6.67	2.85	2.32	1.5	G, S	3
—	10.35	6.66	2.79	2.11	—	G	8
12.34	10.66	6.69	—	—	—	S	16 ^b

a. G, potentiometry with a glass electrode; S, spectrophotometry. b. at 20°C.

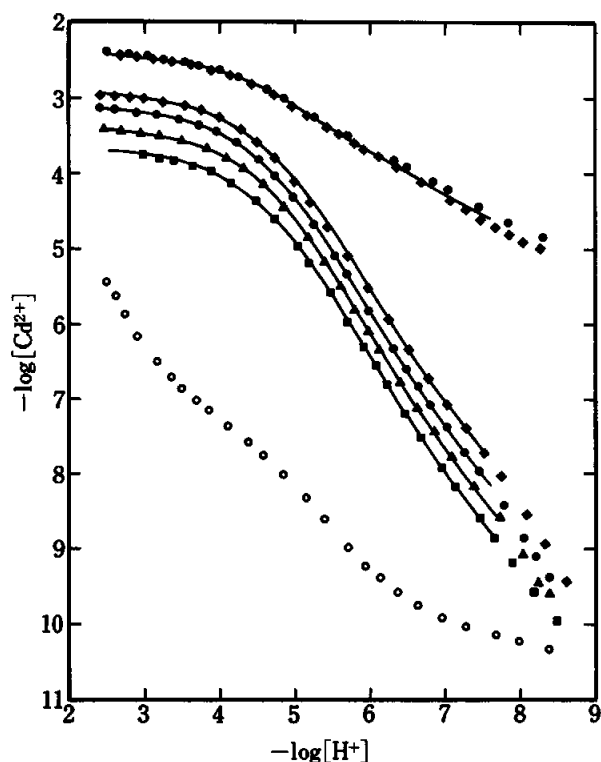


Fig. 2 $-\log[\text{Cd}^{2+}]$ vs. $-\log[\text{H}^+]$. See Table 2 for experimental conditions. Open circles show the detection limit in the Xylenol Orange solution. The solid lines are calculated with the constants in Table 3.

the free cadmium ion concentration at $-\log[\text{H}^+] > 8$.

Mononuclear species

The formation of a cadmium complex with Xylenol Orange is generally expressed as



Only mononuclear species, MH_qL , are formed when the total concentration of H_3L is larger than that of cadmium ion. These total concentrations are expressed as

$$C_M = [\text{M}] + \sum[\text{MH}_q\text{L}]$$

$$C_L = \alpha[\text{H}_3\text{L}] + \sum[\text{MH}_q\text{L}]$$

where α is the side reaction coefficient of H_3L taking into account the protonation of XO, and is given by $(K_4K_5K_6[\text{H}^+]^3 + K_4K_5[\text{H}^+]^2 + K_4[\text{H}^+] + 1 + 1/K_3[\text{H}^+])$. When $Y = K_{1q}[\text{H}^+]^{(q-2)}$, the value can be calculated by

$$Y = \frac{(C_M - [\text{M}])\alpha[\text{H}^+]}{[\text{M}](C_L - C_M + [\text{M}])}$$

If only MH_2L is formed, the plot of $\log Y$ vs. $-\log[\text{H}^+]$ would yield a straight line with a slope of $(2-q)$.

The results are shown in Fig. 3. All the experimental points lay on a single curve, whose slope changes from

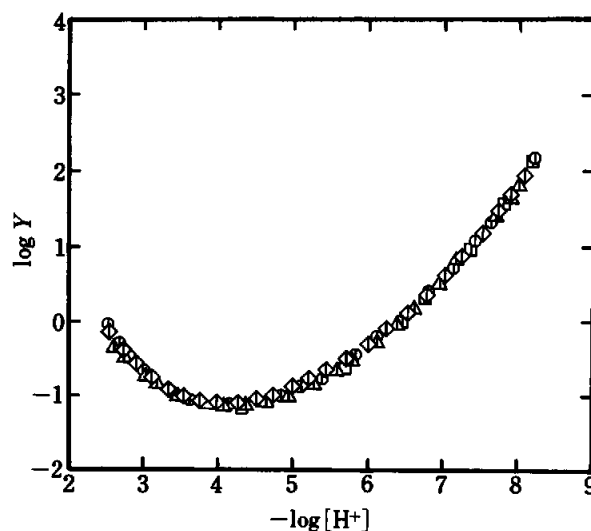


Fig. 3 $\log Y$ vs. $-\log[\text{H}^+]$. See Table 2 for experimental conditions.

Table 3 Stability constants of cadmium Xylenol Orange complexes (25°C; 0.1 mol dm⁻³ KNO₃)

Equilibrium	Logarithmic constant
$K_{13} = [\text{MH}_3\text{L}]/[\text{M}][\text{H}_3\text{L}]$	2.19
$K_{12} = [\text{MH}_2\text{L}][\text{H}]/[\text{M}][\text{H}_3\text{L}]$	-1.26
$K_{11} = [\text{MHL}][\text{H}]^2/[\text{M}][\text{H}_3\text{L}]$	-6.46
$K_{10} = [\text{ML}][\text{H}]^3/[\text{M}][\text{H}_3\text{L}]$	-14.54
$K_{21} = [\text{M}_2\text{HL}][\text{H}]^2/[\text{M}]^2[\text{H}_3\text{L}]$	-3.23
$K_{20} = [\text{M}_2\text{L}][\text{H}]^3/[\text{M}]^2[\text{H}_3\text{L}]$	-8.03

-1 through 0 to 1. These suggest the presence of MH_3L , MH_2L and MHL , respectively. From the intercepts of the tangents, the stability constants for each species were obtained.

At $-\log[\text{H}^+] > 8$, MHL further deprotonates to form ML . Since the ion selective electrode does not work properly under these conditions as described above, the protonation constant of the complex, $K_{\text{MHL}}^{\text{H}}$ was determined by the data obtained with only a glass electrode. The stability constant for this species was calculated with the relation: $K_{10} = K_{11}/K_{\text{MHL}}^{\text{H}}$.

Binuclear species

When $2C_L > C_M > C_L$, binuclear species $\text{M}_2\text{H}_q\text{L}$ predominate in the solution. Similar numerical treatment showed the presence of M_2HL and M_2L . Their stability constants were obtained.

Refinement of the stability constants

With all the data, these stability constants were refined to give a minimum error square sum about $-\log[\text{Cd}^{2+}]$. The constants thus obtained are summarized in Table 3. The solid lines in Fig. 2 were calculated with these constants. Distribution of each

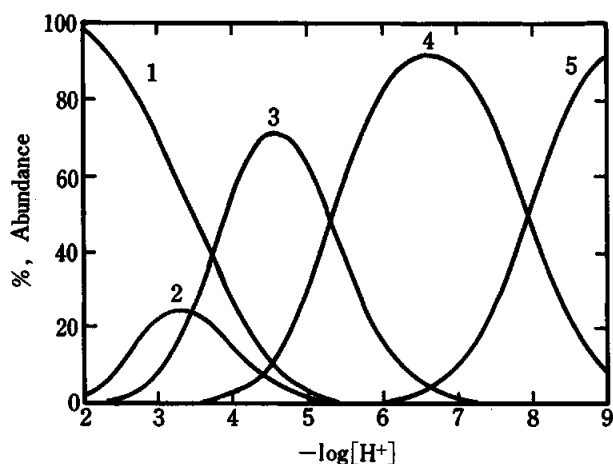


Fig. 4 Distribution of cadmium species in cadmium-Xylenol Orange system. $C_M=0.3 \times 10^{-3} \text{ mol dm}^{-3}$; $C_L=3 \times 10^{-3} \text{ mol dm}^{-3}$. Species: (1) M^{2+} (2) MH_3L (3) MH_2L (4) MHL (5) ML .

species about cadmium ion is shown for $C_M=0.3$ and $C_L=3 \text{ mmol dm}^{-3}$ in Fig. 4.

Further evidence

When stability constants of metal complexes are determined by potentiometry with only a glass electrode, the average number of proton attached to the ligand, \bar{n} is utilized for the numerical analysis. The \bar{n} value could be obtained also in this study and is shown as a function of $-\log[H^+]$ by various symbols in Fig. 1.

On the other hand, when all the equilibrium constants are known, \bar{n} can be calculated by

$$\bar{n}_{\text{calc}} = \frac{\sum \sum q[M_p H_q L]}{C_L}$$

The \bar{n} calculated with the constants obtained above well reproduces the experimental points, as shown in Fig. 1.

The absorption spectra of the solutions containing $10^{-5} \text{ mol dm}^{-3}$ cadmium and XO were recorded at various $-\log[H^+]$ values as shown in Fig. 5A. The solution became colored above $-\log[H^+] 5$, but a clear isobestic point was not observed.

Distribution of the various species of XO is calculated under the same conditions and is shown as a function of $-\log[H^+]$ in Fig. 5B. As total concentrations of cadmium and Xylenol Orange are far lower than those in Fig. 4, all the complexes are more dissociated. Among these species, H_2L , HL , L , MHL , ML and M_2L are deeply colored, because the phenolic proton is dissociated. The main reaction between $-\log[H^+] 5$ and 7 is that between M and H_3L , which forms colored MHL as described previously⁷, but H_2L , MH_2L , ML and M_2L also exist as minor species. The change of the absorption spectra is just as expected

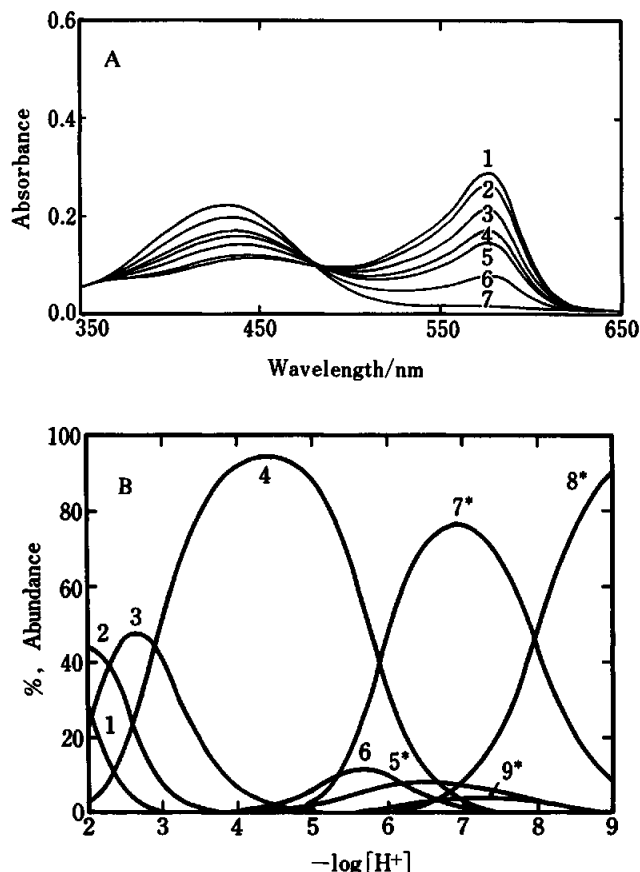


Fig. 5A Absorption spectra of solutions containing cadmium ion and Xylenol Orange. $C_M=1 \times 10^{-5} \text{ mol dm}^{-3}$; $C_L=1 \times 10^{-5} \text{ mol dm}^{-3}$. $-\log[H^+]$: (1) 6.62 (2) 6.42 (3) 6.12 (4) 5.94 (5) 5.81 (6) 5.53 (7) 4.94.

Fig. 5B Distribution of Xylenol Orange species in cadmium-Xylenol Orange system. $C_M=1 \times 10^{-5} \text{ mol dm}^{-3}$; $C_L=1 \times 10^{-5} \text{ mol dm}^{-3}$. Species: (1) H_6L (2) H_5L (3) H_4L (4) H_3L (5) H_2L (6) MH_2L (7) MHL (8) ML (9) M_2L . Species given by the numbers with * are deeply colored.

from the distribution diagram. These two findings confirm that our constants are reasonable.

Discussion

For comparison, the stability constants obtained in this study were recalculated so as to refer to the reaction of M with H_iL to form MH_iL (Table 4). For this recalculation, $K_1=10^{12.23}$, $K_2=10^{10.56}$ and $K_3=10^{6.67}$ were used.³ Murakami *et al.* have studied this system⁶, and found only three species, MHL , ML and M_2L under almost the same experimental conditions. Although there was inconsistency that $K_1 K_{MHL}^M$ is not equal to $K_{ML}^M K_{MHL}^M$, these values are also listed in Table 4 as they are.

Each species is estimated to have the structure proposed previously.⁶ K_{MHL}^M is almost the same as K_{MHL}^{Mida} (5.3); this suggests the coordination by only an iminodiacetate moiety in this species, although transfer of proton from nitrogen to phenolate is necessary

Table 4 Logarithmic stability constants of cadmium Xylenol Orange complexes(25°C; 0.1 mol dm⁻³ KNO₃)^a

$K_{MH_3L}^M$	$K_{MH_2L}^M$	K_{MHL}^M	K_{ML}^M	$K_{M_2HL}^M$	$K_{M_2L}^M$	$K_{MH_3L}^H$	$K_{MH_2L}^H$	K_{MHL}^H	$K_{M_2HL}^H$	Ref.
2.19	5.41	10.77	14.92	3.23	6.51	3.45	5.20	8.08	4.80	this work
—	—	7.84	9.67	—	8.54	—	—	8.03	—	5

a. See text for details.

before coordination. MH₃L and M₂HL also have the coordination by the same moiety, but they have smaller constants than K_{Mida}^M , because the transfer of proton is very disadvantageous in these cases. On the other hand, the larger constants for K_{MHL}^M , K_{ML}^M and $K_{M_2L}^M$ imply the coordination of or the interaction with phenolate or ketone group in these species. The literature values for K_{MHL}^M (7.84) and K_{ML}^M (9.67) are too small.

Protonation constant of phenol proton is decreased from 6.67 to 5.20 and that of the second nitrogen proton from 10.56 to 8.08 by replacement of hydrogen with cadmium ion on the other moiety. These imply that donor atoms attached to two phenol rings are not independent and influence each other through a triphenyl methane group.

Formation of binuclear species is characteristic of this ligand. Coordination of the second metal is expected to be less favorable than that of the first one because of the influence discussed above. Actually we found a large difference between K_{ML}^M and $K_{M_2L}^M$ (8.4) or between K_{MHL}^M and $K_{M_2HL}^M$ (7.5). The difference in the literature values, 1.1 between K_{ML}^M and $K_{M_2L}^M$ is too small.⁶

Thus the relation between our equilibrium constants is consistent with the proposed structure. Similar studies on copper(II) and lead complexes with XO will be published elsewhere.

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