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The Complexation Reaction of 1-(Hydroxy-4-methyl-2-phenylazo)-2-naphthol-4-sulfonic Acid (Calmagite) with Divalent Metal Ions and Use as a Metallochromic Indicator

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In previous papers,[1,2] the complexation reaction of 1-(1-hydroxy-2-naphthylazo)-6-nitro-2-naphthol-4-sulfonic acid (Eriochrom Black T, BT) with divalent metal ions in the presence of aminopolycarboxylate was studied spectrophotometrically. In the present paper, solution equilibria between 1-(hydroxy-4-methyl-2-phenylazo)-2-naphthol-4-sulfonic acid (common name, calmagite) and metal(II)-aminopolycarboxylate chelates were dealt with in the same way as in the BT system, and the use of calmagite as a metallochromic indicator in the chelatometric titrations of zinc(II), cadmium(II) and lead(II) was studied.

Apparatus and experimental procedures were those used previously.[1,2] Commercial calmagite was purified by employing the procedure proposed by Lindstrom and Diehl.[3] The C.H.N. analysis and spectrophotometric measurement showed that the purity of calmagite was 93%.

The Complexation Reaction of Calmagite. Typical absorption curves of calmagite and its metal(II) chelates were shown in Fig. 1. In copper(II)-ethylenediaminetetraacetic acid(EDTA), zinc(II)-nitrilotriacetic acid (NTA), lead(II)-NTA and cadmium(II)-*N'*-(hydroxyethyl)-ethylenediamine-*N*,*N*,*N'*-triacetic acid (EDTA-OH) systems, the exchange reaction of calmagite with metal(II)-

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[1] M. Kodama and H. Ebine, This Bulletin, **40**, 1857 (1967).

[2] M. Kodama and C. Sasaki, *ibid.*, **41**, 127 (1968).

[3] F. Lindstrom and H. Diehl, *Anal. Chem.*, **32**, 1123 (1960).

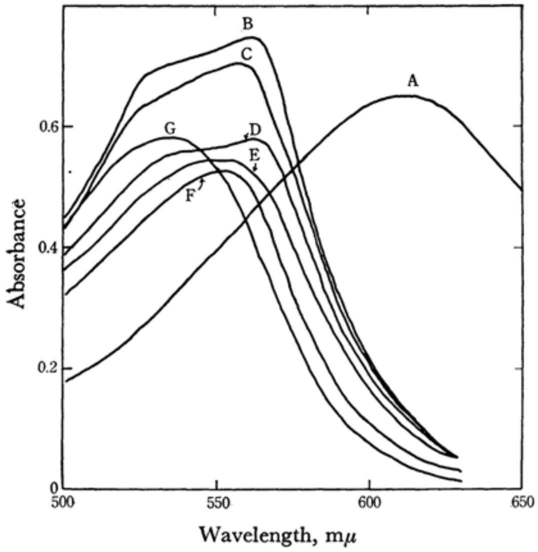

Fig. 1. Absorption curves of calmagite and its metal(II) chelates.
pH=9.79, μ=0.30
Concentration of calmagite=$3.3_0\times10^{-5}$ M
A : no metal(II), 10.0 mM EDTA
B : Ni(II)-NTA chelate 10.0 mM, NTA 10.0 mM
C : Zn(II)-NTA chelate 20.0 mM, NTA 5.0 mM
D : Co(II)-NTA chelate 10.0 mM, NTA 10.0 mM
E : Cd(II) 10.0 mM, ammonia 0.1 M
F : Pb(II)-NTA chelate 30.0 mM, NTA 5.0 mM
G : Cu(II)-NTA chelate 10.0 mM, NTA 10.0 mM

TABLE 1. STABILITY CONSTANTS, log K_{MD} (μ=0.30)

	Cu(II)	Ni(II)	Co(II)	Zn(II)	Cd(II)	(Pb(II)
Calmagite	21.70	21.63	21.03	14.73	12.59	12.90
BT[1,2]	21.38	20.8	20.0	12.31	12.74	13.19

TABLE 2. END POINT INDICES (Δ_1 AND Δ_2)

System	Metal concentration	Δ_1	Δ_2
Zn(II) ammonia buffer (0.1 M, pH=10.0)	0.1	6.78	3.03
	0.01	5.78	3.03
	0.001	4.78	3.03
Cd(II) ammonia buffer (0.1 M, pH=10.0)	0.1	8.27	4.84
	0.01	7.27	4.84
	0.001	6.27	4.84
Pb(II) 0.1 M tartrate (pH=10.0)	0.1	6.25	6.36
	0.01	5.25	6.36
	0.001	4.25	6.36

aminopolycarboxylate chelates proceeds very rapidly. Hence, the composition and stability constants of calmagite chelates of these metal(II) ions were determined from $\log(A_{HD}-A)/(A-A_{MD})$ *vs.* $\log[MZ]/([Z]_f\ [1+K_2[Z]_f/(a_H)])$ plots.[1,2] In nickel(II)-EDTA-OH and cobalt(II)-EDTA system, however, the reaction is very slow. Therefore, as in BT system, solution equilibria were determined from a $\log\ [(A_{HD}-A)/(A-A_{MD})[m-(A_{HD}-A)/(A_{HD}-A_{MD})]$ *vs.* $\log\ [Z]_f$ plot.[4,5] The notations here are those used previously.[1,2,4,5] Under the present experimental conditions, calmagite invariably forms chelates of a 1-to-1 composition. Results are given in Table 1. The numerical values used in the calculation of stability constants of calmagite chelates were estimated from the related con-

TABLE 3. EDTA TITRATIONS OF METAL (II) USING CALMAGITE AS INDICATOR (pH=10.0)

	Concentration of metal(II) M	Volume of metal solution ml	Concentration of EDTA M	Volume of EDTA solution added, ml	
				Calcd	Obsd
Zn(II) ammonia buffer (0.1 M)	1.00×10^{-2}	5.00	$1.38_1\times10^{-2}$	3.62	3.63
		10.00		7.24	7.22
		15.00		10.86	10.83
	1.00×10^{-3}	5.00	$1.38_1\times10^{-3}$	3.62	3.60
		10.00		7.24	7.22
		15.00		10.86	10.85
Cd(II) ammonia buffer (0.1 M)	$0.958_4\times10^{-2}$	5.00	$1.38_1\times10^{-2}$	3.47	3.50
		10.00		6.94	6.90
		15.00		10.41	10.43
	$0.958_4\times10^{-3}$	5.00	$1.38_1\times10^{-3}$	3.47	3.40
		10.00		6.94	6.96
		15.00		10.41	10.43
Pb(II) 0.1 M tartrate	$1.02_4\times10^{-2}$	5.00	$1.38_1\times10^{-2}$	3.71	3.69
		10.00		7.42	7.47
		15.00		11.13	11.17

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4) M. Kodama, This Bulletin, **40**, 2575 (1967).

5) M. Kodama, C. Sasaki and M. Murata, *ibid.*, **41**, 2333 (1968).

stants[1-3,6-8] in a solution of ionic strength 0.10 in the same way as previously.[1] On the basis of general relation between stability constant and dissociation constant, the stability constant of metal(II)-calmagite chelate would be larger than that of metal(II)-BT chelate. In contrast to this prediction, log K_{MD} values of cadmium (II) and lead(II) chelates of calmagite were slightly less than those of BT. This abnormal behavior can not be explained in a simple manner, but may partially be attributed to π-back donation, to steric interaction or other effects. It can also be mentioned here that the Irving-Williams series applies to calmagite and BT chelates of copper(II), nickel(II), cobalt(II) and zinc(II).

The Use of Calmagite as an Indicator in Chelatometric Titrations of Zinc(II), Cadmium(II) and Lead(II). Thermodynamically, because of its larger log K_{MD} value, calmagite can not be used as a metallochromic indicator in EDTA titrations of copper(II), nickel(II) and cobalt(II). In the cases of zinc(II), cadmium(II) and lead(II), as shown in Table 2, end point indices, Δ_1 and Δ_2,[9] calculated using stability constants of metal-(II)-EDTA,[7] -calmagite, tartrate[10] and ammine[8] complexes, and dissociation constants of EDTA[6] and calmagite,[3] clearly suggest that calmagite can be used successfully as an indicator in EDTA titrations of zinc(II), cadmium(II) and lead(II). This prediction was examined experimentally. At the end point, the color transition from red to bluish-violet occurred sharply. Typical results are given in Table 3. Experimental equivalence points agreed well with stoichiometric ones. Aqueous solutions of calmagite and its metal(II) chelates were much more stable than those of BT, in good agreement with the findings of Lindstrom and Diehl.[3]

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6) G. Schwarzenbach and G. Anderegg, *Helv. Chim. Acta*, **40**, 4170 (1957).

7) G. Schwarzenbach, R. Gut, and G. Anderegg, *ibid.*, **37**, 937 (1954).

8) A. Ringbom, "Complexation in Analytical Chemistry," Interscience Publishers, New York (1963), p. 301.

9) C. N. Reilley and R. W. Schmid, *Anal. Chem.*, **31**, 887 (1959).

10) V. E. Panova, *Zhur. neorg. Khim.*, **1**, 422 (1956).