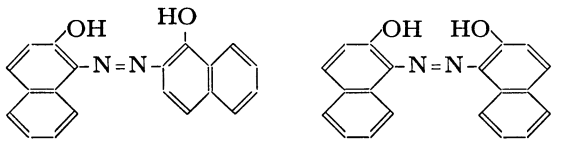
1,1′-Dihydroxy-2,2′-azonaphthalene-4,4′-disulfonic Acid as a New Reagent for Magnesium

Yasuko NODA* and Haruo MIYATA

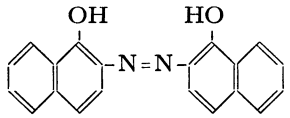
Department of Chemistry, Faculty of Science, Okayama University, Tsushima, Okayama

(Received May 31, 1971)

Eriochrome Black T (EBT) has been used exclusively as the metallochromic indicator in the chelatometric titration of magnesium with EDTA. Also, Patton and Reeder's dye (HSN, 2-hydroxy-1-(2-hydroxy-4-sulfo-1-naphthylazo)-3-naphthoic acid) has been used for calcium. The acid dissociation constants of these indicators are 6.3 and 11.6 for EBT,[1] and 9.2_6 and 13.6_7 for HSN[2] respectively, as pK_a values; the skeletal structures are as follows:



for EBT for HSN



Structure 1

We expected that the pK_a values of the reagent with a skeletal structure such as Structure 1 would be lower than those of EBT or HSN, and that the conditional stability constant for its magnesium chelate would be higher. Therefore, 1,1′-dihydroxy-2,2′-azonaphthalene-4,4′-disulfonic acid[3] was synthesized as a reagent for magnesium from the diazotized 2-amino-1-naphthol-4-sulfonic acid, which was coupled with 1-naphthol-4-sulfonic acid. The pK_a values of this reagent are 5.0 and 11.1. A color change from blue to red upon treatment by this reagent with the magnesium ion is very sharp at pH 10. The absorption spectra of the reagent and its magnesium chelate are shown in Fig. 1. The absorption spectrum of calcium chelate at pH 7.7 is almost the same as that of the reagent itself at pH 6.46 (Curve 2) in Fig. 1. The existence of a 1-to-1 chelate was verified by the continuous-variation method, its conditional stability constant, K', and the stability constant, K, are listed in Table 1.

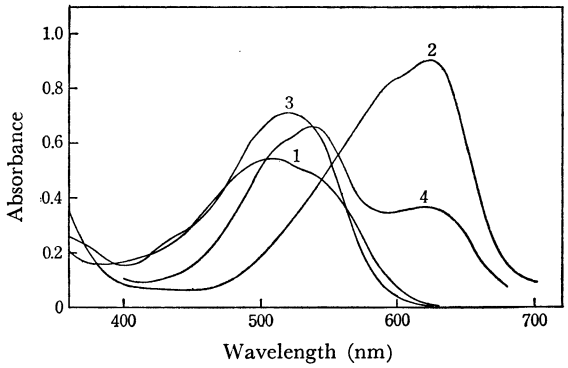


Fig. 1. Absorption spectra of the reagent and its magnesium chelate: 1 at pH 1.71; 2 at pH 6.46; 3 at pH 13; and 4 (magnesium chelate) at pH 7.69.
reagent concentration: 2.46×10^{-5} M
magnesium concentration, 2.46×10^{-3} M

By a comparison of these data, it was found that the reagent is a valuable indicator for the chelatometric titration of the magnesium ion at pH 10, and that also, it can be used in the colorimetric determination of magnesium in the presence of the calcium ion. Further details on the magnesium chelate will be reported elsewhere.

TABLE 1. ACID DISSOCIATION CONSTANTS OF THE REAGENTS, AND CONDITIONAL STABILITY CONSTANTS AND STABILITY CONSTANTS OF THESE CHELATES ($t=25°C$, $\mu=0.1$)

Reagent	pK_{a1}	pK_{a2}	log K		log K' (at pH 10)	
			Mg	Ca	Mg	Ca
the reagent	5.0	11.1	7.0	4.7	5.9	3.6
EBT[1]	6.3	11.6	7.0	5.4	5.4	3.8
HSN[2]	9.2_6	13.6_7		5.8_5		
Calmagite[4]	8.14	12.35			5.69	3.68

* Present address: Yanagimoto Mfg. Co., Ltd., Kyoto.

1) G. Schwarzenbach and W. Biedermann, *Helv. Chim. Acta*, **31**, 678 (1948).

2) A. Itoh and K. Ueno, *Analyst*, (London), **95**, 586 (1970).

3) Found: C, 41.66; H, 3.50; N, 4.75%. Calcd for $C_{20}H_{12}O_8N_2S_2Na_2\cdot4H_2O$: C, 40.68; H, 3.41; N, 4.74%.

4) F. Lindstrom, *Anal. Chem.*, **32**, 1126 (1960).