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Heterocyclic Azomethine Compounds and Their Reduction Products as Analytical Reagents. II. The Reaction of 1-Picolylideneamino-2-naphthol with Zinc(II)

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The acid dissociation constants of 1-picolylideneamino-2-naphthol in aqueous dioxane media of various concentrations and the stability constant of the zinc(II) chelate in a 50 v/v% aqueous dioxane medium were determined potentiometrically at 25 °C and $\mu=0.1$. The acid dissociation constants, pK_{a1}, pK_{a2}, and pK_{a3}, at the zero dioxane mole fraction, evaluated by means of a least-squares treatment of the experimental data, are 3.1_6, 4.3_1, and 10.3_1 respectively. The overall stability constant of the zinc chelate was calculated be to $\log\beta_2=12.7_9$. 1-Picolylideneamino-2-naphthol can be used as a sensitive reagent for the extractive spectrophotometric determination of zinc. The zinc chelate extracted into chloroform has an absorption maximum at 520 nm. The bathochromic shift is as large as 120 nm. The color system obeys Beer's law over a concentration range up to 2×10^{-5} M. The molar absorptivity is 4.5×10^4 l/mol·cm at 520 nm.

In a preceding paper,$^{1)}$ the acid dissociation constants of picolinaldehyde 2-hydroxyanil and some of its derivatives and their reactions with metal ions have been reported. The applicability of these compounds as sensitive reagents for the extractive spectrophotometric determinations of certain divalent-metal ions has also been pointed out. There has, however, been no reported characterization of metal complexes derived from the Schiff bases of 1-amino-2-naphthol or any of its ring-substitution products. In the present work, the chelate formation between 1-picolylideneamino-2-naphthol, a new heterocyclic azomethine compound, and zinc(II) and its application to the extractive spectrophotometric determination of traces of zinc are investigated. Of the divalent-metal chelates with this reagent which can be extracted into chloroform, the zinc chelate has the largest molar absorptivity.

Experimental

Materials and Apparatus. 1-Picolylideneamino-2-naphthol is synthesized as follows. A suspension of 1-amino-2-naphthol (0.05 mol)(purified by Kurzer's method$^{2)}$) in benzene(300 ml) is refluxed with freshly-distilled picolinaldehyde (0.055 mol) for a period of 15 min. The resulting crude product is recrystallized from a mixture of methanol and benzene (1 : 1) to obtain yellow fine crystals (4 g, 33%); mp 186—187 °C (with decomposition); IR (KBr): 1627 cm^{-1} (-CH=N-). Found: C, 77.49; H, 4.64; N, 11.26%. Calcd for $C_{16}H_{12}ON_2$: C, 77.40; H, 4.87; N, 11.28%.

A 1×10^{-4} M solution of the reagent in chloroform and a 1×10^{-2} M stock solution of zinc perchlorate are used for the spectrophotometric study. An Iwaki model KM mechanical shaker is used for the shaking.

All the other reagents and apparatus used have been reported previously.$^{1)}$

Potentiometric Titrations. As the reagent and the zinc chelate are insoluble in water, the titration is carried out in an aqueous dioxane medium. The experimental conditions and the method for the determination of the acid dissociation constants have been described previously.$^{1)}$ For the determination of the stability constant, a 50 v/v% dioxane solution containing the ligand (2.5×10^{-3} M), sodium perchlorate (0.1 M), and zinc perchlorate (1.25×10^{-3} M) is titrated with a 0.1850 M sodium hydroxide solution at 25±0.1 °C.

Standard Procedure for the Zinc Determination. An aliquot of a zinc solution is transferred into a 50-ml separatory funnel along with a 5 ml of a 1 M sodium perchlorate solution and 2 ml of a 1 M tris(hydroxymethyl)aminomethane-hydrochloric acid buffer solution (pH 8.5). The solution is diluted to 10 ml with water and then shaken for 1 min with 10 ml of the reagent solution. The absorbance of the chloroform extract is then measured at 520 nm against the reagent blank.

Results and Discussion

Acid Dissociation Constants. The potentiometric titration curves of the monosodium salt of 1-picolylideneamino-2-naphthol with perchloric acid show that this reagent behaves as a tribasic acid, the equations used to calculate the acid dissociation constants being:

$$\frac{(1-R)[\mathrm{H}^+]}{R-2}=\frac{R[\mathrm{H}^+]}{R-2}\cdot\frac{1}{K_{a1}}+K_{a2} \tag{1}$$

$$\frac{2-R}{R[\mathrm{H}^+]^2}=\frac{R-1}{R[\mathrm{H}^+]}\cdot\frac{1}{K_{a2}}+\frac{1}{K_{a1}K_{a2}} \tag{2}$$

and:

$$K_{a3}=\frac{(R-2)[\mathrm{H}^+]}{3-R} \tag{3}$$

where $R=\{(3-a)C_A+[\mathrm{H}^+]-[\mathrm{OH}^-]\}/C_A$, and where C_A is the total concentration of the ligand, and a, the degree of neutralization. The pK_a values of the ligand acid in aqueous dioxane media of various concentrations are given in Table 1. The values of pK_{a1} and pK_{a2} are attributed to the removal of protons from the azomethine and the pyridine nitrogens respectively, whilst that of pK_{a3} is attributed to the dissociation of the naphtholic proton. The values of pK_{a1} and pK_{a2} decrease, and that of pK_{a3} increases, with an

TABLE 1. ACID DISSOCIATION CONSTANTS OF 1-PICOLYLIDENEAMINO-2-NAPHTHOL IN AQUEOUS DIOXANE MEDIA
$\mu=0.1$, 25°C

Mole fraction of dioxane	pK_{a1}	pK_{a2}	pK_{a3}
0	3.1_6	4.3_1	10.3_1
0.1122(37.5 v/v%)	3.0_5	4.2_4	10.7_5
0.1739(50 v/v%)	2.9_5	4.1_7	11.4_0
0.2598(62.5 v/v%)	2.8_6	4.0_9	11.5_3
0.3872(75 v/v%)	2.7_4	4.0_3	12.2_8

increase in the mole fraction of dioxane. On plotting each pK_a value against the mole fraction of dioxane, an approximately linear relationship is obtained in every case. The value of pK_a's at the zero dioxane mole fraction, evaluated by a least-squares treatment of the experimental data, are also included in Table 1.

The pK_{a3} value for 1-picolylideneamino-2-naphthol in the 50 v/v% dioxane medium is lower by 0.9 log unit than the pK_{OH} value for PAN[3] under the same conditions. Contrary to this observation, it has been found that the pK_{a3} values for picolinaldehyde 2-hydroxyanil and its methyl and chloro derivatives are somewhat higher than those for the corresponding azo dyes.[1,4] These results may be explained according to Hadzi's observation[5] that *o*-hydroxyazonaphthols exist as azo-hydrazo tautomers, whereas *o*-hydroxyazophenols are true azo compounds.

Stability Constant of the Zinc Chelate. The results of the continuous variation method show that zinc reacts with the reagent in a neutral to a slightly basic medium to form a 1 : 2 metal-to-ligand chelate easily extractable into chloroform. Therefore, the potentiometric titration is carried out in the molar ratio of 1 : 2. The titration curves of the reagent in a 50 v/v% dioxane medium in both the presence and absence of zinc are shown in Fig. 1. The pH inflection at a=2.5 in the former case suggests that the formation reactions of the 1 : 1 chelate, ZnL$^+$, and the 1 : 2 chelate, ZnL$_2$, proceed predominantly below and above a=2.5 respectively. The successive stability constants can be obtained from the following relationships[6]:

$$L=\frac{K_{a2}K_{a3}(3C_A+[OH^-]-[Na^+]-[H^+])}{2[H^+]^2+[H^+]K_{a2}} \tag{4}$$

$$\bar{n}=\frac{C_A-(K_{a2}K_{a3}+[H^+]K_{a2}+[H^+]^2)L/K_{a2}K_{a3}}{C_M} \tag{5}$$

where C_A and C_M are the total concentrations of the ligand and of zinc respectively. The values of $\bar{n}$ and L at each point of the titration curve are calculated from Eqs. (4) and (5). From these data, the formation curve is then plotted, a symmetrical pattern being followed. The successive stability constants are estimated from the values of pL at $\bar{n}$=0.5 and $\bar{n}$=1.5 to be 7.6_0 for log K_1 and 5.1_9 for log K_2, by means of the equations given by Schrøder.[7] These values are considerably lower than those for the zinc-PAN chelate (log K_1= 11.2, log K_2=10.52[3]) and the zinc-picolinaldehyde 2-hydroxyanil chelate (log K_1=10.8, log K_2=8.0[4]), but higher than those for the zinc chelates of salicylidene-2-aminopyridine (log K_1=5.8, log K_2=4.3[4]) and *o*-aminophenol (log K_1=5.99, log K_2=4.96[8]). 1-Picolylideneamino-2-naphthol, therefore, acts as a terdentate ligand toward zinc to form two five-membered chelate rings. This consideration is supported by the spectral properties of the other divalent-metal chelates with the reagent in chloroform, as will be shown below.

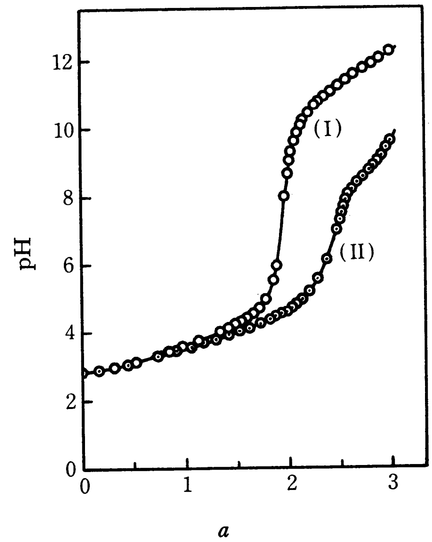

Fig. 1. Potentiometric titration curves of 1-picolylideneamino-2-naphthol and its zinc chelate in 50 v/v% aqueous dioxane, μ=0.1, 25 °C; abscissa a represents moles of alkali added per mole of ligand (tribasic acid).
(I): Ligand, 2.50×10^{-3} M.
(II): Ligand, 2.50×10^{-3} M; Zn, 1.25×10^{-3} M

Extractive Spectrophotometric Determination of Zinc. As has already been shown above, the 1 : 2 zinc-1-picolylideneamino-2-naphthol chelate is readily extracted into organic solvents, such as chloroform, 1,2-dichloroethane, *o*-dichlorobenzene, and nitrobenzene, to give a reddish-violet color. Chloroform is chosen because the largest absorbance is obtained in it. The color system obeys Beer's law. It is, therefore, tested for the extractive spectrophotometric determination of traces of zinc. However it is not possible to obtain the distribution coefficients of the reagent and the zinc chelate because of their low stability.

Absorption Spectra: The absorption spectra of the reagent and its zinc chelate in chloroform are shown in Fig. 2, the absorption maximum of the zinc chelate against the reagent blank being found at 520 nm. It may be noted that the bathochromic shift observed on chelation with the reagent is about 120 nm, much larger than that observed with PAN, *i.e.*, 80 nm. This is an advantage in the spectrophotometric determination of metals.

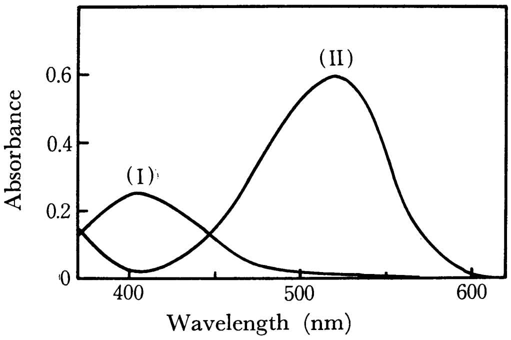

Fig. 2. Visible absorption spectra of 1-picolylideneamino 2-naphthol and its zinc chelate in chloroform.
(I): Reagent, 5.0×10^{-5} M; reference, CHCl$_3$.
(II): Zn, 1.30×10^{-5} M (8.5 μg); reagent, 2.0×10^{-4} M; pH, 8.5; reference, reagent blank.

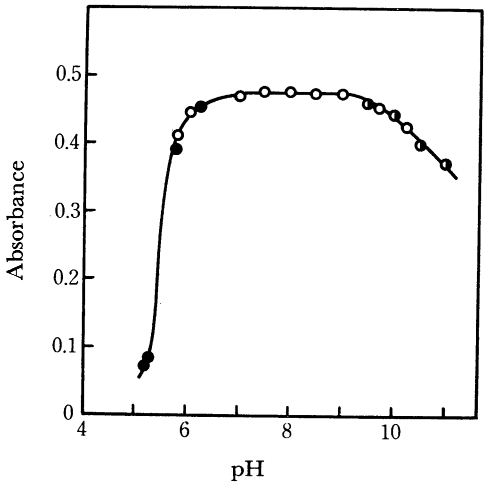

Fig. 3. Effect of pH.
Zn, 1.07×10^{-5} M (7.0 μg); reagent, 2.0×10^{-4} M; reference, reagent blank; ●, hexamethylenetetramine-HCl buffer; ○, tris(hydroxymethyl)aminomethane-HCl buffer; ◑, ammonia-ammonium chloride buffer.

Effect of pH: The absorbance of the organic phase is measured as a function of the pH of the aqueous phase, the results being shown in Fig. 3. At any pH examined, the absorption maximum of the chloroform extract is found at 520 nm, indicating that only one species is extracted. The zinc chelate is extracted above pH 5. The absorbance of the extract is at its maximum at pH 7.5—9.0

Color Stability and Effect of the Shaking Time: The zinc chelate is not very stable in either the aqueous or the organic phase. The absorbance of the chloroform extract decreases by 4.0% per 30 min for 7.3 μg of zinc. The absorbance is thus measured within 5 min after extraction. The maximum absorbance is obtained when a zinc solution is shaken with a chloroform solution of the reagent for 45 s to 2 min at pH 8.5.

Effect of the Reagent Concentration: About a 10-fold excess of the reagent is enough to obtain a constant absorbance.

Beer's Law and Sensitivity: Beer's law is obeyed over the concentration range up to 2×10^{-5} M (13 μg of zinc in 10 ml). At 520 nm, the molar absorptivity is 4.5×10^4. The spectrophotometric sensitivity is estimated to be 1.5×10^{-3} μg of zinc per cm^2, corresponding to log $I_0/I=0.001$. The sensitivity of the present method is much higher than that of the methods using zincon (molar absorptivity, $\varepsilon=1.9\times10^4$ at 610 nm[9]) or xylenol orange ($\varepsilon=2.74\times10^4$ at 550 nm[10]); however, it is lower than those with PAN ($\varepsilon=5.6\times10^4$ at 550 nm[11]), 5-chloro-PAN ($\varepsilon=8.4\times10^4$ at 564 nm[12]), or dithizone ($\varepsilon=9.6\times10^4$ at 532 nm[13]).

Reactions with Other Divalent-metal Ions. 1-Picolylideneamino-2-naphthol reacts with many divalent-metal ions in a neutral or slightly basic medium to form extractable colored chelates. The cobalt(II) chelate, however, changes in color from reddish-violet to brown during the course of extraction with chloroform at pH 8.5, giving a precipitate on the interface. This is probably due to the oxidation of the cobalt(II) chelate to the cobalt(III). In addition, magnesium(II) gives an orange red color to the organic phase during the course of extraction at pH 11, but the color fades away in a moment.

Table 2. Spectral properties of the metal chelates extracted into chloroform

Metal	Absorption maximum (nm)	Molar absorptivity $\times10^{-4}$ (l/mol·cm)	pH
Cd(II)	524	3.6	9.8[b]
Co(II)	523	partly precipitated	8.5
Cu(II)	540	1.5	7.4[b]
Fe(II)[a]	520	0.7	8.5[b]
Hg(II)	530	3.5	6.3[b]
Mn(II)[a]	523	3.7	9.8[b]
Ni(II)	537	3.5	8.5[b]
Pb(II)	520	1.5	9.8[b]
UO_2(II)	510	0.4	6.0
Zn(II)	520	4.5	8.5

a) in the presence of NH_2OH. b) pH value at which the maximum absorbance is obtained.

Table 2 summarizes the spectral properties of several divalent-metal chelates with this reagent extracted into chloroform. The spectrum of each chelate shows a broad, intense band well separated from that of the reagent, the shift being larger than 100 nm. The results tabulated in Table 2 imply that 1-picolylideneamino-2-naphthol can also be used as a sensitive reagent for the extractive spectrophotometric determination of cadmium(II) and manganese(II).

The disadvanatge of the present reagent is that its solution and chelates are not very stable. As it is much more sensitive for cadmium(II), manganese (II), and zinc(II) than copper(II), though, a further search for more stable analogs is in progress.

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References

1) Part I: M. Otomo, and K. Kodama, This Bulletin, **46**, 2421 (1973).

2) F. Kurzer, *J. Chem. Soc.*, **1949**, 3434.

3) A. Corsini, I. Mai-Ling Yih, Q. Fernando, and H. Freiser, *Anal. Chem.*, **34**, 1090 (1962).

4) W. J. Geary, G. Nickless, and F. H. Pollard, *Anal. Chim. Acta*, **26**, 575 (1962); *ibid.*, **27**, 71 (1962).

5) D. Hadzi, *J. Chem. Soc.*, **1956**, 2143.

6) A. Young and T. R. Sweet, *J. Amer. Chem. Soc.*, **80**, 800 (1966).

7) K. H. Schrøder, *Acta. Chem. Scand.*, **20**, 1401 (1966).

8) R. G. Charles and H. Freiser, *J. Amer. Chem. Soc.*, **74**, 1385 (1952).

9) R. M. Rush and J. H. Yoe, *Anal. Chem.*, **26**, 1345 (1954).

10) T. V. Gurkina and A. H. Igoshin, *Zh. Analit. Khim.*, **20**, 778 (1965).

11) S. Shibata, *Bunseki Kagaku*, **21**, 551 (1972).

12) J. E. Going and P. T. Pflaum, *Anal. Chem.*, **40**, 1098 (1970).

13) S. Ashizawa, *Bunseki Kagaku*, **10**, 350 (1951).