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Evaluation of PAC, TAC, 2-IAC as Metallochromic Indicators in the EDTA Titrations of Nickel

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The rates of color change of 2-(2-pyridylazo)-4-methylphenol (PAC), 2-(2-thiazolylazo)-4-methylphenol (TAC) and 2-(2-imidazolylazo)-4-methylphenol (2-IAC) during EDTA–nickel titration have been determined. The rate is a thousand times greater for TAC and 2-IAC than for PAC. From equilibrium considerations, the rate of color change and the color contrast change, an evaluation of PAC, TAC, and 2-IAC as metallochromic indicators for nickel is given. The optimum pH ranges with TAC and 2-IAC are from 6 to 7 and from 5 to 7, respectively, at 80 °C. With PAC, the titration should be conducted with boiling at pH 4—5. 2-IAC is the best indicator due to the good visual color contrast and the wide pH range over which it is applicable.

In EDTA titrations, the sharpness of the color change of metallochromic indicators is governed by the reaction rate for substitution of the metal-indicator chelate with EDTA, as well as the equilibrium conditions involved. Usually, the reaction rate for substitution of nickel-indicator chelates with EDTA being slow, the rate of indicator color change is important. The PAC[2-(2-pyridylazo)-4-methylphenol],[1] TAC[2-(2-thiazolylazo)-4-methylphenol],[2] and 2-IAC[2-(2-imidazolylazo)-4-methylphenol][3] synthesized previously can be used as indicators for nickel–EDTA titrations. In a previous paper,[4] the reaction rate for substitution of nickel–TAC chelates with EDTA was determined and the mechanism of the color change was proposed. Since PAC, TAC, and 2-IAC have different heterocyclic rings, differences in the rate of color change is expected.

In the present paper, the substitution reaction rate for PAC and 2-IAC are presented and PAC, TAC, and 2-IAC are evaluated as metallochromic indicators for nickel–EDTA titration.

Experimental

Reagents. PAC, TAC, and 2-IAC, which had been previously synthesized and purified, were dissolved in dioxane and 10^{-3} M solutions were prepared.

A nickel(II) solution was prepared from reagent grade nickel nitrate and standardized with dimethylglyoxime by gravimetry.

EDTA·2Na was recrystallized from water and standardized against zinc metal(99.99% pure).

An MES[2-morpholino-1-ethanesulfonic acid]–potassium hydroxide solution was used as a buffer.

All other reagents used were of reagent grade.

Apparatus. A Union Giken RA-401 Stopped-Flow Spectrophotometer, a Union Giken SM-401 High-Sensitivity Spectrophotometer, and a Radiometer PHM 26c pH meter were used.

All experiments were carried out in 20% dioxane solutions at $\mu=0.1$ (KNO_3) and at 25±1 °C.

Results

The Reaction for Substitution of Ni–PAC or Ni–2-IAC with EDTA. In the presence of a large excess of PAC or 2-IAC, nickel forms a 1 : 2 chelate (NiL_2) over the pH range from 5 to 7, as well as in the case of TAC. When EDTA is added to the nickel chelate solution in highly excessive amounts, the following substitution reaction proceeds to completion:

$$NiL_2 + \text{edta}' \longrightarrow Ni(\text{edta})^{2-} + 2L', \tag{1}$$

where L is an anion of the PAC or 2-IAC. The rate law can be expressed as

$$-\frac{d[NiL_2]}{dt} = k_{0(L,EDTA,H)}[NiL_2], \tag{2}$$

where $k_{0(L,EDTA,H)}$ is the conditional rate constant involving the indicator, EDTA, and hydrogen ion concentrations. By representing the absorbances at reaction times 0, t, and ∞ by A_0, A_t, and A_∞, we obtain

$$\log(A_t - A_\infty) = -\frac{k_{0(L,EDTA,H)}}{2.303}t + \log(A_0 - A_\infty). \tag{3}$$

A solution containing nickel, an indicator and a buffer was vigorously mixed with a solution containing

TABLE 1. FIRST-ORDER RATE CONSTANTS $k_{0(L,EDTA,H)}$ FOR PAC UNDER VARIOUS CONDITIONS

$C_{Ni}=1.86\times10^{-5}$ M, 25 °C, $\mu=0.1$, dioxane 20%v/v.

C_{EDTA} ($\times10^{-3}$ M)	C_{PAC} ($\times10^{-4}$ M)	pH	$k_{0(L,EDTA,H)}$ ($\times10^{-3}$ s^{-1})
7.00	1.00	5.56	1.61
		5.65	1.52
		5.75	1.20
		6.02	0.833
	1.13	5.55	1.42
	1.25	5.55	1.22
		5.75	1.05
	1.50	5.52	1.12
	2.00	5.37	0.993
		5.43	0.917
		5.46	0.907
		5.50	0.889
		5.57	0.872
		5.74	0.604
		5.92	0.600
	3.00	5.74	0.412
	4.00	5.52	0.417
		5.75	0.333
	5.00	5.52	0.333
9.05	1.00	5.49	2.19
	2.00	5.47	1.27
13.00	2.00	5.41	1.76

TABLE 2. FIRST-ORDER RATE CONSTANTS $k_{0(\mathrm{L,EDTA,H})}$ FOR 2-IAC UNDER VARIOUS CONDITIONS

$C_{\mathrm{Ni}}=5.00\times10^{-6}$ M, 25 °C, $\mu=0.1$, dioxane 20%v/v.

C_{EDTA} $(\times10^{-4}\,\mathrm{M})$	$C_{\mathrm{2\text{-}IAC}}$ $(\times10^{-4}\,\mathrm{M})$	pH	$k_{0(\mathrm{L,EDTA,H})}$ $(\times10^{-2}\,\mathrm{s}^{-1})$
2.00	1.00	5.82	6.25
		5.90	5.53
		5.95	5.30
		6.05	4.60
		6.10	4.55
		6.25	3.98
		6.33	3.45
	1.20	5.95	4.37
		6.33	2.95
	1.40	5.89	4.48
		5.95	3.78
		6.33	2.54
3.00	1.00	5.95	7.65
		6.22	5.59
		6.34	5.07
4.00	1.00	5.95	10.3
		6.22	7.25
		6.34	6.95

EDTA and a buffer, and the absorbance at 570 nm for PAC or at 555 nm for 2-IAC was recorded as a function of the reaction time. From plots of $\log(A_t-A_\infty)$ *vs.* the reaction time (t), Reaction 1 was recognized to be of pseudo first-order with respect to $\mathrm{NiL_2}$ in both cases. The conditional rate constants, $k_{0(\mathrm{L,EDTA,H})}$, obtained are shown in Tables 1 and 2.

These results indicate that the values of $k_{0(\mathrm{L,EDTA,H})}$ are proportional to the EDTA concentration and to the reciprocal of the indicator concentration in both cases, as for the case of TAC. Plots of $k_{0(\mathrm{H})}$ *vs.* $[\mathrm{H^+}]$ give straight lines (Fig. 1).

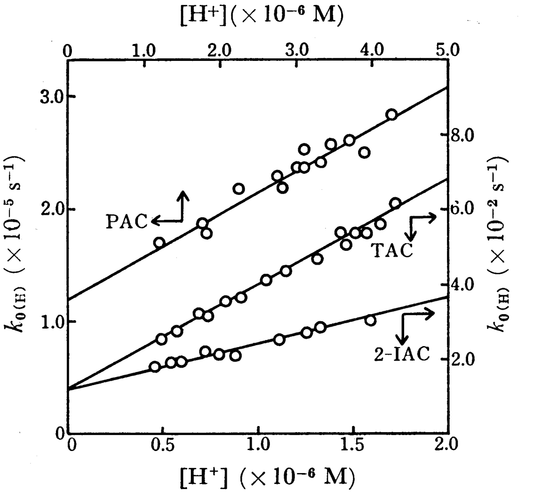

Fig. 1. Plots of $k_{0(\mathrm{H})}$ *vs.* $[\mathrm{H^+}]$.

Therefore, the rate law can be expressed as

$$-\frac{\mathrm{d[NiL_2]}}{\mathrm{d}t}=k_{0(\mathrm{H})}\frac{[\mathrm{NiL_2}][\mathrm{edta'}]}{[\mathrm{HL}]}$$

$$=(k_1'[\mathrm{H^+}]+k_2')\frac{[\mathrm{NiL_2}][\mathrm{edta'}]}{[\mathrm{HL}]}, \qquad (4)$$

where [edta′] is the total concentration of the EDTA not combined with nickel ions. The reaction mechanism is the same as that in the case of TAC:

$$\mathrm{NiL_2 + H^+ \rightleftarrows NiL^+ + HL}, \qquad (5)$$

$$\mathrm{NiL^+ + edta'} \xrightarrow{k_1} \mathrm{Ni(edta)^{2-} + HL}, \qquad (6)$$

$$\mathrm{NiL_2 + H_2O \rightleftarrows NiL(OH) + HL}, \qquad (7)$$

$$\mathrm{NiL(OH) + edta'} \xrightarrow{k_2} \mathrm{Ni(edta)^{2-} + HL + OH^-}. \qquad (8)$$

Reactions 5 and 7 precede Reactions 6 and 8, and the reactions of $\mathrm{NiL^+}$ and NiL(OH) with EDTA are the rate-determining steps. Equation 4 can be rewritten as

$$-\frac{\mathrm{d[NiL_2]}}{\mathrm{d}t}=k_1[\mathrm{NiL^+}][\mathrm{edta'}]+k_2[\mathrm{NiL(OH)}][\mathrm{edta'}], \qquad (9)$$

where $k_1=k_1'K^{\mathrm{L}}_{\mathrm{NiL_2}}/K^{\mathrm{H}}_{\mathrm{HL}}$ and $k_2=k_2'K^{\mathrm{L}}_{\mathrm{NiL_2}}/K^{\mathrm{H}}_{\mathrm{HL}}K^{\mathrm{OH}}_{\mathrm{NiL(OH)}}K_{\mathrm{W}}$. The values of k_1' and k_2' are obtained from the slopes and y-intercepts, respectively, of the straight lines in Fig. 1. For PAC and 2-IAC, the values of $K^{\mathrm{OH}}_{\mathrm{NiL(OH)}}$ could not be estimated. The rate constants are summarized in Table 3.

TABLE 3. RATE CONSTANTS

25 °C, $\mu=0.1$, dioxane 20%v/v.

	PAC	TAC	2-IAC
$k_1'(\mathrm{M^{-1}\,s^{-1}})$	3.7	2.7×10^4	1.3×10^4
$k_1(\mathrm{M^{-1}\,s^{-1}})$	6.9×10	2.1×10^3	3.9×10^3
$k_2'(\mathrm{s^{-1}})$	1.2×10^{-5}	1.3×10^{-2}	1.2×10^{-2}
$k_2(\mathrm{M^{-1}\,s^{-1}})$	—	7.9×10^6	—

Discussion

As shown in Table 4, the basicities of donor atoms of TAC are less than those of PAC, and the rate constants for TAC are smaller than those for PAC. In the substitution reactions of copper(II)–PAC and TAC chelates with EDTA, the same results were observed.[5] On the other hand, although the basicity of 2-IAC is larger than that of PAC, the rate constants for 2-IAC are much greater than those for PAC and are almost equal to those for TAC. This is in good agreement with the correlation between the reagent basicities and the nickel chelates stabilities, *i.e.*, in spite of the larger 2-IAC basicity, the formation constants for nickel chelates are smaller than those for nickel–PAC chelates. The coordination bond of the nitrogen atom in the imidazole ring of 2-IAC should be weaker than that in the pyridine ring of PAC. The characteristics of the nitrogen in the imidazole ring may be somewhat different from those of the nitrogen in the pyridine ring due to the resonance between pyridine-like and pyrrole-like nitrogens.

TABLE 4. EQUILIBRIUM CONSTANTS

25 °C, $\mu=0.1$, dioxane 20%v/v.

	PAC	TAC	2-IAC
pk_1	2.22	<0.5	3.68
pk_2	9.58	8.34	9.22
log K_{NiL}	11.18	8.00	8.95
log $K_{\mathrm{NiL_2}}$	10.85	7.24	8.70

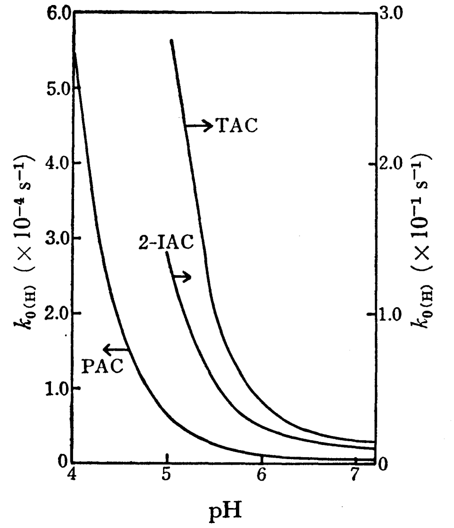

Fig. 2. Dependence of the rate of color change on pH.

Table 5. Amounts of nickel titration in an acetate buffer at 80 °C

pH	Ni taken (mg)	Ni found (mg)		
		PAC	TAC	2-IAC
4	5.78	5.88		
	11.55	11.61		11.44
4.5	5.78	5.89	5.50	5.77
5	5.78	6.21	5.64	5.78
	11.55	11.70	11.31	11.54
5.5	2.89		2.87	2.88
	5.78		5.75	5.78
	11.55		11.48	11.56
6	5.78		5.78	5.78
	11.55		11.56	11.56
6.5	2.89		2.90	2.90
	5.78		5.78	5.78
	11.55		11.57	11.56
7	5.78		5.78	5.83

The rate constants, $k_{0(\mathrm{H})}$, are plotted against the pH in Fig. 2. In the titration of nickel, the rate of indicator color change decreases with increasing pH, so that titration at lower pH results in a higher rate of indicator color change. However, the equilibrium conditions and the color contrast between the free indicator and the nickel chelate restrict the pH range for titration to pH 6—8 (PAC), pH 6—7 (TAC), and pH 6—8 (2-IAC). Within these pH ranges, free PAC, TAC, and 2-IAC are yellow and the nickel chelates are red-violet for PAC and 2-IAC, and blue for TAC. At higher pH values, the free indicators are red-orange due to dissociation of the phenolic proton, and visual detection of end point is difficult due to the poor color contrast. The results of nickel titrations using PAC, TAC, and 2-IAC are shown in Table 5. When titration using PAC was carried out at pH 4 and at 80 °C, the end point was overshot. Thus, titration should be performed slowly with boiling. Since the conditional formation constant for the nickel–TAC chelate is too small for pH values less than 6, using TAC the end point appeared too soon. If the nickel concentration is large, even at pH values higher than 6, a negative error often occured because of the poor visibility of the color change from blue to yellow-green. In the case of 2-IAC, although the conditional formation constant for the nickel–2-IAC chelate is of the same order as that of the nickel–TAC chelate, the end point was correctly detected, even at pH 5, because it is easy for the human eye to detect the color change from red-violet to yellow or yellow-green. At pH values higher than 7, a positive error occured due to the slow rate of indicator transition. From these results, the optimum pH ranges for nickel titrations are pH 4—5 with PAC, 6—7 with TAC, and 5—7 with 2-IAC. Thus, of these three, 2-IAC is the best indicator for nickel from the standpoints of good visibility of the color change and a wide optimum pH range.

By the addition of a small amount of 1,10-phenanthroline, titrations can be carried out at 50 °C using TAC[4] or 2-IAC,[3] while in the case of PAC, the rate of color change is not sufficiently enhanced.

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