Spectrophotometric Determination of the Acid Dissociation Constants of Phenylazochromotropic Acid Derivatives

Kyoji Tôei, Haruo Miyata and Toshiya Shibata[*1]

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

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Various phenylazochromotropic acid derivatives having functional groups in the ortho, meta, or para position of the phenyl group have been synthetized, and their behavior as analytical reagents has been studied.[1] Moreover, their acid dissociation constants have been estimated spectrophotometrically.[2]

This paper will report on the synthesis of 3- and 4-(1, 8-dihydroxy-3, 6-disulfo-2-naphthylazo)-phenoxyacetic acid and on the spectrophotometric determination of their acid dissociation constants

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[*1] Present address: Osaka Gas Co., Ltd., Osaka.

[1] For example, H. Miyata, This Bulletin, **36**, 382 (1963).

[2] H. Miyata, *ibid.*, **37**, 426 (1964).

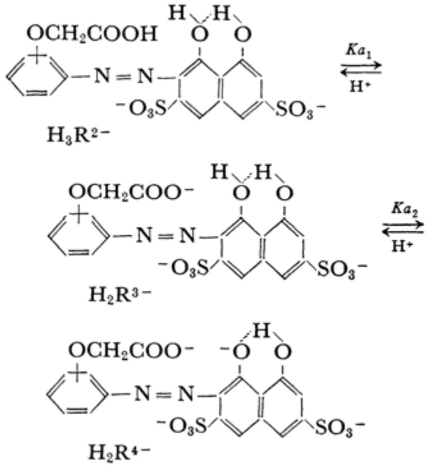
Synthesis of the Reagents. *Synthesis of 3-(1, 8-Dihydroxy-3, 6-disulfo-2-naphthylazo)phenoxyacetic Acid (abbr. 3-PAC).* The acetylation of *m*-aminophenol with acetic anhydride afforded the acetyl derivative which was then converted to the *m*-acetaminophenoxyacetic acid[3] by reaction with monochloroacetic acid in an alkaline medium.

m-Aminophenoxyacetic acid[4] was obtained by the hydrolysis of the corresponding acetamino derivative with hydrochloric acid.

3-PAC was prepared by coupling chromotropic acid with diazotized *m*-aminophenoxyacetic acid. The disodium salt was obtained as greenish needles by the recrystallization of the crude product from water.

Synthesis of 4-(1, 8-Dihydroxy-3, 6-disulfo-2-naphthylazo)phenoxyacetic Acid (abbr. 4-PAC). The disodium salt of the reagent was obtained as reddish brown needles in a manner similar to that described for 3-PAC.[5]

Acid Dissociations of the Reactions. The acid dissociations of the reagents are as follows:



The constants of the above dissociation, K_{a_1} and K_{a_2}, are:

$$K_{a_1} = [\mathrm{H}][\mathrm{H_2R}]/[\mathrm{H_3R}] \quad (1)$$

and

$$K_{a_2} = [\mathrm{H}][\mathrm{HR}]/[\mathrm{H_2R}] \quad (2)$$

respectively. If the two dissociation steps are separated widely enough, these dissociation equilibria can be treated independently. In this case, the concentrations are proportional to the absorbances, and $\mathrm{p}K_{a_1}$ and $\mathrm{p}K_{a_2}$ are obtained by the following equations:

$$\mathrm{p}K_{a_1} = -\log[\mathrm{H}] - \log\{(E_{\mathrm{H_3R}} - E)/(E - E_{\mathrm{H_2R}})\} \quad (3)$$

$$\mathrm{p}K_{a_2} = -\log[\mathrm{H}] - \log\{(E_{\mathrm{H_2R}} - E')/(E' - E_{\mathrm{HR}})\} \quad (4)$$

where $E_{\mathrm{H_3R}}$, $E_{\mathrm{H_2R}}$ and E_{HR} represent, respectively, the absorbances of H_3R, H_2R, and HR at a constant wavelength, and where E and E' represent the absorbances of a mixture of H_3R and H_2R or H_2R and HR respectively.

Absorption Spectra. The procedure of the measurements of the absorption spectra has been described earlier.[2]

The pH values of the solutions of the 3- and 4-PAC were adjusted with perchloric acid, sodium hydroxide, or a buffer solution, while the ionic strength was adjusted with sodium perchlorate to 0.1. An EDTA solution was added to mask trace amounts of calcium or magnesium possibly present in the sodium hydroxide or ammonium chloride.

The spectra were observed with a Hitachi automatic recording spectrophotometer, EPS-2 type, while the absorbances were measured with a Shimadzu spectrophotometer, QR-50 type, equipped with 1-cm cells, using water as a reference. The pH values were measured with a Toa-Denpa, Model HM-8A, pH meter. All the measurements

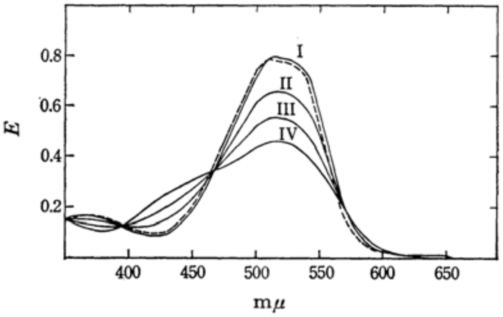


Fig. 1. Absorption spectra of 3-derivative.

Broken line		pH 0.97
Curve	I	5.79
	II	9.27
	III	9.88
	IV	12.10

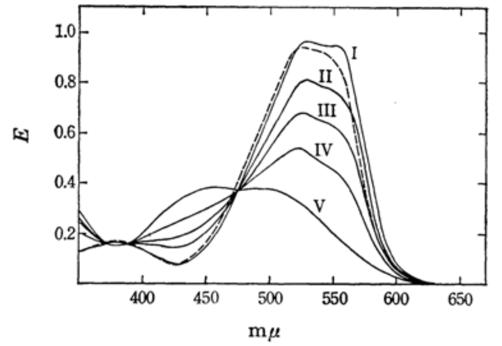


Fig. 2. Absorption spectra of 4-derivative.

Broken line		pH 1.0
Curve	I	5.76
	II	8.58
	III	8.98
	IV	9.33
	V	12.71

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3) W. A. Jacobs and M. Heidelberger, *J. Am. Chem. Soc.*, **39**, 2192 (1917).

4) C. C. Howard, *Ber.*, **30**, 547 (1897).

5) W. A. Jacobs and M. Heidelberger, *J. Am. Chem. Soc.*, **39**, 2196 (1917).

were made at 25°C.

The absorption spectra in the range from 350 to 700 mμ of 3- and 4-PAC (2.5×10^{-5} M) in perchlorate solutions with an ionic strength of 0.1 over various pH values are shown in Figs. 1 and 2 respectively.

The Acid Dissociation Constants. The pK_a values were determined spectrophotometrically from the absorbance-pH data, using Eqs. (3) and (4). The absorbances were measured at 510 mμ for pK_{a_2} of 3-PAC, at 580 mμ for pK_{a_1}, and at 550 mμ for pK_{a_2} of 4-PAC. The results are shown in Table 1.

The first dissociation constant of the 3-PAC could not be obtained, because the difference in absorbance between H_2R and H_3R was small, even though the concentration of the reagent increases up to 5×10^{-5} M. Therefore, it was found too hard to determine it spectrophotometrically.

As Figs. 1 and 2 show, the absorption spectrum of H_3R is almost the same as that of H_2R, which corresponds with the dissociation of the $-OCH_2COOH$ group, while the spectrum of H_2R is different from that of HR. This means that the dissociation of a proton from the $-OCH_2COOH$ group will hardly influence the resonance structures of the reagent, even if in the ortho[6] and para positions with regard to the azo group.

TABLE 1. pK_a VALUES OF 2-, 3- AND 4-(1,8-DIHYDROXY-3,6-DISULFO-2-NAPHTHYLAZO)-PHENOXYACETIC ACIDS
(25°C, μ=0.1)

	pK_{a_1}*	pK_{a_2}
2-PAC[6]	2.9_9	9.7_6
3-	—	9.4_8
4-	3.0_4	9.0_3

* The values were obtained from 5×10^{-5}M solution.

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[6] K. Toei, H. Miyata, T. Shibata and S. Miyamura, This Bulletin, **38**, 334 (1965).