

Polarographic Analysis of Reductive Fading Reactions of 4-Aza-2'-Methyl-4'-Diethylaminophenyl-Quinones

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This paper concerns the effect of substituent groups of phenolic couplers on dark stability of cyan quinonimine dyes deduced from the polarographic analysis of the solutions of two structure types of this class of dyes. These dyes were prepared by oxidative coupling of CD-2 developing agent (2-amino-5-diethylaminotoluene) with *m*-cresol or a 2-,5-diacylaminophenol. Polarographic measurements of these dyes were carried out in a mixture of ethanol and Britton-Robinson (borate-acetate-phosphate) buffer solution (volume ratio, 1.5 : 1) as a supporting electrolyte at $20 \pm 0.2^\circ\text{C}$, bubbled with nitrogen gas. Plots of E versus $\log\{i/(i_d - i)\}$ reveal that the leuco dye formations of these dyes are two-electron processes. In the case of the *m*-cresol dye, the proton number calculated from a plot of pH versus $E_{1/2}$ was 2.8 in the range of pH 6.1~6.9, and 2.0, pH 7.1~7.8. Consequently, the fading reaction of the dye can be written as follows: $\text{Dye} + 2e + 3\text{H}^+ \rightarrow \text{Leuco Dye} \cdot \text{H}^+$ (Protonated Leuco Dye), in the lower pH region, and $\text{Dye} + 2e + 2\text{H}^+ \rightarrow \text{Leuco Dye}$, in the higher pH region. The half-wave potential of the acylaminophenol dye was much more negative than that of the *m*-cresol dye. Thus, the fading reaction of the dye does not proceed easily in the presence of a reducing agent. The proton number that the dye required was approximately 2.0 in the pH range 5.9~7.6. The chemical equation for the redox reaction of the dye can be expressed as follows: $\text{Dye} + 2e + 2\text{H}^+ \rightarrow \text{Leuco Dye}$. The *m*-cresol dye could be easily reduced and thus fade in the presence of thiosulfate or EDTA-Fe(II), because there was a big difference between the half-wave potential of the dye and these reducing agents. For example, in the faded solution with thiosulfate polarographic waves of the leuco dye and tetrathionate ions were observed separately. Therefore, the leuco dye formation of *m*-cresol dye in the fading reaction with reducing agent can be written as follows: $\text{Dye} + 2\text{Red.} + 3\text{H}^+ \rightarrow \text{Leuco Dye} \cdot \text{H}^+ + 2\text{Ox.}$ in the lower pH region, $\text{Dye} + 2\text{Red.} + 2\text{H}^+ \rightarrow \text{Leuco Dye} + 2\text{Ox.}$ in the higher pH region. On the other hand, the half-wave potential of the acylaminophenol dye is close to those of the reducing agents. As a result, the polarographic waves of the leuco dye and the oxides of the reducing agents were not observed separately. It is suggested that the cyan dye image formed with an acylaminophenol dye would be much more stable than a *m*-cresol dye under the reductive conditions. Consequently, some basic information to predict dark stability of cyan quinonimine dye images under reductive conditions can be obtained by measurement of the half-wave potential of dye solutions.

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Introduction

Dark fading of chromogenic cyan dye image is a concern where certain reducing agents exist: for instance, residual cyan coupler, retained thiosulfate, ferrous ions and ballasted hydroquinones. Any of these might cause reductive fading of cyan dye to produce the leuco form^{1,2,3}. In the previous paper⁴, T. Miyagawa and Y. Shirai reported reductive fading reactions of both a pyrazolone azomethine dye (magenta) and a naphthoquinonimine dye (cyan) which had simple structures. This paper presents basic information on the stability of quinonimine dyes, deduced from polarographic analysis on fading of dyes with reducing agents such as thiosulfate and EDTA-Fe (II). These dyes were prepared from CD-2 developing agent and couplers—*m*-cresol (Dye I) or an acylaminophenol (Dye II)—in order to study the effects of substituent groups on half-wave potentials of redox systems of dyes.

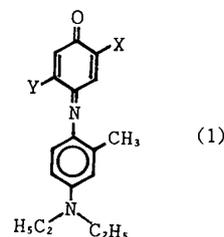
Preparation and Characteristics of Dyes

These dyes (1) were synthesized by means of oxidative coupling of CD-2 developing agent (2-amino-5-diethylaminotoluene) with the corresponding couplers, *m*-cresol (Dye I) or 2-,5-diacylaminophenol (Dye II), in the presence of hydrogen peroxide and silver powder catalyst. Dyes were purified by means of column chromatography using silica gel (Wako Gel C-200) and solvent (benzene: acetone = 9: 1 volume

ratio). The characteristics of the dyes are shown in Table I. Dye I has a 5-methyl group as its only substituent, while Dye II has two different acylamino groups in the 2- and 5-positions.

Polarographic Analysis of Dye Solution

Polarographic measurements on these dyes were carried out to clarify the redox mechanisms of leuco dye formation. In these experiments, the concentration of dye 1.2×10^{-4} mol/l, and a mixture of ethanol and Britton-Robinson buffer (borate-acetate-phosphate) solution (volume ratio, 1.5 : 1) was employed as a supporting electrolyte at $20 \pm 0.2^\circ\text{C}$, bubbled with nitrogen gas. An H-type cell with a calomel electrode was used to contain the solution. From the relation between the square root of the height of the mercury head, \sqrt{h} , and limiting current i_l , we conclude that diffuse current predominantly contributes to the



Dye I -X: -H -Y: -CH₃

Dye II

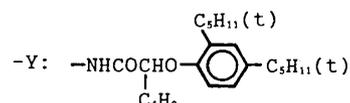
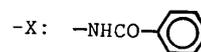


Table I. Characteristics of Dyes

No.	Melting Point ($^\circ\text{C}$)	Characteristics in Ethanol Solution	
		λ_{max} (nm)	Molar Extinction Coefficient
Dye I	115~116	632	2.26×10^4
Dye II	78~79	664	8.13×10^3

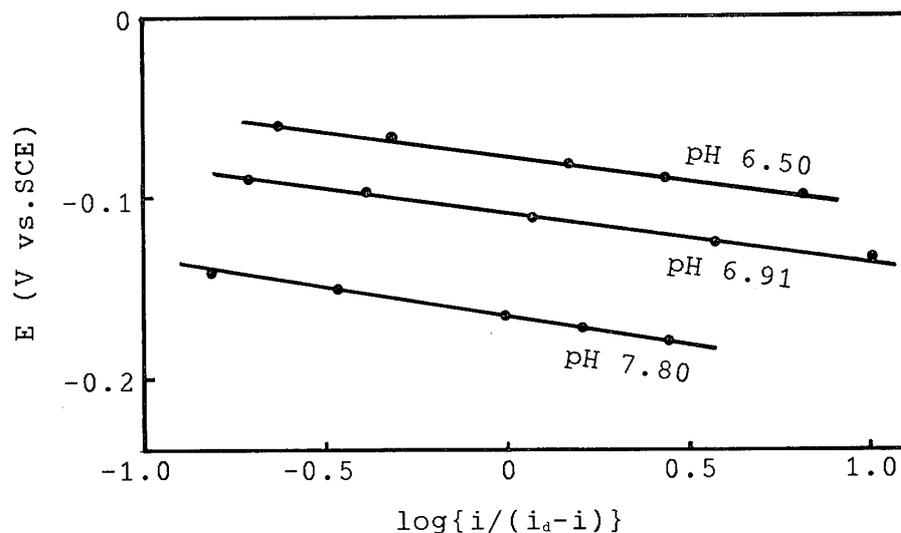
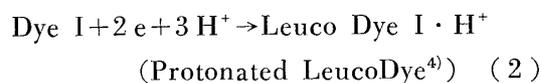


Figure 1. $E-\log\{i/(i_d-i)\}$ plots of Dye I solution at various pHs.

redox reaction of dyes on a mercury electrode. The numbers of electrons and protons these dyes required in the reaction process to produce leuco dye were calculated. In the case of Dye I, plots of E versus $\log\{i/(i_d-i)\}$ for the dye solution in the range of pH 6.5~7.8 were parallel to each other, as shown in Fig. 1. These straight lines have about a 30 mV slope. Thus, slope of $E-\log\{i/(i_d-i)\}$ plottings

of Dye II is similar to that of Dye I. This means that leuco dye formation for these dyes is a two-electron process.

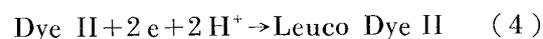
Half-wave potentials of these dyes depend on pH value as shown in Fig. 2. These lines were drawn by means of the least square method. In the case of Dye I, the slope of half-wave potential versus pH is about 82 mV in the range of pH 6.1~6.9, but it changes to about 58 mV in the range of pH 7.1~7.8. Consequently, the proton numbers calculated are 2.8 at lower pHs, and 2.0 at higher pHs. From these results, chemical equations proposed for the reductive fading of Dye I to form leuco dye are as follows: in the lower pH region,



in the higher pH region,



The redox reaction system of Dye II can be expressed in the following equation, over the whole range of pH 5.9~7.6:



Dye II has much more negative potential than Dye I. It seems that the reductive fading of 2-,5-diacylaminophenol dye is much more dif-

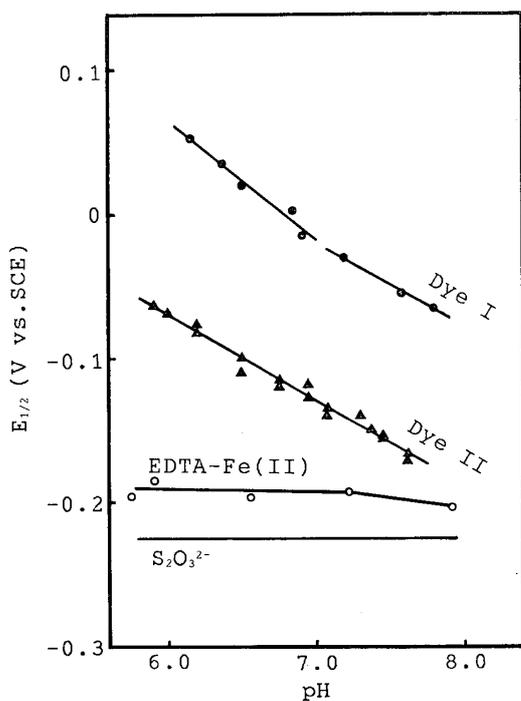


Figure 2. Relation between pH values and $E_{1/2}$ of dyes and reducing agents.

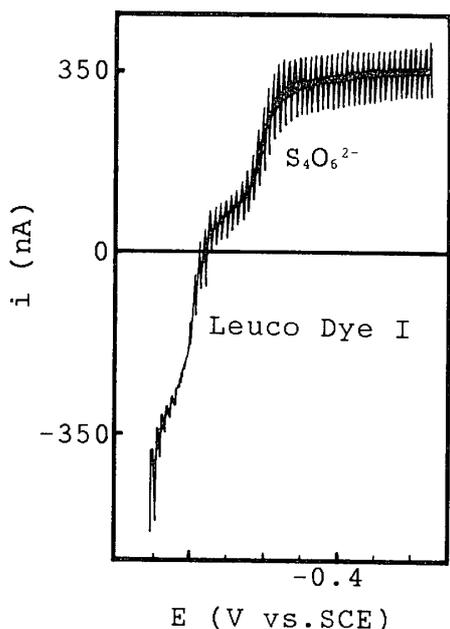


Figure 3. Polarogram of reduced Dye I solution by thiosulfate at pH 7.00. 1.2×10^{-4} mol/l. concentration of Dye I and 1.2×10^{-4} mol/l. of thiosulfate were mixed at the initial time of reaction. Polarographic waves of Leuco Dye I and tetrathionate are observed separately to each other.

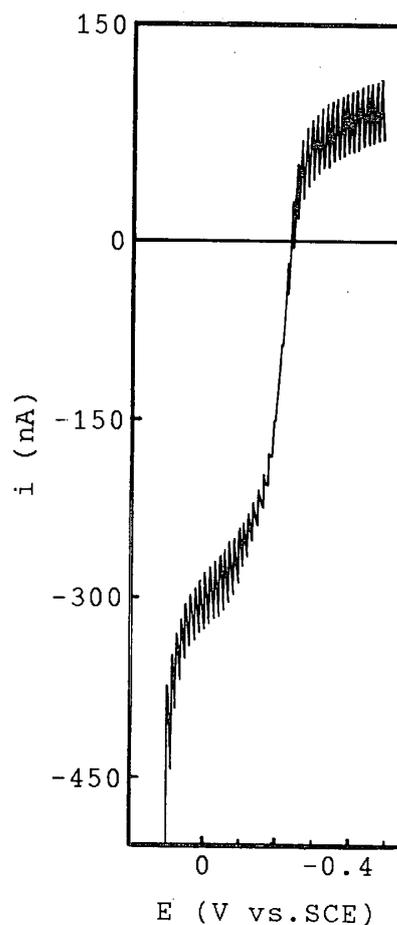


Figure 4. Polarogram of partially reduced Dye II solution by thiosulfate at pH 6.21. 1.2×10^{-4} mol/l. concentration of Dye II and 1.2×10^{-4} mol/l. of thiosulfate were mixed at the initial time of reaction. Polarographic waves of Leuco Dye II and tetrathionate are not separated to each other, because half-wave potential of Dye II is close to that of thiosulfate.

Table II. Half-Wave Potentials of Dye I and Leuco Dye I (V vs. SCE)

pH	Dye I	Leuco Dye I	
		With thiosulfate	With Fe(II)
6.00	+0.03	+0.04	+0.01
6.68	0.00	0.00	+0.01
7.00	-0.04	-0.03	-0.03
7.82	-0.06	-0.07	-0.06

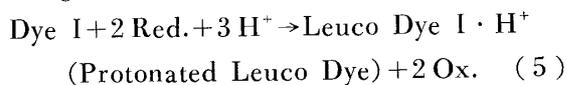
ficult compared with the m-cresol dye.

Polarographic Analysis of The Solution Containing Dye and Reducing Agents

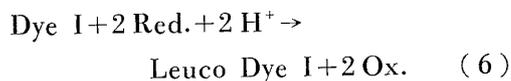
The polarogram of a Dye I solution which was reduced by thiosulfate or EDTA-Fe (II) supported the redox mechanism of the dye fading reaction. In these experiments, sodium thiosulfate or EDTA-Fe (II) was added into the dye solution. The mixed solution was

prepared to contain 1.2×10^{-4} mol/l of dye and 0.3×10^{-4} mol/l to 1.2×10^{-4} mol/l of reducing agent. One of these results is shown in Fig. 3. As Dye I became Leuco Dye I, the polarographic wave of the dye fell to the bottom of the chart, and that of thiosulfate rose to the upper portion, showing the change to tetrathionate. Half-wave potentials of Dye I and the leuco dye which is formed by two different reducing agents are shown in Table II. These values are very close to each other over the whole pH range of the experiments. From these results, the leuco dye formation in the fading

reaction of Dye I with thiosulfate or EDTA-Fe (II) can be written as follows: in the lower pH region,



in the higher pH region,



Half-wave potentials of reducing agents are also illustrated with those of Dye I and Dye II in Fig.2. The potential of thiosulfate is independent of pH value, as is well-known. In the case of EDTA-Fe (II), slightly lower values are observed in the higher pH region. The latter is similar to the result illustrated in T. H. James' book⁵⁾.

On the other hand, polarographic waves of Leuco Dye II and oxides of reducing agents were not observed separately as shown in Fig. 4, because the half-wave potential of Dye II was much more negative and it was close to the reducing agents. It is suggested that the redox reaction system may come into an equilibrium with little action after mixing.

Discussion

Both Dye I and Dye II were prepared from CD-2 developing agent as stated above. Reductive fading of Dye I with thiosulfate or EDTA-Fe(II) is facile, because there is a big difference in half-wave potential between the dye and reducing agents. On the other hand, Dye II has a resistance to reductive fading due to a more negative half-wave potential. From the viewpoint of chemical structure of the dye molecules, Dye I has only one methyl group in the 5-position, a strong electron releasing group, while Dye II has two different acylamino groups in both the 2- and 5- positions. Although the electron releasing property of an acylamino group is somewhat weaker than a

methyl group, these two substituent groups are in co-operation to protect both double bonds of keto and azomethine structures from reducing action (prevention against change into single bonds). As a result, substitutions of acylamino groups both in the 2- and 5- positions make the half-wave potential of Dye II much more negative. In other word, a cyan image formed with Dye II would be more stable under reductive conditions. Consequently, some basic information to predict the dark stability of cyan quinonimine dye images under reductive conditions can be obtained by measurement of the half-wave potentials of dye solutions.

Conclusion

Reductive fading reactions of two kinds of cyan dyes prepared from CD-2 with m-cresol (Dye I) or 2-,5-diacylaminophenol (Dye II) were studied by means of polarographic analysis.

1) Redox reaction of Dye I to form leuco dye is as shown in Eq. (2) in the lower pH region, and in Eq. (3) in the higher pH region. The reaction system of Dye II can be expressed by Eq. (4) for the whole pH range of the experiments.

2) Leuco dye formation in the fading reaction of Dye I with thiosulfate or EDTA-Fe (II) can be written as shown in Eq. (5), in the lower pH region, and in Eq. (6) in the higher pH region.

3) Dye II has a resistance to reductive fading in the presence of thiosulfate or EDTA-Fe (II), due to a more negative half-wave potential close to those of the reducing agents used in this study.

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