呈色試藥의 發色에 미치는 陽이온 表面活性劑의
영향(第 1 報). Zephiramine 의 存在下에서
여러가지 술포프탈레인 指示藥의 解離常數

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The Influence of the Cationic Surfactant on the Coloration of Chromogenic Reagents(I). The Dissociation Constants of Sulfophthalein Indicatiors in the Presence of Zephiramine

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要 約. 양이온 표면활성제인 Zephiramine 의 存在下에서 여러가지 술포프탈레인 指示藥의 吸收스 펙트럼과 해리상수를 測定하여 수용액에서의 값과 비교했다. 鹽基性赤色型은 吸收 극대가 6~21 nm 長波長쪽으로 移動하며 吸收度는 약간 증가하는 反面, 黃色型은 吸收극대가 오히려 4~20 nm 短波 長으로 移動하고 吸收度도 약간 감소했다. pKa 값은 $-1.38 \sim +0.37$ 정도 변화했다. 이와같은 呈色 反應을, 色素分子가 미셀 表面에 吸着됨으로서 더 安定한 共面구조를 形成하기 때문이라는 假定으 로 說明했다.

ABSTRACT. The absorption spectra and the dissociation constants of various sulfophthaleins have been measured in the presence of a cationic surfactant. In the presence of 2.0×10^{-5}M zephiramine and an ionic strength of 0.05 at $25 \pm 1°C$ the absorption maxima of the basic forms are shifted to red by 6~21 nm and their molar absorptivities are increased, while the absorption maxima of the yellow forms are shifted to blue by 4~20 nm and their molar absorptivities are decreased. The decreases in pKa values are of the order of ranging $-1.38 \sim 0.37$.

The characteristic of the observed changes has been explained by the assumption that the dye molecule adsorbed on micellar surface forms a stable coplanar structure easily and then the conjugation in the dye molecule is elevated.

INTRODUCTION

Recently, many absorptiometric determinations of metal ions have been investigated in the presence of a cationic surfactant of long-chain quaternary ammonium salt[1~6]. The addition of relatively small amount of a cationic surfactant to the colored solution of a metal causes a mark-

ed color change with a bathochromic shift and increase in sensitivity. From the analytical viewpoint, this mode of reaction is the most interesting, because it is considered to be more generally applicable and one of the most sensitive method available for the absorptiometric determination of metal ions.

Many explanations have been given for the reaction mechanism involving the color change[7~9]. The protolytic dissociation of an acid dye molecule is promoted on the micellar surface on account of the preferential adsorption of the anion. The chelate reaction seems to be affected by micellar ions[10], and it has been suggested that a ternary[11] or a higher-order complex[8] is formed with the micellar ion, and that this complex is more stable than the original chelate. However, the color changes, bathochromic shifts and the increase in sensitivity, could not be explained only in terms of both the promotion of the protolytic dissociation of the dye and the formation of a stable ternary complex on the micellar surface. Bunton et al.[12,13] have suggested a sandwich model for the adsorption of organic acids on the micelle and interpreted the promotion of the protolytic dissociation in terms of the attractive force due to both the electric and hydrophobic properties between the micelle cation and acid anion. This suggestion seems to be applicable to a simple organic acid such as benzoic acid or phenol, but it can not successfully explain the color change of a complicating acid dye such as the sulfophthalein.

The present study was initiated for the purpose of the elucidation of the coloration mechanism. The absorption spectra and the dissociation constants of various sulfophthalein indicators were measured in the presence of zephiramine and compared each other, and an adsorption model has been postulated to account for the nature of observed changes.

EXPERIMENTAL

Materials. All chemicals used throughout this work were of reagent grade and used without further purification. Zephiramine (tetradecyldimethylammonium chloride) was Dotite-grade reagent, and measurements were made on solutions in concentration of $2.0 \times 10^{-3} M$. All sulfophthaleins used were obtained from different sources commercially available. The chemicals used for buffer solutions were as follows; monochloroacetic acid and sodium monochloroacetate for pH 2~3.8, acetic acid and sodium acetate for pH 3.8~5.5, triethanolamine and hydrochloric acid for pH 5.5~8, and ammonia and ammonium chloride for pH 8~10.5.

Measurements. The absorption spectra were recorded on Hitachi 124 spectrophotometer using 1 cm cells. All pH measurements were made using TOA HM-7A pH meter.

The acid dissociation constants were determined spectrophotometrically. All absorbance and pH measurements were made on solutions of a constant ionic strength at $25 \pm 1\,^{\circ}C$. For an ionic strength of 0.05, a stock solution, A, was prepared containing $0.45 M$ of a salt of a monobasic weak acid or of a salt of a monoacidic weak base. The pH was varied by adding various amounts of a stock solution, B, which contained either $1 M$ weak acid or weak base. A series of an indicator solution of varing of pH and constant ionic strength, 0.05, was prepared in the following manner: 20~30mg of an indicator was dissolved in 10 m*l* of $1 N$ potassium hydroxide solution and diluted to 100.0 m*l* with water. 5 m*l* of this solution was placed in each 100 m*l* flask, followed by 10 m*l* of the stock solution A and 5 m*l* of $4 \times 10^{-2} M$ zephiramine. Stock solution B was added to adjust the pH to the desired value, then the mixture was diluted to 100.0 m*l* with water. After the absorbance had been measured, the pH value of

solutions were measured. The pK values were calculated by the conventional method.

Most sulfophthalein indicators in water exhibit two color change intervals; one from ~yellow to the strongly colored basic form and the other from yellow to the strongly colored acidic form. The present paper deals with only the pK values in relation to the color change of the former. In the case of the chlorophenol red, the plot of pH $vs.$ log(Base)/(Acid) gives a straight line with a slope of 1.74 as shown in $Fig.$ 1, and the pK value calculated from this curve could not give a constant. Therefore, the pH value at the midpoint, (Acid) = (Base), was taken as the pK value.

RESULTS

The structure of sulfophthaleins is formulated as I, in which one or more pairs of substituents
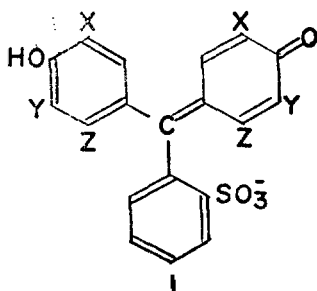
such as CH_3, $CH(CH_3)_2$, OH, COOH, Cl or Br are bonded at the positions denoted X, Y or Z. $Table$ 1 shows the wavelengths of the absorption maximum and the molar absorptivities in the presence of zephiramine. These values were measured at the selected pH at which the ionic species of each indicator was the same whether zephiramine is present or not except for the combination of the indictor anion with the micelle cations. The pK values and molar absorptivities of bromophenol blue, o-cresol red and bromocresol green in the presence of zephiramine have been reported by other and there are

small differences between those values and those of this work. However, these differences seem to be ascribed to the differences in ionic strength and the concentration of zephiramine.

The absorption maxima of the strongly colored basic forms were shifted to red by the order of 6~21 nm and their molar absorptivities were increased to a small extent by the addition of zephiramine. On the other hand, the absorption maxima of the yellow forms were shifted to blue by 4~20 nm and their molar absorptivities were decreased except for those of thymol blue and bromothymol blue.

$Table$ 2 shows the pK values of sulfophthaleins in the presence and in the absence of zephiramine. In the presence of zephiramine, the pK values of most sulfophthaleins are decreased but those of m-cresol purple and pyrogallol red are little varied and those of thymol blue and Eriochrome Cyanine R are increased. The decreases in pK value by the addition of zephiramine is proportional to the pK value of the indicator, but it does not show a fine
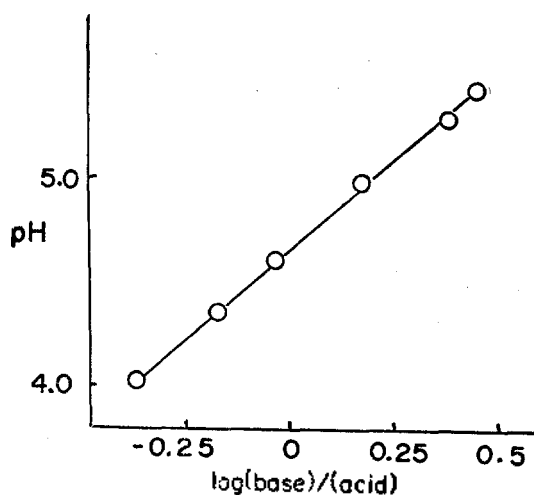

$Fig.$ 1. The plot of pH $vs.$ log (Base)/(Acid) for chlorophenol red in the presence of zephiramine. Chlorophenol red: $1.80\times10^{-5}M/l$, zephiramine: $2.0 \times10^{-3}M/l$, $\mu=0.05$.

Table 1. Abrorption maxima and molar absorptivities of sulfophthalein indicators in the presence of zephiramine at 25°C, $\mu=0.05$, zephiramine: $2\times10^{-3}M/l$.

Indicators	Yellow form				Basic red form			
	no zep.		in zep.		no zep.		in zep.	
	λ_{max}	$\epsilon\times10^{-4}$	λ_{max}	$\epsilon\times10^{-4}$	λ_{max}	$\epsilon\times10^{-4}$	λ_{max}	$\epsilon\times10^{-4}$
Bromophenol blue	434	2.93	423	2.56	588	8.40	604	8.86
Bromocresol green	440	2.31	423	2.23	614	5.20	629	5.20
Chlorophenol red	435	1.68	430	1.64	580	3.73	595	5.54
Bromocresol purple	430	1.69	415	1.60	586	7.37	592	7.80
Pyrogallol red	400	1.26	396	1.15	542	2.19	563	2.58
Bromothymol blue	430	1.78	410	1.80	614	3.53	626	3.80
Pyrocatechol violet	448	1.60	442	1.50	595	1.85	610	2.63
Phenol red	431	2.16	422	2.08	557	4.23	572	4.90
o-Cresol red	435	2.41	425	2.17	570	6.45	583	5.91
m-Cresol purple	434	1.64	420	1.53	576	2.34	590	3.24
Thymol blue	453	1.56	440	1.61	595	3.12	605	3.42
Eriochrome cyanine R	442	1.06	430	0.70	585	2.74	596	1.85

Table 2. pK values of sulfophthalein indicators in the absence and in the presence of zephiramine at 25° C, $\mu=0.05$, zephiramine: $2\times10^{-3}M/l$.

No.	Indicators	Substituted group			pK		ΔpK
		X	Y	Z	In aq.[a]	In zep.	
1	Bromophenol blue	Br	Br	H	4.00	2.86	1.14
2	Bromocresol green	Br	Br	CH₃	4.70	3.88	0.82
3	Chlorophenol red	H	H	Cl	6.05	4.67	1.38
4	Bromocresol purple	Br	CH₃	H	6.21	5.14	1.07
5	Pyrogallol red	H	OH	O—	6.54	5.61	0.93
6	Bromothymol blue	CH(CH₃)₂	Br	CH₃	7.13	6.87	0.26
7	Pyrocatechol violet	OH	H	H	7.82	7.76	0.06
8	Phenol red	H	H	H	7.84	7.22	0.62
9	o-Cresol red	CH₃	H	H	8.30	7.92	0.38
10	m-Cresol purple	H	H	CH₃	8.32	8.35	−0.03
11	Thymol blue	(CH(CH₃)₂	H	CH₃	8.95	9.32	−0.37
12	Erio chrome cyanine R	COOH	CH₃	H	12.1[b]	13.0[b]	−0.90

[a] Reference 15. [b] Reference 6

linear relation between them as shown in *Fig.* 2. However, no relation between the difference in pK value and the shift of the absorption maxima or the variation of the molar absorptivities was observed.

DISCUSSION

When a sulfophthalein anion is adsorbed on the positively charged surface of micellar aggregates, the conjugation in the molecule may be-
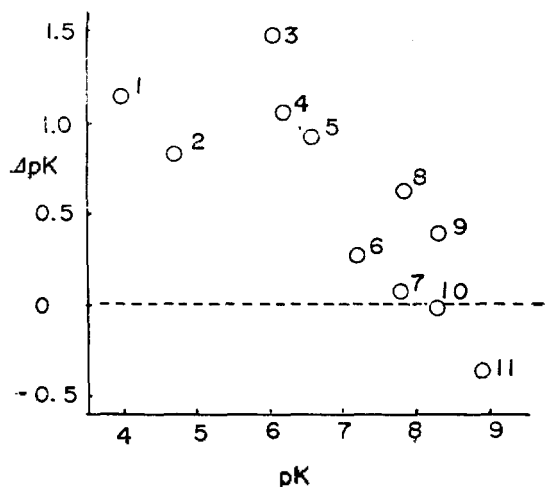
Fig. 2. The plot of $\Delta pK(pK_{aq}-pK_{sep})$ vs. pK_{aq} of sulfophthalein indicators[a]. [a]Numbers refer to Table 2

Scheme 1.

inhibited to some extent because of the localization of the electron which is ascribed to the interaction between positive charges of micelles and the anion site, and therefore, it can be expected that a hypsochromic shift occurs in the absorption band of the molecule on the micellar surface. This is in agreement with the fact that the absorption maxima of the yellow forms of sulfophthaleins are shifted to blue by the order of 4~20 nm. On the other hand, however, the absorption maxima of the strongly colored basic forms are shifted to red and their absorbances are increased on the micellar cation in spite of the inhibition of the conjugation. This effect of micellar aggregates on the coloration of the basic form may be assumed to be caused by some structural changes in the indicator molecule as a result of adsorption on the micellar surface. The structural change will be discussed with phenol red for an example.

Phenol red dissociates in aqueous solution as Scheme 1 [14].

When yellow form(II) is ionized into red form(I), the color change is accompanied by a structural change. In the yellow form(II), the
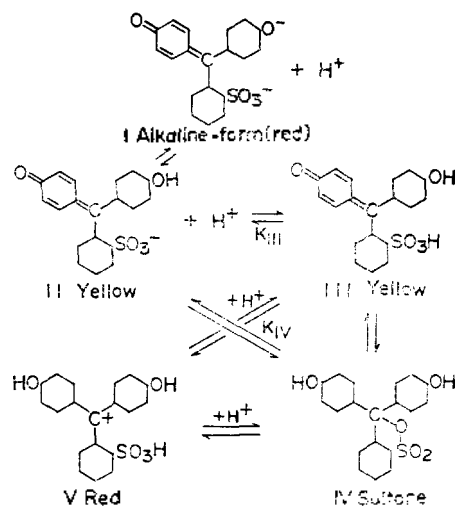
tricovalent carbon has a positive charge attributed to the resonance of the quinoid group and may form a tetrahedral bonding-structure as a result of the attractive force between it and the adjacent sulfonate ion. This structure may be similar to that of sultone(IV). In red form(I), the conjugation in the phenolate group is extended to the other phenolate though the tricovalent carbon, on which the influence of the sulfonate ion is eliminated as a result of the extended electron conjugation. The tricovalent carbon has, therefore, sp^2 hybridization and the two phenolic rings become coplanar to one another involving the tricovalent carbon. The idea that the influence of the sulfonate ion on the tricovalent carbon is related to the coloration of sulfophthaleins, is supported by the fact that most sulfophthalein indicators in a strong acid solution become red in spite of the both phenolic groups being not dissociated as form(V).

When this coplanar bonding-structure is kept more preferentially under a certain condition, the molar absorptivity must be increased as the probability of electron transition is increased. The micellar aggregates are very bulky and

their surface can be regarded as a plane by comparison with the indicator molecule. It can be expected that attractive force of positive charges of micelle acts on the oxygen of phenolate, carbonyl group, and the sulfonate ion of the indicator molecule. *Fig.* 3 shows the postulated adsorption model of phenol red on the micellar surface. It is clear that the molecule adsorbed on the micellar surface in this mode forms a planar structure more preferentially and that the conjugation easily extends to both phenolic groups with the tricovalent carbon. In addition, the adsorption of the sulfonate ion, which is bonded weakly at the tricovalent carbon and thus interferes with the conjugation, may contribute the conjugation as another effect. Therefore, the ease of forming the coplanar structure causes the bathochromic shift and promotes the protolytic dissociation of the phenol. The decrease in pKa value by the addition of zephiramine, as given in *Table* 2, is nearly proportional to the electrophilicity of the substituent group on the phenolic ring, and in the case of the

same substituent group the *m*-substituent (*Z* position in the structural formula I) exert more remarkable effect than that bonded at *o*-position (*X* or *Y* position). For example, the pK value of *o*-cresol red decreases more than that of *m*-cresol purple in the presence of zephiramine. These results seem to be ascribed to the fact that the electron density of the tricovalent carbon is decreased by the substitution of electron-attracting groups, then the electrostatic force between the carbonium ion and the sulfonate ion is increased. Therefore, when the sulfonate is strongly adsorbed, the effect of a cationic surfactant on the protolytic dissociation of such a sulfophthalein as substituted by electron-attracting groups is more marked than that substituted by electron-donating groups.

The fact that the pK value of thymol blue and Eriochrome Cyanin R are increased in the presence of zephiramine, can be explained in terms of these molecules forming a coplanar structure on the micellar surface. The isopropyl radical in thymol blue is electron-donating and bulky. When this molecule is adsorbed on the micellar surface and become a coplanar structure as formula II, the electron-donating effect of the isopropyl group seems to be increased, and thus the dissociation of phenolic proton may be difficult. In the case of the yellow form of Eriochrome Cyanine R the hydroxyl groups form a hydrogen bond with the adjacent carboxylate ion. When the carboxyl ion and the
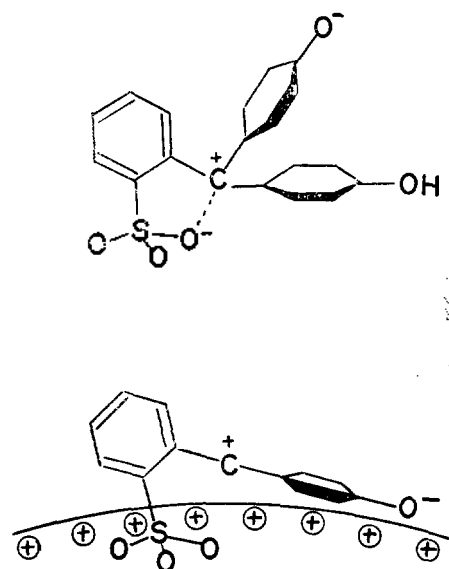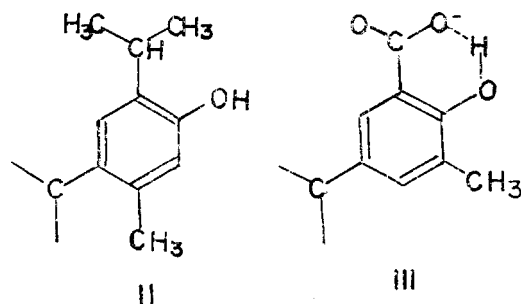

Fig. 3 The schematic adsorption model of phenol-sulfophthalein at micellar surface.

II

III

benzener ing are laid in the same plane on the micellar suface, the hydrogen bond becomes stable and make it difficult to dissociate the proton as shown in formula III.

REFERENCES

1. B. W. Bailay, J. E. Chester, R. M. Dagnal and T. S. West, *Talanta*, **15**, 1359 (1968).
2. V. Svoboda and V. Chromy, *Talanta*, **13**, 237 (1966).
3. Keihei Ueno, *Bunseki Kagaku*, **20**, 736 (1971).
4. Y. Shijo and T. Takeuchi, *ibid*, **20**, 980 (1971).
5. H. Nishida and T. Nishida, *ibid*, **21**, 997 (1972).
6. H. Nishida and T. Nishida, *ibid*., **22**, 963 (1973).
7. H. Kohara, *ibid*, **17**, 1147 (1968).
8. H. Kohara, N. Ishibashi and K. Fukamachi, *ibid*., **17**, 1400 (1968).
9. H. Nishida, *ibid*., **20**, 1080 (1971).
10. C. F. Hiskey and T. A. Downey, *J. Phy. Chem.*, **58**, 835 (1954).
11. J. E. Chester, R. M. Dagnal and T. S. West, *Talanta*, **17**, 13 (1970).
12. C. A. Bunton, M. J. Minch, J. Hidalgo and Luis Sepulveda, *J. Amer. Chem. Soc.*, **95**, 3262 (1973).
13. C. A. Bunton and M. J. Minch, *J. Phy. Chem.*, **78**, 1490 (1974).
14. I. M. Kolthoff, S. Bhowmik and M. K. Chantooni Jr., *Proc. Nat. Acad. Soc.*, **56**, 1370 (1966).
15. H. Yoshimura, H. Matsushida and T. Morimoto, "pH NO RIRON TO SOKUTEIHO" P. 74, Maruzen, Tokyo, 1968.