報 文

New Amphoteric Surfactants Containing a
2-Hydroxyalkyl Group. VI*Alkaline Fading Rate of Triphenylmethane Dye in
the Presence of Amphoteric Surfactant

Hisao HIDAKA, Hayashi KUBOTA, and Shuji YOSHIZAWA

Department of Chemistry, Faculty of Science and Engineering, Meisei University
(337, Hodokubo, Hino-shi, Tokyo)

The fading rate of triphenylmethane dye, crystal violet(CV), in an alkaline solution has been measured in the presence of amphoteric surfactant micelles by following the decrease in the maximum of the visible absorption spectrum of CV. The amphoteric surfactant used, *N*-(2-hydroxydodecyl)-*N*-(2-hydroxyethyl)- β -alanine (HAA), can exist in three different forms of cationic (C-HAA), zwitter ionic(Zw-HAA), and anionic(A-HAA) types depending on pH value.

The fading was expressed by a pseudo-first order rate and the rate was in the order of C-HAA > A-HAA > Zw-HAA. The surface electrostatic states affected the fading rate occurring in or on micelles. The effect of addition of electrolyte was also examined and the fading was gradually accelerated with increasing concentration of electrolyte.

The ratio of CV solubilized in micelles to CV existing the outside of micelles was calculated from the fading rate curves. The solubilization of CV decreased with increasing electrolyte concentration.

1 Introduction

Dye-containing micelles solution systems would be suitable for the study of models of photochemical energy transfer mechanism. Catalysis in micellar and macromolecular systems has been reviewed by Fendler and Fendler¹⁾. The effects of electrolyte and of structure of various surfactants were also examined by using an anion which was competitive to OH⁻ ion in the Stern layer of micelle surface. The micellar effect on an equilibrium between crystal violet(CV) and OH⁻ ion obeys the Hartley's "sign rule"²⁾. LDuynstee and Grundwald revealed that the nucleophilic reaction between CV and OH⁻ ion was accelerated in a cationic micelle system, while it was retarded in an anionic micelle system^{3),4)}. Effects of surfactant concentration and structure as well as the role of added electrolyte on the alkaline fading of CV have been reported by Albrizzio *et al*⁵⁾.

We studied the fading rate of CV in alkaline solution using amphoteric surfactant which can exist in three ionic forms, *i.e.* cationic, zwitter ionic, and anionic, depending on pH value. The characteristic of this study is that the rate can be measured for a charge-changeable surfactant without the change of the skeleton. The effects of the additions of electrolyte or alcohol on the fading rate were also investigated in order to examine micelle formation and bulky structure. Furthermore, an amount of CV solubilized in micelle was calculated from the break point of the log (OD_t-OD_∞) *versus* time plots.

2 Experimental

Materials

The CV used was special grade (Wako Pure Chem. Ind. Co. Ltd.). The preparation and purification of HAA were the same as described in the previous paper⁶⁾. HAA and equivalent NaOH was refluxed with stirring for 2 h in an alcoholic aqueous solution, followed by removal

* Previous paper; H. Hidaka, S. Yoshizawa, M. Takai, and M. Moriya, *Yukagaku*, **31**, 489 (1982).

of the solvent to give white crystal of A-HAA. In a similar way, the cationic type (C-HAA) was obtained by adding equivalent HBr to HAA in an alcoholic aqueous solution.

Measurement of Fading Rates

Fading rate measurements were carried out spectrophotometrically with a Shimadzu Double-40 D spectrophotometer. In a three neck Erlenmeyer flask equipped with a stirrer, which varies a revolution number in the reaction system, are placed a mixture of 10 ml CV solution (3×10^{-5} M) and 10 ml surfactant solution (3×10^{-2} M) in a thermostated bath maintained at 25°C. The addition of an alkaline solution was followed by the disappearance of the maximum absorption peak of CV near 592 nm. The reaction was initiated by the addition of 10 ml of 0.3 N NaOH solution. There is an equilibrium reaction between CV and OH⁻ ion as shown in the following equation.

The reaction can be expressed as a pseudo-first order under the condition of OH⁻ ion $\gg$ CV. The optical density of CV absorption peak was measured at regular time intervals. The rate constant of a pseudo-first order reaction was calculated as follows:

$$k = (1/t) \cdot [\ln(\text{OD}_0 - \text{OD}_\infty) / (\text{OD}_t - \text{OD}_\infty)]$$

where k is the pseudo-first order rate constant, t reaction time (s), OD_0 the optical density at the starting step, OD_∞ one after the reaction time of 24 h, and OD_t one after t time. In order to examine the effects of addition of electrolyte or alcohol, the appropriate amount of NaCl, NaBr or C₂H₅OH was added to the above systems.

The effects of agitation on the fading rate constant were also examined. The rate constant as a function of revolution number of a stirrer for a sodium dodecyl sulfate (SDS)-CV system was measured to give the following results; $4.79 \times 10^{-4} \text{ s}^{-1}$ (200 rpm), $5.17 \times 10^{-4} \text{ s}^{-1}$ (300 rpm), $5.20 \times 10^{-4} \text{ s}^{-1}$ (400 rpm), and $5.00 \times 10^{-4} \text{ s}^{-1}$ (500 rpm), respectively. The rate constant reaches a plateau value at 400 rpm or above, which is in good agreement with the Duynstee's results⁴⁾

of the rate constant $k = 4.9 \sim 5.2 \times 10^{-4} \text{ s}^{-1}$ for the same SDS-CV system, although the agitation condition was not mentioned in the report⁴⁾. Therefore, the rate measurements for the HAA-CV system were all carried out at 400 rpm.

3 Results and Discussion

Three ionic types of HAA are expressed as follows:

From the measurements of potentiometric titration, the isoelectric point pI, the dissociation constants pK_1 and pK_2 are 6.80, 5.15, and 8.45, respectively as reported previously⁷⁾. The cationic type holds at the range below pK_1 , while the anionic type is at the pH range above pK_2 . In the intermediate range between pK_1 and pK_2 , the surfactant has zwitter ionic properties. The critical micelle concentration (cmc) of Zw-HAA was determined to be 2.2 mM by the Wilhelmy's surface tension method⁸⁾. Further, the dependence of cmc on pH value was also measured and the cmc of A-HAA having -COO⁻Na⁺ group was lower than that of C-HAA having [-N⁺H<] Br⁻ group⁷⁾. Since a cmc value is inversely proportional to an aggregation number from the estimation of Anacker's results^{9), 10)}, the aggregation number of A-HAA is presumed to be larger than that of C-HAA. The experiment of fading described in this paper was carried out in the micellar solution of 10 mM which corresponds to about 5 times more than the cmc of Zw-HAA.

Visible and ultraviolet spectra were recorded for CV solution with C-HAA, Zw-HAA, or A-HAA, respectively. The visible spectrum of CV has the maximum absorption peak at 592 nm, attributed to $n \rightarrow \pi^*$ transition. It was reported by Duynstee and Grundwald that the anionic SDS system showed a red shift for CV which is basic dye^{33, 42)}. In contrast, SDS showed no shift and hexadecyltrimethylammonium bromide (CTAB) showed a red shift for an acidic dye^{33, 42)}. The electrostatic state was known to affect the shift of dye in micelles. With respect to the CV solution, A-HAA caused a red shift of 8 nm, Zw-HAA caused no shift, and

C-HAA was again caused a red shift of 5 nm. The $\lambda_{\max}$ 315 nm of CV attributed to Π - Π^* transition hardly shifted in each spectrum for the solution with C-HAA, Zw-HAA, or A-HAA. In all reactions, each optical density against reaction time was measured at the fixed wavelength of 592 nm which was the maximum absorption peak of CV.

The relationship between $\log(\text{OD}_t - \text{OD}_\infty)$ and reaction time is plotted in Fig.-1.

Fig.-1 Effect of the fading rate on A-HAA, Zw-HAA, and C-HAA micelles at 25°C.

The fading rate decreased in the order of C-HAA > A-HAA > Zw-HAA. The k_ϕ/k_0 ratio of CV fading rate was calculated, where k_ϕ and k_0 are the observed pseudo-first order rate constants for the attainment of equilibrium in the presence and absence of surfactant. The k_ϕ/k_0 ratio was 0.19 for C-HAA, 0.13 for A-HAA, and 0.09 for Zw-HAA, respectively. For comparison, it was cited that the ratios were 14.1 for CTAB and 0.06 for SDS as summarized in Table-1. The fading rate of CV in a cationic micelle system was faster than that in an anionic

micelle system in regard to the effect of cationic and anionic surfactant. The anionic micelle system was slower than the system in the absence of surfactant from the result of Duynstee and Grunwald^{3),4)}. However, the system in the absence of HAA exhibited the most rapid fading in all systems in the presence of HAA. Since the ammonium group of CTAB is positively charged on the surface of micelles, the penetration of OH^- ion into the charged micelle containing CV is achieved and hence the rate constant k_ϕ increases.

The charge of $-\text{COO}^-$ and that of $>\text{NH}^+$ are cancelled from the consideration of surface potential, evaluated from the titration method for a zwitter ionic surfactant¹⁰⁾. That is, the surface electrostatic potential in or on micelles is zero. (but the different point between a zwitter ionic surfactant system and a nonionic surfactant one is that a gross charge of a zwitter ionic surfactant is large.) Consequently, the penetration of OH^- ions into the micelles where CV was solubilized was lowered because of neither attraction nor repulsion of electron and the fading rate decreased. However, on adding NaOH to C-HAA or Zw-HAA, the atmosphere of reaction field changes to alkaline side. Although C-HAA or Zw-HAA is altered to A-HAA, it should be allowed that the neutralization and the fading occur competitively.

When CV and HBr were added simultaneously with NaOH, the fading rate was also measured for comparison as shown in Fig.-2. Since excess NaOH was immediately reacted with HBr, the fading rate was more rapid than that for the system free from the surfactant. The reason was presumed to be due to an electrolyte

Table-1 Pseudo-first order rate constants*.

Surfactant	Rate constant (k_ϕ , s^{-1})	k_ϕ/k_0 ratio	References
C-HAA	15×10^{-4}	0.19	present work
A-HAA	10×10^{-4}	0.13	present work
Zw-HAA	7.4×10^{-4}	0.09	present work
no surfactant	79×10^{-4} (k_0)		present work
SDS	$\sim 1 \times 10^{-4}$ ***	0.06	3)
CTAB	240×10^{-4}	14.1	3)
no detergent	17×10^{-4} (k_0)		3)

* at approximately 25°C for the fading of 10^{-5} M CV in 10^{-2} M surfactant solution.

** other kinetic data⁴⁾ $k_\phi = 4.9 \sim 5.2 \times 10^{-4}$

Fig.-2 Effect of reaction conditions for the fading rate at 25°C.

effect of NaBr which was formed from HBr and NaOH. In addition to this, the fading for the system of CV and A-HAA without the addition of NaOH was very slow. When A-HAA was hydrolyzed in part to form OH^- ion, CV was consumed. The reaction of HBr with NaOH was fast when CV, Zw-HAA, and HBr were simultaneously added with NaOH. The fading rate for the above system of CV, Zw-HAA, NaOH, and HBr showed the same tendency as that for CV, Zw-HAA, and NaOH.

The fading rates were measured immediately and at 24 h after CV was added to each HAA derivative and CV was solubilized in micelles. The addition time of OH^- ion after the solubilization of CV in HAA micelles had no appreciable influence on the reaction rate. This fact means that both micelle formation and solubilization were very rapid.

Fig.-3 Dependence of the fading rate on the addition of electrolyte (NaCl) in or on A-HAA micelles at 25°C.

The addition effects of electrolyte on the fading

rate are illustrated in Fig.-3. The fading proceeds in two steps: The one is the consumption step of CV outside micelles by OH^- ions and the other the consumption one of CV solubilized in micelles. The two steps made more clear by the addition of electrolyte. The rate of the former step was faster with the increase in the concentration of electrolyte. Subsequently, approximately 10 min later, the rate reached almost a plateau value. Since the slope for the $\log(\text{OD}_t - \text{OD}_\infty)$ versus time plots is the same, the fading process of CV solubilized in micelles by the penetration of OH^- ions has the constant rate in spite of the added amount of electrolyte. The fading rate in NaBr solution is almost similar to that in NaCl solution. The cmc decreased by further addition of electrolyte as stated by Shinoda *et al.*⁽¹¹⁾ We also reported the effect of electrolyte for Zw-HAA as the following equation; $\log \text{cmc} = -2.66 - 0.248 \cdot [\text{C}]$ where $[\text{C}]$ = molar concentration of NaCl.⁽⁶⁾ The relationship between cmc and aggregation number per one micelle is in reverse proportion from the results of light scattering experiments reported by Anacker *et al.*^{(8), (9)} The addition of electrolyte lets a cmc lower and an aggregation number increases. The product of aggregation number and micelles number is clearly a constant at a fixed concentration. Counterion increased with the increase in the concentration of an electrolyte so that the charge in or on the surface of micelles decreased for a Gouy-Chapman electric double layer. Therefore, as the intermolecular force weakens, the aggregation number increases and water-soluble CV becomes difficult to enter into the micelles. Consequently, CV of monomeric state in the outside of micelles reacts immediately with OH^- ion.

Fig.-4 shows the effects of electrolyte addition on the cmc of Zw-HAA and the solubilization percentage of CV for the dye used. The percentage can be calculated from the point of intersection, of which the two lines of the decreased line in the initial step and the line in the subsequent consumption step of CV solubilized in micelles were extrapolated. Solubilization is closely related to micellization and changes in the addition of electrolytes are known to alter the cmc and aggregation number of the surfact-

Fig.-4 Effect of CV solubilized in A-HAA micelles on the cmc for the addition of electrolyte at 25°C.

ant as well as the solubilization. In this study, the solubilization percentage of CV decreased with the increase in electrolytes added. Although the solubilization percentage was 43.3% in the absence of NaCl, the percentage fell to *ca.* 10% by adding 0.8 mol of NaCl. Thus, CV became difficult to be solubilized in micelles by adding electrolytes. The cmc decreased and the aggregation number inversely increased with the increase in electrolytes from the assumption of Anacker's results^{8), 9)} and Mukerjee's data¹²⁾. If it is assumed that fixed amount of space of micelle is available for solubilization, the micelles in the presence of electrolyte would have a compacted structure of surfactants. The solubilization of CV was the same in both NaCl solution and NaBr solution. Consequently due to various parameters involved, solubilization patterns for the CV-HAA system are difficult to predict the solubilization even qualitatively.

The effect of ethyl alcohol addition on the fading rate is shown in **Fig.-5**. The reaction rate became faster with the increase in the concentration of alcohol. The solubilization behavior for alcohol addition is different from that for electrolyte addition. Although the addition of a small amount of alcohol have little influence on the fading rate, the reaction rate suddenly increased with further more addition of alcohol. The site of incorporation of solubilized molecules depends on the change of a spherical micelle structure by alcohol addition. Alcohol molecules would enter into micelles and hence the micelles

Fig.-5 Dependence of the fading rate in A-HAA micelles on the addition of ethyl alcohol at 25°C.

Fig.-6 Dependence of the cmc and the reaction rate of A-HAA on temperature.

have a bulky or loosed structure.

The activation energy of the fading reaction in alkaline solution was calculated from the Arrhenius' equation; $\log k = -E_a/2.303 RT$. The E_a was evaluated to be 10.9 kcal/mol for the A-HAA micelle system from the slope as shown in **Fig.-6**. The micelle formation energy reported in the previous paper⁷⁾ was +1.5 kcal/mol at pH 11, zero at pH 6.2, and -2.15 kcal/mol at pH 2. The micelle formation energy is lower than the activation energy for alkaline fading. This fact suggests that after the micelles were formed, CV was solubilized and then the fading was caused.

The solubilized model of CV is illustrated in **Fig.-7**. It was assumed by Infelta *et al.* that the solubilisation distribution over the micelles follows Poisson's law^{13)~15)}. In this paper, the location (the surface or core of micelles) of CV solubilized can not be determined. The cationic type (C-HAA) system has positive

Fig.-7 Schematic representation of the CV-alkaline fading for A-HAA, Zw-HAA, and C-HAA micelles.

system has negative charges on the surface of micelles. Therefore, OH^- ions are difficult to approach to the CV solubilized in micelles and the rate is slow.

Since Zw-HAA exhibits electrostatic stabilization and no effective charge, the solubility of Zw-HAA for water was dropped. The cmc of Zw-HAA is lower than that of A-HAA or C-HAA. Therefore, the hydrophobic interactions are enhanced and the aggregation number increased. Thus, the attack of water-soluble OH^- ions is hindered due to the hydrophobic factor. Consequently, the rate for Zw-HAA system is assumed to be the slowest. Moreover, the structural factor in regard to not only the location of amino group but also the steric hindrance of two hydroxy groups of 2-hydroxydodecyl and 2-hydroxyethyl groups are closely related to the fading rate.

Acknowledgments

We gratefully acknowledge Dr. M. Moriya and Dr. M. Takai for their support in this work. We would also like to thank Mr. Y. Takahashi and Mr. K. Watanabe for their technical assistance.

(Received Oct. 4, 1982)

References

- 1) J.H. Fendler and E.J. Fendler, "Catalysis in Micellar and Macromolecular Systems", Academic Press, New York (1975) p. 198.

charges on the surface of micelles. The OH^- ions facilitate the approach to the CV molecules solubilized in micelles and so the fading rate is fast. But, fading rate for C-HAA is slow in comparison with the C-TAB system. This finding implies that the $-\text{COOH}$ group on the surface of micelles prevents the attack of OH^- ions.

Whereas, the anionic type (A-HAA)

- 2) G.S. Hartley, *Trans. Faraday Soc.*, **30**, 444 (1934).
- 3) E.F.J. Duynstee and E. Grundwald, *J. Am. Chem. Soc.*, **81**, 4540 (1959).
- 4) E.F.J. Duynstee and E. Grundwald, *J. Am. Chem. Soc.*, **81**, 4542 (1959).
- 5) J. Albrizzio, J. Archila, T. Rodulfo, and E.H. Cordes, *J. Org. Chem.*, **37**, 871 (1972).
- 6) M. Takai, H. Hidaka, M. Moriya, *J. Am. Oil Chem. Soc.*, **56**, 537 (1979).
- 7) H. Hidaka, M. Moriya, and M. Takai, *J. Am. Oil Chem. Soc.*, **56**, 914 (1979).
- 8) E.W. Anacker and A.L. Underwood, *J. Phys. Chem.*, **85**, 2463 (1981).
- 9) E.W. Anacker and H.M. Ghose, *J. Am. Chem. Soc.*, **90**, 3161 (1968).
- 10) F. Tokiwa and K. Ohki, *J. Phys. Chem.*, **71**, 1824 (1967).
- 11) K. Shinoda, T. Yamaguchi, and R. Hori, *Bull. Chem. Soc. Jpn.*, **34**, 237 (1961).
- 12) P. Mukerjee, K.J. Mysels, and P. Kapauan, *J. Phys. Chem.*, **71**, 4166 (1967).
- 13) P.P. Infelta, M. Grätzel, and M. Thomas, *J. Phys. Chem.*, **78**, 1906 (1974).
- 14) P.P. Infelta, *Chem. Phys. Lett.*, **61**, 88 (1979).
- 15) P.P. Infelta and M. Grätzel, *J. Chem. Phys.*, **70**, 179 (1979).

2-ヒドロキシアルキル基を有する 新両性界面活性剤 (第6報)

両性界面活性剤存在下でのトリフェニル メタン色素のアルカリ退色速度に 関する研究

日高久夫・窪田 快・吉沢秀二

明星大学理工学部 (東京都日野市程久保 337)

両性界面活性剤存在下で、トリフェニルメタン色素〔クリスタルバイオレット (CV)〕のアルカリ溶液中における退色速度を CV 色素の可視吸収スペクトルの吸光度 (592 nm) の減少から測定した。

両性界面活性剤、*N*-(2-ヒドロキシドデシル)-*N*-(2-ヒドロキシエチル)- β -アラニン (HAA) は pH 変化により陰イオン型 (C-HAA)、両性イオン型 (Zw-HAA) と陽イオン型 (A-HAA) になり、同一骨格で荷電状態を変化させることが可能である。

退色速度は偽一次反応で表され、速度は $\text{C-HAA} > \text{A-HAA} > \text{Zw-HAA}$ の順に低下する。

表面電荷状態がミセル内部または表面で起きる退色速度に影響を与える。電解質添加の影響も調べ、添加量の増加と共に徐々に退色速度は速くなる。

ミセル内部に可溶化した CV とミセル外部に存在する CV 色素の割合を退色速度曲線から計算した。CV の可溶化量は電解質濃度に伴って減少した。