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ORIGINAL CONTRIBUTION

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Investigation on the basic hydrolysis of crystal violet in mixed reverse micelles formed with AOT and nonionic surfactants

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Abstract The kinetics and thermodynamics of the basic hydrolysis of crystal violet (CV) in mixed reverse micelles formed with anionic surfactant AOT and nonionic surfactants have been investigated. It was found that the mixed reverse micelles had inhibitory effects on CV hydrolysis compared with the normal aqueous solution, and the equilibrium constant K of the reaction in mixed reverse micellar systems is smaller than that in pure water. The influence of water content and surfactant composition in reverse micelles on the second-order rate constant k_1 of the positive reaction, on the first-order rate constant k_{-1} of the reverse reaction, as well as on the equilibrium constant K of the reaction has been studied, and the results obtained were interpreted in terms of the nature of surfactants and the properties of microenvironment where the reaction took place.

Key words Mixed reverse micelles – AOT – nonionic surfactant – crystal violet – basic hydrolysis

Introduction

Reverse micelles or water-in-oil microemulsions are thermodynamically stable isotropic dispersions of water in nonpolar solvents stabilized by interfacial film of surfactants. Since the system is optically transparent and the change in the system could be followed by different spectroscopic methods; moreover, the parameters such as the waterpool size; the nature and the concentration of surfactants, the pH of waterpool can be easily adjusted, the interior waterpool of reverse micelles is a desirable microreactor where chemical reactions can take place. In such a microenvironment, the kinetic rate constant of chemical reactions can be changed by several orders of magnitude [1].

Among the surfactants capable of forming reverse micelles, the anionic surfactant AOT(sodium bis(2-ethylhexyl)sulfosuccinate) has received particular attention because it can form reverse micelles under a wide range of conditions, such as water content (usually expressed in terms of $W_0 = [H_2O]/[AOT]$), temperature, solvent, electrolyte, and concentration, without the need for a cosurfactant. A variety of chemical reactions such as ester hydrolysis, aminolysis, hydration of electron, photoelectron transfer reactions, antibody catalysis, etc., have been investigated in AOT reverse micelles [2, 3]. In order to build a better microreactor and increase microenvironment diversity in AOT reverse micelles, a fourth component such as bile salt [4], electrolyte [5, 6], polymer [7, 8], urea, amines [6], fatty alcohol, and nonionic surfactants [9, 10] have been added. The effect of these additives on the structure and properties of the reverse micelles has been investigated. However, the kinetics of chemical reaction in these systems has seldom been studied. In this article, the mixed reverse micelles formed with AOT and nonionic surfactants have been chosen to be the medium for the basic hydrolysis of crystal violet ($CV^+ + OH^- \rightleftharpoons CVOH$). The reaction $CV^+ + OH^- \rightleftharpoons CVOH$ is chosen because its kinetic behavior in aqueous media is well known [11–14] and this reaction can be easily followed by spectroscopic method.

The basic hydrolysis of CV has been considerably studied in the medium of anionic, nonionic, and cationic reverse micelles [15–24]. While the anionic surfactants sodium dodecyl sulfate [19] and AOT [15, 17, 18, 20] decrease and the cationic surfactant cetyltrimethylammonium bromide [16, 19, 21, 22] enhances the rate of the reaction, the results obtained from nonionic surfactant is quite confusing. Triton X-100 [23] hardly affects the kinetics of the process, but a large increase in the reaction rate was observed in the system of propane-2-ol/hexane/water microemulsions [20]. A surprising and interesting report was that the reaction rate could be considerably accelerated by using an anionic reverse micelle of H_2O/AOT/ethane under supercritical conditions [24]. As to the effect of a fourth composition, 1-hexanol, 1-butanol, and 1-octanol [16, 19, 20] were added to CTAB reverse micelles, and an inhibitory effect was observed. The addition of electrolytes, such as NaCl and $KClO_4$ [15], has shown inhibitory effects on the reaction in AOT reverse micelles. Till now, the effect of a cosurfactant is mainly focused on the cationic reverse micelles, seldom work was related to the system formed with anionic surfactant AOT because of its ability of forming reverse micelles without the need of a cosurfactant. However, adding a cosurfactant to AOT reverse micelles may give rise to a better microreactor and an increased microenvironmental diversity, so the initial purpose of this article is to investigate how a fourth component – addition of a nonionic surfactant – in AOT reverse micelles affects the reaction

$$CV^+ + OH^- \rightleftharpoons CVOH. \qquad (1)$$

In addition, the hydrolysis of CV is a reversible reaction, the study of the effect of reverse micellar systems on the thermodynamics of reaction $CV^+ + OH^+ \rightleftharpoons CVOH$ may provide another method in understanding the reverse micellar catalysis. In this article, the equilibrium constant K of the hydrolysis reaction was measured, and the factors affecting the constant K were discussed.

Experimental

Materials

The surfactant AOT (sodium bis(2-ethylhexyl)sulfosuccinate, Sigma), Brij30 (polyoxyethylene(4) lauryl ether, Acros Organics) and Igepal CO-210, Igepal CO-520, Igepal CO-720(polyoxyethylene(2) nonylphenol, polyoxyethylene(5) nonylphenol, polyoxyethylene(12) nonylphenol, Aldrich) were used without purification. The solvent, *n*-heptane (A. R. grade), was dried with 4 Å molecular sieves and redistilled. Crystal violet and sodium hydroxide (A.R. grade) were products of Beijing Chemical Factory. Doubly distilled water was used throughout the study.

Kinetic measurements

Kinetic measurements and spectral studies were carried out on a 752C UV–vis spectrophotometer (Shanghai No. 3 Analytical Instrument Factory, China) with a thermostated cell holder by measuring the disappearance of the violet color from crystal violet ($\lambda = 592$ nm) in the course of reaction. The reverse micellar solutions containing all components except CV was used as blank. All experiments were carried out at 25 °C. The concentration of crystal violet was always much lower than that of OH^- in order to keep the experimental results fit the pseudo-first order rate equation. By taking into account the restrictions imposed by the need of a suitable absorbance measurement to follow the kinetics, the concentrations of CV were determined depending on the microemulsion composition, and were 7.5×10^{-4} M, 5×10^{-4} M, 2.5×10^{-4} M, respectively, when $W_0 = 5, 10, 15$. For each reaction system with constant water content and CV concentration, experiments under five OH^- concentrations were carried out. In all the cases the reactant concentration is referred to the aqueous phase and not to the entire (surfactant + oil + water) system. The total concentration of surfactants was 0.10 M in *n*-heptane.

Reaction was started by adding certain amount of a water solution containing OH^- with a syringe to mixtures already containing all other components. Before data acquisition, the mixtures were shaken vigorously until a transparent solution was achieved.

Data treatment

A typical absorbance–time plot for the basic hydrolysis of crystal violet in reverse micelles was shown in Fig. 1. Initially, the absorbance decreases exponentially, then passes through a minimum, and increases gradually until reaching a certain value. This restoration of the decreased absorbance after a certain time was explained by Leis and coworkers [15] in terms of the shift of the equilibrium (1) to the left because of the disappearance of OH^- due to AOT hydrolysis.

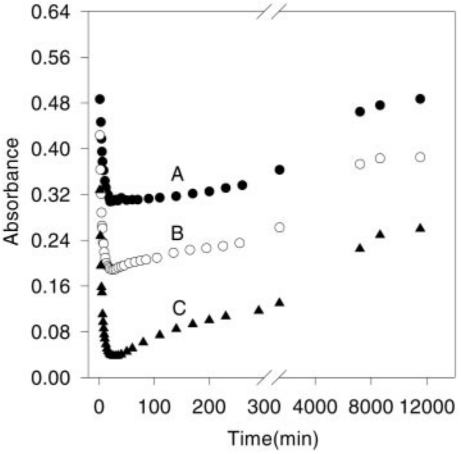

Fig. 1 Absorbance (592 nm)–time plot for the basic hydrolysis of CV in reverse micelles. $W_0 = 5$, $[\mathrm{OH}^-] = 0.10$ M, $[\mathrm{CV}] = 7.5 \times 10^{-4}$ M. Surfactant composition: (A) 0.10 M AOT; (B) 0.07 M AOT + 0.03 M Brij30; (C) 0.03 M AOT + 0.07 M Brij30

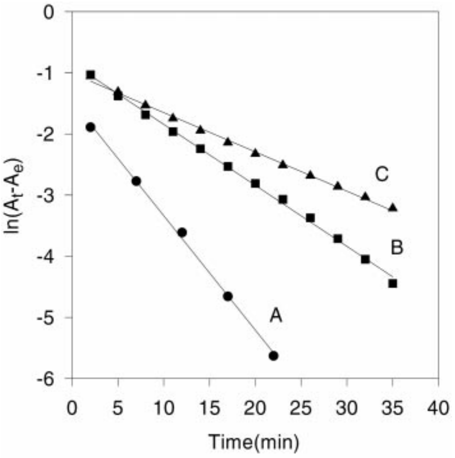

Fig. 2 $\ln(A_t - A_e)$ vs. time plot in AOT reverse micelles at 298 K. (A) $W_0 = 5$, (B) $W_0 = 10$ (C) $W_0 = 15$

Equation (1) can be written for convenience as

$$\mathrm{CV}^+ + \mathrm{OH}^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{CVOH}\ . \tag{2}$$

Then we have

$$\frac{\mathrm{d}[\mathrm{CV}^+]}{\mathrm{d}t} = -k_1[\mathrm{CV}^+][\mathrm{OH}^-] + k_{-1}[\mathrm{CVOH}]\ , \tag{3}$$

$$\frac{\mathrm{d}[\mathrm{CVOH}]}{\mathrm{d}t} = k_1[\mathrm{CV}^+][\mathrm{OH}^-] - k_{-1}[\mathrm{CVOH}]\ . \tag{4}$$

Since the initial $[\mathrm{OH}^-]$ value is kept much higher than the initial $[\mathrm{CV}^+]$ value, $[\mathrm{OH}^-]$ can be considered constant during the reaction time and the above set of differential equations (3) and (4) becomes linear and can be analytically solved, the result is as follows:

$$[\mathrm{CV}^+] = [\mathrm{CV}^+]_\mathrm{e} + ([\mathrm{CV}^+]_0 - [\mathrm{CV}^+]_\mathrm{e})\mathrm{e}^{-\lambda t}\ , \tag{5}$$

where $[\mathrm{CV}^+]_0$ is the initial concentration of CV^+, $[\mathrm{CV}^+]_\mathrm{e}$ is the concentration of CV^+ at the equilibrium, and λ is given by:

$$\lambda = k_1[\mathrm{OH}^-] + k_{-1}\ . \tag{6}$$

In Eq. (5), the concentration $[\mathrm{CV}^+]$ can be substituted by the absorbance A, and it is obtained that

$$A_t = A_\mathrm{e} + (A_0 - A_\mathrm{e})\mathrm{e}^{-\lambda t} \tag{7}$$

where A_0, A_t and A_e are the absorbance of the reactant system at the initial time, at time t and at the equilibrium. By bearing in mind that the basic hydrolysis of AOT is very slow [25], the minimum absorbance as shown in Fig. 1 can be approximately considered as the equilibrium value (A_e) of the reaction system. Then λ value can be obtained from the slope of the $\ln(A_\mathrm{t} - A_\mathrm{e})$ vs. time plots, just as shown in Fig. 2. For a reaction system with constant surfactant composition and water content, λ is plotted vs. $[\mathrm{OH}^-]$, which gives a straight line with the slope k_1 and the ordinate intercept k_{-1} as known from Eq. (6). From above treatment, it is obvious that both the rate constants of the positive and reverse reaction of the basic hydrolysis of crystal violet can be obtained from the spectrometric measurements of the reaction system. The results for the reaction system 0.05 M + 0.05 M Brij30/*n*-heptane are presented in Fig. 3. Having obtained k_1 and k_{-1}, the

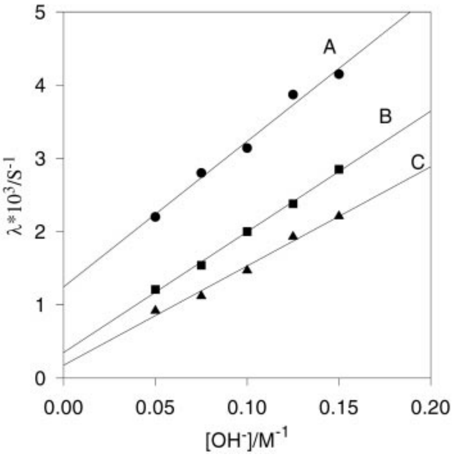

Fig. 3 $\lambda(\lambda = k_1[\mathrm{OH}^-] + k_{-1})$ vs. $[\mathrm{OH}^-]$ plot in 0.05 M AOT + 0.05 M Brij30/*n*-heptane mixed reverse micelles at 298 K. The rate constants k_1 and k_{-1} of the reversible basic hydrolysis of crystal violet can be obtained from the slope and the ordinate of the straight line. (A) $W_0 = 5$, (B) $W_0 = 10$ and (C) $W_0 = 15$

equilibrium constant K corresponding to reaction (1) is calculated from $K = k_1/k_{-1}$.

Results and discussions

The absorbance–time profile of the reaction in reverse micelles

Figure 1 is a typical absorbance-time plot of the reverse micellar system formed with AOT and nonionic surfactants where the basic hydrolysis of CV takes place. Initially, the absorbance decreases exponentially as expected from the normal hydrolysis, however, after a definite time, the absorbance passes through a minimum and increases gradually until reaches a certain value. Similar absorbance-time profile was also observed by Leis and coworkers [15], and the unusual restoration of the absorbance was explained by the shift of the equilibrium (1) to the left because of the disappearance of OH^- due to AOT hydrolysis.

To shed light on the nature of absorbance-time profile, the absorbance of systems with different surfactant compositions was recorded, and the results were shown in Fig. 1. It can be known from Fig. 1 that the decrease of AOT content in the system results in a decrease of the absorbance, which verifies the interpretation that the restoration of the absorbance can be ascribed to the basic hydrolysis of AOT. Leis [15] et al. has observed that, after 24–36 h, the absorbance in AOT reverse micellar systems can reach its initial value, which means that the initial concentration of CV has been recovered. This is not the case in our experiment, where the restored absorbance value was found to be a function of AOT concentration, or more precisely, a function of the molar ratio of AOT to OH^-. The recovered absorbance increases as the ratio of AOT to OH^- becomes greater. This seems more reasonable because the AOT hydrolysis can only change the concentration of OH^- and hence the equilibrium concentration of CV hydrolytic product – carbinol, but cannot make carbinol disappear completely.

It was also shown in Fig. 1 that the absorbance of the system increases very slowly after its minimum, indicating that the basic hydrolysis of AOT is very slow. This is in accordance with the results obtained by Fletcher et al. [25]. Accordingly, the disappearance of OH^- due to the hydrolysis of AOT can be ignored before the absorbance reaches its minimum, and it is reasonable to assume that the minimum absorbance can be regarded as the equilibrium absorbance of the system.

Rate dependence on the medium composition

The measured second-order rate constants k_1 of positive reaction and first-order rate constant k_{-1} of reverse reaction for reversible basic hydrolysis of crystal violet in mixed reverse micelles with different composition are shown in Tables 1 and 2. All experimental results show a decrease in rate constant k_1 in reverse micellar systems compared with that in normal aqueous solution. The phenomenon has been interpreted by Izquierdo et al. [20] from two respects. (i) a strong stabilization of the crystal violet because of their interaction with the anionic surfactant headgroups, and (ii) a more difficult approaching process in respect to aqueous solution.

Tables 1 and 2 show that the system composition has a significant influence on the rate constant k_1 and k_{-1} of the hydrolytic reaction. For rate constant k_1 of the positive reaction, increasing the content of nonionic surfactant leads to an increase of the rate constant, whereas an apparent inhibitory effect is observed as the water content increases. The effect of EO chain length of nonionic surfactant on the rate constant k_1 is quite confusing. When water content is lower (e.g., $W_0 = 5$), the increase of the EO chain length leads to a decrease of the rate constant k_1, whereas

Table 1 Second-order rate constants (k_1) for the positive reaction of the basic hydrolysis of crystal violet in AOT/nonionic surfactants/water/*n*-heptane mixed reverse micelles at 298 K

Surfactant composition	$10^2 k_1$ ($M^{-1} s^{-1}$)		
	$W_0 = 5$	$W_0 = 10$	$W_0 = 15$
0.10 M AOT	1.04 ± 0.01	0.68 ± 0.01	0.64 ± 0.01
0.09 M AOT + 0.01 M Brij30	1.18 ± 0.16	0.91 ± 0.10	0.81 ± 0.08
0.07 M AOT + 0.03 M Brij30	1.43 ± 0.09	1.24 ± 0.05	1.07 ± 0.04
0.05 M AOT + 0.05 M Brij30	1.95 ± 0.04	1.64 ± 0.03	1.29 ± 0.01
0.03 M AOT + 0.07 M Brij30	2.45 ± 0.11	2.09 ± 0.05	—
0.09 M AOT + 0.01 M Igepal CO-210	1.11 ± 0.01	0.71 ± 0.01	0.55 ± 0.11
0.09 M AOT + 0.01 M Igepal CO-520	0.99 ± 0.12	0.72 ± 0.10	0.59 ± 0.12
0.09 M AOT + 0.01 M Igepal CO-720	0.84 ± 0.06	0.71 ± 0.09	0.61 ± 0.02

k (pure water) = 0.2 $M^{-1} s^{-1}$.

Table 2 First-order rate constants (k_{-1}) for the reverse reaction of the basic hydrolysis of crystal violet in AOT/nonionic surfactants/water/*n*-heptane mixed reverse micelles at 298 K

Surfactant composition	$10^3 k_{-1}$ (s^{-1})		
	$W_0 = 5$	$W_0 = 10$	$W_0 = 15$
0.10 M AOT	1.21 ± 0.01	0.66 ± 0.01	0.48 ± 0.01
0.09 M AOT + 0.01 M Brij30	1.35 ± 0.17	0.59 ± 0.11	0.38 ± 0.08
0.07 M AOT + 0.03 M Brij30	1.29 ± 0.09	0.50 ± 0.05	0.27 ± 0.04
0.05 M AOT + 0.05 M Brij30	1.21 ± 0.04	0.38 ± 0.04	0.18 ± 0.01
0.03 M AOT + 0.07 M Brij30	0.95 ± 0.12	0.35 ± 0.06	—
0.09 M AOT + 0.01 M Igepal CO-210	1.51 ± 0.01	0.74 ± 0.01	0.58 ± 0.12
0.09 M AOT + 0.01 M Igepal CO-520	2.04 ± 0.13	0.90 ± 0.11	0.67 ± 0.13
0.09 M AOT + 0.01 M Igepal CO-720	3.30 ± 0.06	1.12 ± 0.09	0.80 ± 0.02

an increase of the k_1 with the EO chain length is observed at greater water content. The EO chain length of nonionic surfactants has different influence on the rate constant k_1 with varying water content.

For rate constant k_{-1} of the reverse reaction, the increase of water and nonionic surfactant content, together with the decrease of EO chain length of nonionic surfactants, result in an decrease of k_{-1}, just as evidenced in Table 2.

In the investigation on various chemical reactions in reverse micelles, a specific reaction field that affords the "multiple field assistance" was proposed by Sunamoto et al. [26], and the rate variation for various reactions was interpreted. Rodenas et al. [19] has investigated the effect of reverse micelles formed with SDS and CTAB on the basic hydrolysis of CV and attributed the variation of reaction rate to the change of the dielectric constant. However, since the systems formed with cationic surfactants or anionic surfactants have different effects on the reaction, it can be said that the nature of surfactants that formed reverse micelles, or electrostatic interactions between the head groups of surfactants and the reactants, should be a dominant factor influencing the reactivity in such a medium.

In the reverse micellar systems formed with AOT and Brij30, the decrease of AOT content gives rise to a decrease of the stabilization of crystal violet by electrostatic interaction, and therefore increases the rate constant k_1 and decrease the rate constant k_{-1}.

When the content of AOT is fixed, the electrostatic interactions between reactants and headgroups of AOT, and the consequent electrostatic effect on the reaction rate can be considered as unchanged. The variation of the micropolarity of the waterpool due to the change of water content and the change of EO chain length of the added nonionic surfactants may be an important factor that influences the reaction rate. The effect of the surfactant composition on the micropolarity of mixed reverse micelles has been investigated by using $Ru(bpy)_3^{2+}$ as fluorescence probe [27, 28], and a conclusion was obtained that the micropolarity of waterpool in reverse micelles increases with increasing water content (W_0) and with decreasing EO chain length of the added nonionic surfactants. In reverse micellar systems formed with AOT and Igepal CO-210, Igepal CO-520, Igepal CO-720 in the same molar ratio, or in reverse micellar systems formed with AOT and nonionic surfactants with varying water content, an increase of rate constant k_1 is observed with increasing the EO chain length of nonionic surfactants (at greater water content) and with decreasing water content in mixed reverse micelles. These results can be interpreted by the decreased micropolarity in the waterpool, or the decrease of the dielectric constant [19]. On the other hand, the decrease of the rate constant k_1 with increasing EO chain length in mixed reverse micelles at lower water content ($W_0 = 5$) may be somewhat complicated, and further investigation is demanded.

Although almost all researchers agree with that the reaction rate of the basic hydrolysis of crystal violet has a close relationship with the surfactant composition and the physical properties of the entrapped water in reverse micelles, different rate constant-surfactant composition profiles and rate constant-water content profiles were observed. The basic hydrolysis of CV in mixed reverse micelles formed with AOT and Tween 20 was studied and a result was obtained that the addition of Tween 20 had an inhibitory effect on the reaction, which was explained in terms of the more rigid interfacial film owing to the addition of Tween 20 [18]. The effect of water content was also investigated by Mukhopadhyay [18] and Leis [15]. In their studies, there exists a maximum rate constant at about $W_0 = 10$. This rate constant – W_0 profile was explained by the exclusion of OH^- from "filled" microdroplet and the reduction of OH^- concentration[15]. All these facts indicate that a further research is demanded for understanding the effect of the system composition on the microstructure of reverse micelles and on the basic hydrolysis of the CV.

The thermodynamic equilibrium

The thermodynamic equilibrium constant K of Eq. (1) in water has been measured by Ritchie and coworkers [29] to be $K = 4 \times 10^4\ \mathrm{M}^{-1}$. This value is much greater compared with the K value obtained in mixed reverse micellar systems (Table 3), which may be mainly ascribed to the strong stabilization of the crystal violet because of their electrostatic interactions with the anionic surfactant head groups.

It is shown in Table 3 that K increases with the increase of water and nonionic surfactant content, but decreases with increasing EO chain length of nonionic surfactants in mixed reverse micelles.

As discussed above, the increased K value with increasing content of the added nonionic surfactant can also be interpreted by the decreased electrostatic attractions between CV^+ and headgroups of AOT and hence the decreased stabilization of CV^+. The nature of the surfactant that formed reverse micelles, or the electrostatic interactions, has a significant effect on the equilibrium of CV hydrolysis, which is in accordance with the results obtained by Bunton and Robinson [30] in aqueous micellar systems where it was reported that the equilibrium constant of reaction (1) was markedly decreased by anionic micelles of sodium lauryl sulfate and increased by the cationic micelles of cetyltrimethylammonium bromide.

With respect to the effect of the water content and EO chain length of the added nonionic surfactant on the equilibrium constant K of the basic hydrolysis of CV, the micropolarity of the reaction field may play a major role. The K value increases as the micropolarity of the waterpool increases due to the increased water content or the decreased EO chain length of the added nonionic surfactants. This effect is opposite to that on the rate constant k_1, but it is not very clear why the variation of the microenvironment has such different effects on the kinetic and thermodynamic behaviors of the basic hydrolysis of crystal violet in reverse micelles.

Conclusions

As a conclusion, reverse micelles formed with AOT and nonionic surfactants have inhibitory effects on the basic hydrolysis of crystal violet. The rate constant of hydrolysis decreases with increasing water content in the system, but increases as the nonionic surfactant content increases. The EO chain length of nonionic surfactants has different influence on the hydrolytic rate at different water contents. The equilibrium constant of the hydrolytic reaction in reverse micellar systems is much smaller than that in pure water, it increases with increasing water and nonionic surfactant content, but decreases with increasing the EO chain length of nonionic surfactants. The above phenomena can be interpreted in terms of the nature of the surfactants that formed the reverse micelles as well as the micropolarity property of the waterpool of reverse micelles. The nature of the surfactants that formed the reverse micelles has a dominant influence on the kinetic and thermodynamic behavior of the basic hydrolysis of crystal violet. Therefore, when nonionic surfactants were added into AOT reverse micelles, the increase of their contents is favorable to the reaction kinetically and thermodynamically due to the decreased electrostatic attractions between CV^+ and the headgroups of anionic AOT. When the ratio of AOT to nonionic surfactant is fixed, the variation of micropolarity of the reaction field owing to the change of water content and EO chain length of nonionic surfactants also has a important effect on the basic hydrolysis of CV in reverse micelles. The increase of the micropolarity results in a decrease of the hydrolytic rate, whereas the equilibrium constant increases with increasing the micropolarity. The decrease of EO chain length of nonionic surfactants and the increase of water content give rise to an enhanced micropolarity of the waterpool in mixed reverse micelles. Therefore, in mixed reverse micelles formed with AOT and nonionic surfactants, the increase of EO chain length is

Table 3 Equilibrium constants (K) for the basic hydrolysis of crystal violet in AOT/nonionic surfactants/water/*n*-heptane mixed reverse micelles at 298 K

Surfactant composition	K (M^{-1})		
	$W_0 = 5$	$W_0 = 10$	$W_0 = 15$
0.10 M AOT	8.60 ± 0.15	10.3 ± 0.31	13.3 ± 0.48
0.09 M AOT + 0.01 M Brij30	8.74 ± 2.3	15.4 ± 4.6	21.3 ± 6.6
0.07 M AOT + 0.03 M Brij30	11.1 ± 1.5	24.8 ± 3.5	39.6 ± 7.1
0.05 M AOT + 0.05 M Brij30	16.1 ± 0.86	43.2 ± 5.3	71.7 ± 4.5
0.03 M AOT + 0.07 M Brij30	25.8 ± 4.4	59.7 ± 12	—
0.09 M AOT + 0.01 M Igepal CO-210	7.35 ± 0.11	9.59 ± 0.26	9.48 ± 3.9
0.09 M AOT + 0.01 M Igepal CO-520	4.85 ± 0.90	8.00 ± 2.1	8.81 ± 3.5
0.09 M AOT + 0.01 M Igepal CO-720	2.55 ± 0.23	6.33 ± 1.3	7.63 ± 0.44

K (pure water) $= 4 \times 10^4\ \mathrm{M}^{-1}$.

favorable to the reaction kinetically but not thermodynamically, whereas the increase of water content is advantageous to the reaction thermodynamically but not kinetically.

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