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ORIGINAL CONTRIBUTION

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# Micellar effects of a triazole-based cationic gemini surfactant on the rate of a nucleophilic aromatic substitution reaction

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**Abstract** The reaction between 2,4-dinitrochlorobenzene (DNCB) and hydroxide ion was studied spectrophotometrically at 25 °C in micelles of a triazole-based cationic gemini surfactant 18-triazole-18 or micelles of the conventional cationic surfactant CTAB. Both CTAB and 18-triazole-18 accelerated this nucleophilic aromatic substitution reaction. The binding constant of the substrate to the micelle, $K_S$, for 18-triazole-18 ($K_S = 335\ M^{-1}$) was found to be much larger than that for CTAB (85 $M^{-1}$) by fitting the kinetic results with pseudophase ion-exchange (PIE) model, which suggests that DNCB binds with gemini micelles more easily than it does with CTAB micelles. It was also found that 18-triazole-18 catalytic system was in accordance with PIE model at surfactant concentrations below ca. 0.5 mM, above which the increase of viscosity and the change of micelle size with increased surfactant concentration may remarkably influence the reaction. This was quite different from the reaction catalyzed by micelles of the conventional surfactant CTAB.

**Keywords** Gemini surfactant · Triazole · Micellar catalysis · Nucleophilic substitution · Pseudophase ion-exchange model

## Introduction

Micellar catalysis and microemulsion catalysis are one of the current active fields in the physical chemistry of surfactant [1–5]. It has been found that such assemblies of surfactants may affect the rates of chemical reactions and the positions of chemical equilibria. In the case of bimolecular reactions the concentration or depletion of reactants in the interfacial region, which is similar to the structure of enzyme, has major effects on reaction rates because the interfacial region differs from water as a reaction medium. Consequently, as a simple and one of the best models for enzyme catalysis, the micellar catalysis has attracted much attention over the past few decades [6–12].

Recently, a new generation of surfactants, gemini surfactants, has attracted great interest [13–15]. They are constituted by two hydrophilic groups and two hydrophobic groups per molecular unit, separated by a spacer. This generation of surfactants has been demonstrated to possess unique properties, such as lower critical micelle concentration (cmc), greater efficiency in lowering the surface tension, lower Krafft temperature, and better solubilization in comparison with the corresponding conventional surfactants (made up by one hydrophilic group and one hydrophobic group), which is due to great difference of molecular structures between gemini surfactants and conventional surfactants. Most investigations on gemini surfactants have focused on their unusual physico-chemical properties, including their high surface activity [13–15], unusual changes of viscosity [16–18], unusual micelle structure and aberrant aggregation behavior [19, 20], and larger solubilization capacity of organic compounds [21, 22]. However, there are few reports on micellar-catalyzed reaction using gemini surfactants till now [23, 24]. It has been found that cationic micelles accelerate nucleophilic aromatic substitution reactions, which is due to interactions between cationic micelles and the negatively charged $\sigma$-complex compound as the transition state formed in the reaction [7]. Owing to the unique micellar properties of gemini surfactants, there may exist some differences between gemini surfactants and the conventional surfactants for micellar catalysis. In the present work, we have chosen the reaction between 2,4-dinitrochlorobenzene (DNCB) and hydroxide ion, a well-known nucleophilic aromatic substitution reaction [25], to examine whether there is any difference between the cationic gemini surfactant and the conventional surfactant for micellar catalysis. A triazole-based cationic gemini surfactant, 3,5-bis(methyleneoctadecyldimethylammonium chloride)-1,2,4-triazole (designated as 18-triazole-18, Scheme 1) was synthesized. Pseudo-first-order rate constants were determined spectrophotometrically at 25 °C, and the kinetic results were explained using pseudophase ion-exchange (PIE) model. The reaction between DNCB and hydroxide ion in micelles of a conventional cationic surfactant cetyltrimethylammonium bromide (CTAB) was also studied kinetically for comparison. It was found that higher microviscosity of 18-triazole-18 at high concentrations may remarkably influence the reaction. This was quite different from the catalytic behavior for CTAB system.

## Experimental

### Materials

Synthetic route of the cationic gemini surfactant 18-triazole-18 was shown in Scheme 1. A mixture solution of 3,5-bis(chloromethyl)-1,2,4-triazole (2.0 g, 12 mmol, synthesized according to literature [26]. WARNING! 3,5-Bis(chloromethyl)-1,2,4-triazole is a severe skin irritant and adequate protection from exposure to this compound is recommended) and *N*,*N*-dimethyloctadecylamine (4.3 g, 14.4 mmol) in 100 mL of absolute ethanol was refluxed with stirring for 48 h. After rotary evaporation of the solvent, a waxy product was obtained. Then 30 mL of acetone was added, and the mixture was heated till it was clear. The solution was cooled in a refrigerator overnight. The precipitate was filtered and repeatedly recrystallized from acetone–ethanol mixture, and the desired product was obtained as a white solid (3.3 g, 36%). Anal. Calcd. for $C_{44}H_{91}N_5Cl_2$ (%): C,69.47; H,11.97; N,9.21. Found: C,69.32; H,12.01; N,9.36. $^1$H-NMR (300 MHz, $CDCl_3$, $\delta$): 0.89 (t, 6H, -$CH_3$), 1.26 (m, 64H, -$(CH_2)_{16}$-), 1.82 (m, 4H, $CH_3(CH_2)_{16}CH_2$-), 3.60 (s, 12H, -$N(CH_3)_2$), 4.42 (s, 1H, NH), 4.88 (d, 4H, triazole-$CH_2$-). IR (KBr, cm$^{-1}$): 2850, 1674, 1468, 1379, 1106, 1012. Critical micelle concentration (cmc) of the surfactant 18-triazole-18, determined by conductivity, is 0.19 mM, and degree ionization of micelles $\alpha$ is 0.28, which was estimated from ratios of slopes, above and below cmc, of the linear plot of specific conductance versus molar concentration of the surfactant.

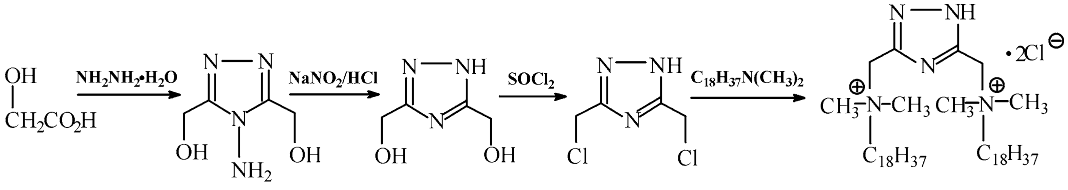
Cetyltrimethylammonium bromide (CTAB) and 2,4-dinitrochlorobenzene were of analytical grade and were purchased from Shanghai Chemical Reagent Co., China, and all other chemicals were also of reagent grade and commercially available.

### Kinetic measurements

The rates of the reaction between 2,4-dinitrochlorobenzene ($1\times10^{-4}$ M) and 0.05 M NaOH were studied spectrophotometrically by measuring the rate of appearance of the 2,4-dinitrophenolate at 358 nm. Since the concentration of $OH^-$ is much higher than that of the substrate DNCB, the reaction could be considered as a pseudo-first-order one, and the obtained rate constants could be treated as pseudo-first-order rate constants. The increase in absorbance with the progress of the reaction was recorded at intervals of 5 s automatically with a Puxi double-beam TU-1901 UV/vis spectrophotometer. The rate constants of each reaction were determined from slope of the plots $\ln(A_\infty - A_t)$ versus time ($A_t$ is the absorbance at time $t$, and $A_\infty$ is the absorbance at equilibrium). $A_\infty$ was not experimentally determined, but calculated by a computer program designed to give the best straight-line fit to data.

## Results and discussion

In order to investigate whether there exits any difference of kinetic behavior between the conventional single-chained surfactant and the gemini surfactant for the reaction between 2,4-dinitrochlorobenzene and $OH^-$,



18-triazole-18

**Scheme 1**

kinetic studies of the reaction of 2,4-dinitrochlorobenzene were carried out at 25 °C in aqueous solutions containing 0.05 M NaOH in the presence of the conventional cationic surfactant CTAB and the cationic gemini surfactant 18-triazole-18, respectively. The results of pseudo-first-order rate constant ($k_\psi$) as a function of surfactant concentration for CTAB and 18-triazole-18 were shown in Figs. 1 and 2, respectively.

The pseudo-first-order rate constant of the reaction between hydroxide ion and 2,4-dinitrochlorobenzene without micellar catalyst was determined to be $7.7\times10^{-6}$ $s^{-1}$. Both CTAB and 18-triazole-18 were found to accelerate this reaction, however, obvious difference in kinetics was observed between these two systems. For the conventional surfactant CTAB, the pseudo-first-order rate constants first increased sharply with an increase in the surfactant concentration, then increased steadily and remained relatively constant with the further increase in the surfactant concentration. Note that high surfactant concentration usually results in a decrease in $k_\psi$ in similar micellar-catalyzed systems [2, 7], which is attributed to the dilution of the reactive counterions in the Stern layer of a higher number of micelles, but no maximum rate constant was observed in this work. This may be due to relatively low surfactant concentration studied in the present work. For gemini surfactant 18-triazole-18, $k_\psi$ increased sharply until a maximum point was reached. Further increase in the surfactant concentration caused a significant decrease in the rate constants, although the values were still larger than the reaction rate constant without micellar catalyst. It can also be found that gemini surfactant 18-triazole-18 exhibited a maximum rate enhancement for the reaction at surfactant concentrations around 0.5 mM, which was much lower than that for system containing the conventional surfactant CTAB (≥ 15 mM, ref. Fig. 1).

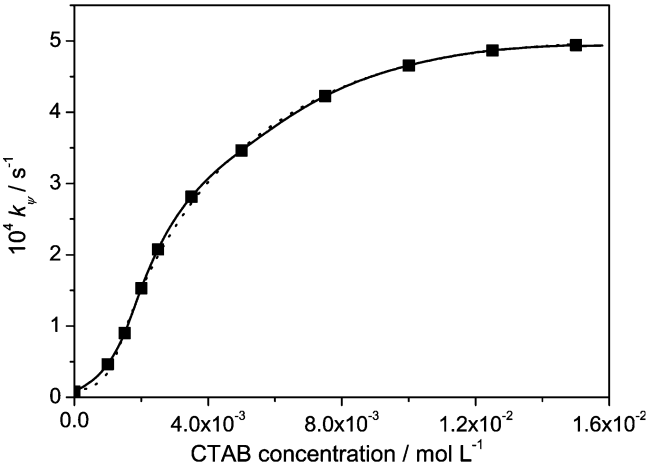
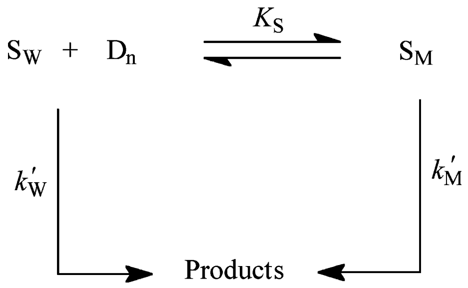


**Fig. 1** Variation of the pseudo-first-order rate constant with CTAB concentration at 25 °C in aqueous solutions containing 0.05 M NaOH. The *solid line* is predicted by Eqs. 5 and 6

The experimental results obtained for the reaction between DNCB and $OH^-$ in the presence of CTAB or 18-triazole-18 can be treated by the pseudophase ion-exchange (PIE) model of bimolecular reactions [7–11]. According to this model the micellar solution consists of a micellar pseudophase and an aqueous phase, and the reaction occurs in both phases as can be seen in Scheme 2.



**Scheme 2**

The subscript M and W denote the micellar and aqueous pseudophases, respectively, and S is the substrate. $D_n$ is the micellized surfactant whose concentration is given by $[D_n] = [D] - \text{cmc}$, where $[D]$ is surfactant concentration. However, for ionic gemini surfactants, which can be considered as the dimer of conventional single-chained surfactants, $D_n$ should be expressed as $[D_n] = 2([D] - \text{cmc})$ according to the PIE model. $K_S$ is the binding constant of the substrate to the micelle calculated from $K_S = [S_M]/[S_W][D_n]$. $k'_W$ and $k'_M$ are the pseudo-first-order rate constants for the reaction in aqueous and micellar pseudophases, respectively, given by

$$k'_W = k_W[OH^-_W], \tag{1}$$

$$k'_M = k_M[OH^-_M]/[D_n], \tag{2}$$

where $k_W$ and $k_M$ are the second-order rate constants for the reaction in aqueous and micellar pseudophases, respectively ($k_M$ is written in terms of the mole ratio of micellar $OH^-$ bound to the micellar head groups). $[OH^-_W]$ and $[OH^-_M]$ are concentrations of $OH^-$ in aqueous and micellar pseudophases, respectively. For competition between $OH^-$ reactive ion and $X^-$ as micelle counterion ($X$ = Br for CTAB, and $X$ = Cl for 18-triazole-18) on the micelle surface, the ion exchange equilibrium can be expressed as [9, 10]

$$OH^-_M + X^-_W \rightleftharpoons OH^-_W + X^-_M \tag{3}$$

with an equilibrium constant

$$K_X^{OH} = \frac{[OH^-_W][X^-_M]}{[OH^-_M][X^-_W]}. \tag{4}$$

**Table 1** The reaction rate constants and the parameters obtained from the fitting of kinetic results for the reaction between DNCB and $OH^-$ in micelles of CTAB or 18-triazole-18 at 25 °C

| Surfactant | cmc (mM) | $\beta$ | $K_S$ ($M^{-1}$) | $K_X^{OH}$ | $10^3$ $k_M^a$ ($s^{-1}$) |
|---|---|---|---|---|---|
| CTAB | 0.9 [1] | 0.80 | 85 | 9.2 | 4.01 |
| 18-triazole-18 | 0.19 | 0.72 | 335 | 13.7 | 4.54 |

[a] Expressed with concentration as a mole ratio of $OH^-$ to the micellized surfactant

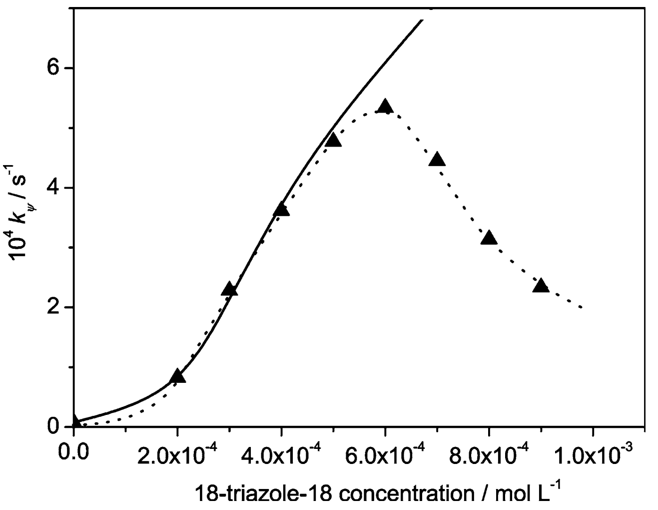


**Fig. 2** Variation of the pseudo-first-order rate constant with 18-triazole-18 concentration at 25 °C in aqueous solutions containing 0.05 M NaOH. The *solid line* is predicted by Eqs. 5 and 6

According to Scheme 2 and Eqs. 1, 2, 3, 4, the pseudo-first-order rate can be derived as [7–10]

$$k_\psi = \frac{k_W[OH_T^-] + (k_M K_S - k_W)[OH_M^-]}{1 + K_S[D_n]}, \tag{5}$$

where $[OH_T^-]$ is the total concentration of $OH^-$ reactive ion calculated from the relation$[OH_T^-] = [OH_W^-] + [OH_M^-]$, and $[OH_M^-]$ can be calculated from:

$$\left\{\frac{[OH_M^-]}{[D_n]}\right\}^2 + \frac{[OH_M^-]}{[D_n]}\left\{\frac{[OH_T^-] + K_X^{OH}[X_T^-]}{\{K_X^{OH} - 1\}[D_n]} - \beta\right\} - \frac{\beta[OH_T^-]}{\{K_X^{OH} - 1\}[D_n]} = 0, \tag{6}$$

where $[X_T^-]$ is the total concentration of counterion, and $\beta$ is the degree of counterion binding ($\beta = 1\text{-}\alpha$, $\alpha$ is degree of ionization of micelles). Experimental results for system containing CTAB were fitted with Eqs. 5 and 6 by using $K_S$,$K_X^{OH}$, and $k_M$ as adjustable parameters, and the result was listed in Table 1. In consideration of the experimental error, values of parameters $K_S$ and $K_X^{OH}$ for CTAB calculated in the present work were quite close to the results reported previously ($K_S$ = 67 $M^{-1}$, and $K_X^{OH} = 12.5$) [11, 12].

However, for gemini surfactant 18-triazole-18, it was quite difficult to fit experimental pseudo-first-order rate constants with Eqs. 5 and 6, as can be seen in Fig. 2. Although reaction rate constants calculated were in agreement of the experimental values at surfactant concentrations below ca. 0.5 mM, they were found to deviate largely from the experimental data at higher surfactant concentrations. Consequently, the traditional analysis of micellar-catalyzed reaction of DNCB with $OH^-$ for traditional single-chained surfactants may not be suitable for gemini surfactant system, and there may exist great differences of catalytic behavior between conventional surfactant and gemini surfactant systems. So, besides pseudophase ion-exchange model, the special physico-chemical properties, such as the significant increase of micelle microviscosity with an increase in the gemini surfactant concentration [16, 17], which have not been observed for conventional surfactants, should be taken into account to analyze the effects of gemini surfactant on micellar-catalyzed reactions.

The studies on gemini surfactants have demonstrated that the microviscosity increased strongly from the single-chained surfactant (monomer) to the gemini surfactant (dimer) [16, 17]. 18-triazole-18 showed a remarkable increase in viscosity in 0.05 M NaOH solution with an increase in surfactant concentration. When the concentration of 18-triazole-18 was higher than 1 mM in NaOH aqueous solution a gel formed, and above this concentration it was difficult to study such a system spectrophotometrically due to significant light scattering effects. So, higher microviscosity of the gemini surfactant may cause a decrease in diffusion coefficient of the reactants in aqueous solution of the gemini surfactant, thus resulting in a decrease in reaction rate. In addition, increased concentration of gemini surfactant may result in a strong tendency for micellar growth and changes of micelle shape [19], while micelles of CTAB remained spherical even at fairly high concentration. For example, a transmission electron microscope study at cryogenic temperature (cryo-TEM) on the microstructure of aqueous solutions of gemini surfactant 12-2-12 revealed significant changes of micelle shape with an increase in surfactant concentration [19, 20]. The micrograph showed spherical micelles and a few short cylindrical micelles at 0.26 wt.%. However, worm-like micelles appeared at 0.5 wt.%, co-existing with spherical micelles. As the concentration was increased from 0.26 to 1 wt.%, the fraction of material under the form of worm-like micelles increased and the number of spherical micelles per unit volume decreased rapidly. At 1 wt.%, branched thread-like micelles as well as closed ring cylindrical micelles were observed. At 1.5 wt.%, the micrograph showed a network of connected cylindrical and closed ring micelles with few isolated spherical and closed ring micelles [20].

According to the reaction mechanism of the micellar catalysis, the increases in micelle size may significantly influence the reaction state between the reactants at the micelle surface region. Firstly, the positive charge density of the cationic micelle surface decreased inversely with the square of the micelle radius, as a result, the concentration of $OH^-$ decreased at the micelle surface region where the reaction takes place, thus leading to a decrease in the reaction rate; and secondly, with an increase in micelle size, the hydrophobic substrate DNCB may enter the interior of the micelles, which is disadvantageous for the contact and reaction of the substrate with $OH^-$ at the micelle surface. Obviously, higher microvisocoty of the gemini surfactant 18-triazole-18, as well as significant increases in micelle size and changes of micelle shape with increased surfactant concentration should be responsible for the large deviation of the experimental data from the predicted values at higher surfactant concentration.

Although such the great deviation was found at high concentration of 18-triazole-18, pseudo-first-order rate constants at surfactant concentration below 0.5 mM were fitted with Eqs. 5 and 6 (Table 1), because significant increase in viscosity was found only at higher surfactant concentrations for 18-triazole-18. On the other hand, kinetic parameters may help us to get a better understanding of the difference between the conventional surfactant CTAB and the gemini surfactant 18-triazole-18 systems for micellar-catalyzed reaction of DNCB with $OH^-$, although these values are less reliable for the reason that they were derived from a limited range of observed data. It can be seen that $K_S$ value (335 $M^{-1}$) for gemini surfactant 18-triazole-18 was much larger than that for CTAB (85 $M^{-1}$), which indicates that DNCB binds with gemini micelles more easily than it binds with CTAB. This result is in accordance with previous studies on solubilization of some organic compounds in micellar solutions of some gemini surfactants, in which the gemini surfactants showed a larger solubilization capacity than conventional surfactants due to unique structure of gemini surfactant micelles [21, 22]. It was found also that $k_M$ value fitted with PIE model for 18-triazole-18 ($4.54\times10^{-3}$ $s^{-1}$) was slightly larger than that for CTAB ($4.01\times10^{-3}$ $s^{-1}$). However, the second-order rate constant in the micellar pseudophase which has the dimension of reciprocal of time cannot be compared directly for different micellar systems. The comparison can be made with the second-order rate constant ($k_M^2$ $M^{-1}$ $s^{-1}$) estimated from a relation $k_M^2 = k_M\ V_m$ [5–7] when the volume of the Stern layer ($V_m$) is taken into account. Although it was difficult for us to determine $V_m$ of 18-triazole-18 accurately, it has been demonstrated that $V_m$'s of gemini surfactants are much larger than that of corresponding single-chained surfactants [27]. As a result, $k_M^2$ for the gemini surfactant 18-triazole-18 system should be smaller than that for micellar system of CTAB. This can be easily explained by the fact that the hydrophobic substrate DNCB is solubilized in the interior of the micelles of 18-triazole-18, while in CTAB system DNCB is located in the micelle surface region.

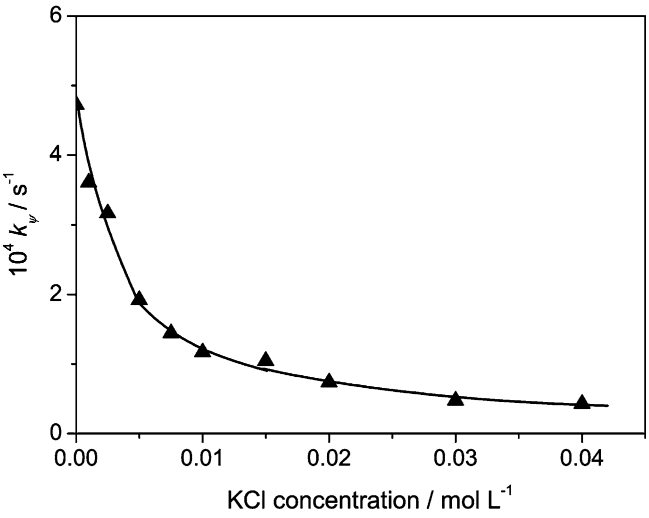


**Fig. 3** The pseudo-first-order rate constants versus KCl concentration. [NaOH] = 0.05 M, and [18-triazole-18] = 0.5 mM

The effect of chloride ion, which is the counterion of 18-triazole-18 micelles, on the reaction between DNCB and $OH^-$ in the precence of gemini surfactant 18-triazole-18 was also investigated. In this case, the total concentration of $Cl^-$ was taken as 2[18-triazole-18] + [KCl]. The pseudo-first-order rate constants obtained for reactions where the concentration of 18-triazole-18 0.5 mM and the reagent ion, NaOH 0.05 M at different concentrations of potassium chloride 1–40 mM are shown in Fig. 3. It can be clearly observed that the addition of KCl retards the reaction of DNCB in 18-triazole-18 micelles. The inhibition effect of added counterions on the micellar-catalyzed reaction of DNCB can be due to the competition between $Cl^-$ and $OH^-$ at micelle surface. $Cl^-$ has a greater affinity for the surface of the micelle, thereby displacing the $OH^-$ ions and resulting in a decrease in the concentration of $OH^-$ ions at the micelle surface. On the other hand, $Cl^-$ may compress the electrical double layer around the micelle surface to a greater extent and, hence, increase the aggregate number of the micelles and the size of the micelles [7]. Consequently, the organic substrate tends to enter the interior of the micelles more deeply, which is not favorable for the reaction at the micelle surface region.

## Conclusions

Micellar-catalyzed reactions between 2,4-dinitrochlorobenzene and hydroxide ion in micelles of a conventional cationic surfactant CTAB and a triazole-based cationic gemini surfactant 18-triazole-18, respectively, were studied. It was found that both CTAB and 18-triazole-18 accelerated the reaction. The binding constant of the substrate to the micelle, $K_S$, for 18-triazole-18 was found to be much larger than that for CTAB by fitting the kinetic results with PIE model, which suggests that DNCB binds with gemini micelles more easily than it with CTAB. Compared with CTAB, the gemini surfactant 18-triazole-18 system has a relatively low second-order rate constant considering the volume of the Stern layer in micellar pseudophase. It was found also that 18-triazole-18 catalytic system was in accordance with PIE model at surfactant concentrations below ca. 0.5 mM, above which higher viscosity and the change of micelle size with increased surfactant concentration may remarkably influence the reaction. This was quite different from micellar-catalyzed reaction of DNCB and hydroxide ion by conventional surfactant CTAB system.

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