# Water−Ethylene Glycol Alkyltrimethylammonium Bromide Micellar Solutions as Reaction Media: Study of the Reaction Methyl 4−Nitrobenzenesulfonate + Br−

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# Water−Ethylene Glycol Alkyltrimethylammonium Bromide Micellar Solutions as Reaction Media: Study of the Reaction Methyl 4-Nitrobenzenesulfonate + Br−

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The $S_N2$ substitution reaction between methyl 4-nitrobenzenesulfonate and bromide ions has been studied in several water−ethylene glycol, EG, cationic micellar solutions, the surfactants being hexadecyltrimethylammonium bromide, tetradecyltrimethylammonium bromide, and dodecyltrimethylammonium bromide. Together with the kinetic experiments, conductivity measurements gave information about the critical micelle concentration and the micellar ionization degree of the water−EG micellar solutions used as reaction media. They also permitted us to gain thermodynamic information about the influence of added EG on the micellization process of the surfactants investigated. A simple pseudophase model was shown to be useful in the discussion of the kinetic results. The importance of the working surfactant concentration range in the reliability of the adjustable parameters obtained from the fittings was stressed. It was found that the reaction was faster in cationic micelles than in water, in the absence as well as in the presence of ethylene glycol. The influence of the surfactant nature as well as of the ethylene glycol content on the equilibrium binding constant describing the distribution of the methyl 4-nitrobenzenesulfonate between the micellar and water−EG bulk phase and on the second-order rate constant for the reaction in the micellar pseudophase was rationalized by considering the polarity of the surface micellar region of the aggregates present in the different reaction media.

## Introduction

In a previous work,[1] we directed our attention to the study of water−ethylene glycol alkyltrimethylammonium bromide micellar solutions as reaction media. It was pointed out that despite the interest shown in ethylene glycol effects on the micellization process of several surfactants,[2−12] no kinetic studies have been carried out in water−EG (EG = ethylene glycol) micellar solutions. The surfactants selected were dodecyltrimethylammonium bromide, DTAB, tetradecyltrimethylammonium bromide, TTAB, and hexadecyltrimethylammonium bromide, CTAB, because there is extensive information about their aqueous micellar solutions.[13] Micellar kinetic effects are divided into two contributions: (i) micellar concentration effects and (ii) micellar medium effects. The former is related to the concentration or depletion of reactants in the interfacial region. The latter is related to the

different characteristics, as compared to the bulk phase, of the interfacial region where the reaction is taking place (polarity, water content, charge−charge interactions, etc.). In our first study, the authors chose a true first-order process, the spontaneous hydrolysis of phenyl chloroformate, to investigate the medium micellar effects, since the micellar concentration effects were ruled out. That is, the effect of the EG addition to the aqueous micellar solutions on the characteristics of the micelle−water interface region and the consequent kinetic micellar effects on the reaction were studied.

In the present work, a bimolecular process was studied: the substitution, $S_N2$, reaction between methyl 4-nitrobenzenesulfonate, MBS, and bromide ions. The mechanism of this process is well-known,[14] and it is not necessary to add bromide ions to the micellar reaction media since the bromide counterions of the surfactant molecules react with the organic substrate. The last point means that no changes in the characteristics of the micellar pseudophase are expected due to the presence of the reactants (the organic substrate concentration is low) compared to those in their absence and, therefore, structural information obtained for the water−EG micellar solutions can be used with confidence in the rationalization of the experimental kinetic data. Given that the process investigated is a bimolecular reaction, it is expected that the concentration micellar effects will be the main contribution to the kinetic micellar effects caused by the addition of EG to the cationic micellar solutions. Taking into account that the bromide counterions are involved in the reaction, the observed rate constant is expected to

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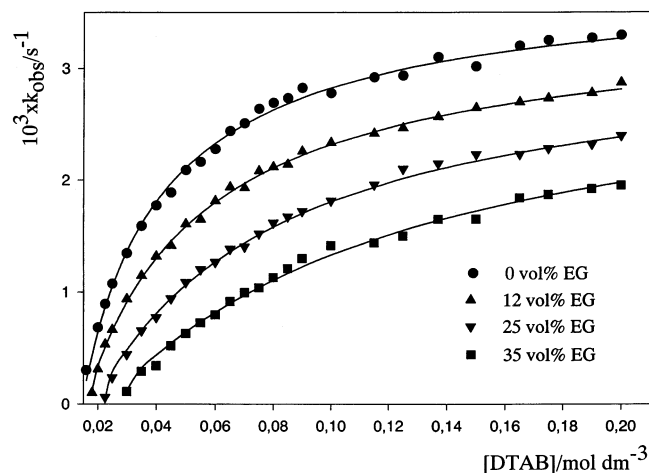
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**Figure 1.** Influence of the surfactant concentration on the observed rate constant, $k_{obs}/s^{-1}$, for the reaction methyl 4-nitrobenzenesulfonate + Br$^-$ in several water−EG DTAB micellar solutions. $T = 298.2$ K.

change substantially if the addition of EG causes changes in the micellar ionization degree. On the other hand, the rate of the methyl 4-nitrobenzenesulfonate + Br$^-$ reaction is also affected by the polarity of the medium in which it is occurring. In the authors' opinion, the investigation and discussion of the kinetic micellar effects provoked by the addition of EG to the cationic micellar solutions on the bimolecular reaction proposed, together with those observed previously in the study of the spontaneous hydrolysis of phenyl chloroformate, can provide valuable information about the water−ethylene glycol alkyltrimethylammonium bromide micellar solutions as reaction media.

## Experimental Section

**Materials.** Methyl 4-nitrobenzenesulfonate was from Fluka as was NaBr. DTAB, TTAB, and CTAB were from Fluka and used as received. Ethylene glycol was from Fluka and used without further purification.

**Conductivity Measurements.** Conductivity was measured with a Crison microCM 2201 conductimeter connected to a water flow thermostat maintained at $298.2 \pm 0.1$ K. The conductivity cell was calibrated with KCl solutions of the appropriate concentration range.

**Kinetics.** The reaction was monitored spectrophotometrically at 298.2 K in a Unicam UV-2 at 280 nm. The substrate was added as freshly prepared solution in acetonitrile. The low solubility of methyl 4-nitrobenzenesulfonate in water made it necessary to prepare its solutions in acetonitrile. Reaction solutions contained 1 vol % of acetonitrile, and the substrate concentration was $1 \times 10^{-4}$ mol dm$^{-3}$.

The temperature for the kinetic runs was maintained at $298.2 \pm 0.1$ K by using a water-jacketed cell compartment. Observed first-order rate constants were obtained from the slopes of the $\ln(A_\infty - A_t)$ versus time plots, $A_t$ and $A_\infty$ being the absorbances at the time $t$ and at the end of the reaction, respectively. Under the working conditions, in all the water−EG micellar solutions investigated, the first-order kinetic plots were linear for more than five half-lives. Each experiment was repeated at least twice, and the observed rate constant was found to be reproducible within a precision of about 5% or better.

## Results and Discussion

Figures 1−3 show the influence of changes in the surfactant concentration on the observed rate constant, $k_{obs}/s^{-1}$, for the reaction methyl 4-nitrobenzenesulfonate + Br$^-$ in several water−EG cationic micellar solutions, the surfactants being DTAB, TTAB, and CTAB. In all cases, an increase in the surfactant concentration results
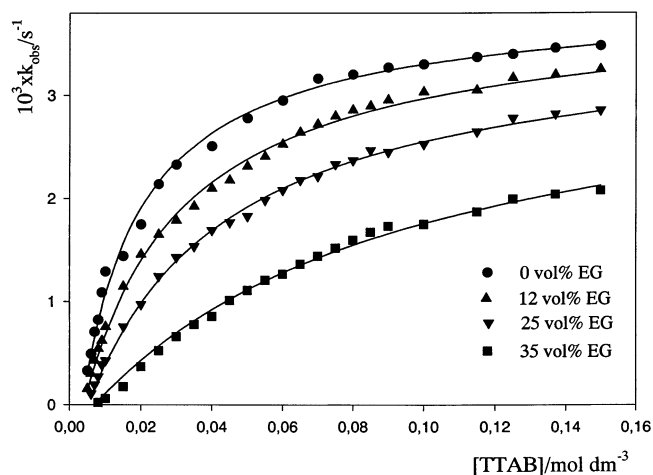


**Figure 2.** Influence of the surfactant concentration on the observed rate constant, $k_{obs}/s^{-1}$, for the reaction methyl 4-nitrobenzenesulfonate + Br$^-$ in several water−EG TTAB micellar solutions. $T = 298.2$ K.
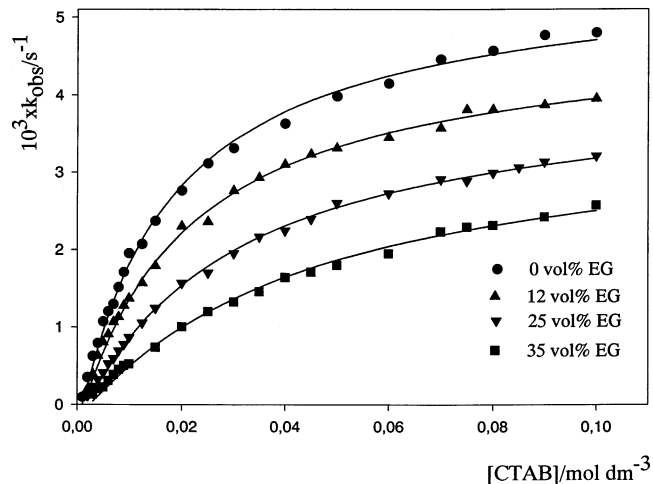


**Figure 3.** Influence of the surfactant concentration on the observed rate constant, $k_{obs}/s^{-1}$, for the reaction methyl 4-nitrobenzenesulfonate + Br$^-$ in several water−EG CTAB micellar solutions. $T = 298.2$ K.

in an increase in the reaction rate. This is an expected result since an increase in [surfactant] causes a further incorporation of the MBS molecules into the cationic micelles, where a high interfacial bromide concentration is present. On the other hand, one can see in Figures 1−3 that an increase in the amount of ethylene glycol present in the micellar solution provokes a decrease in the observed rate constant, for the three surfactants studied. To rationalize the influence of EG on the reaction rate, information about the effect of the volume percent of EG on the characteristics of the cationic micellar aggregates, in which part of the reaction is taking place, has to be obtained.

Table 1 summarizes the values of the critical micelle concentrations, cmc, and of the micellar ionization degrees, α, of the different water−EG micellar solutions. These magnitudes were obtained through conductivity measurements. The values corresponding to the aqueous DTAB, TTAB, and CTAB micellar solutions are in agreement with those in the literature.[8,13] The calculation of the cmc and α values deserves some comments. The authors, when using conductivity measurements, usually determined the cmc values from inflections in plots of conductivity, $\kappa$, against the surfactant concentration (Williams method[15]). The data points above and below

**Table 1. Critical Micelle Concentrations, cmc, Micellar Ionization Degrees, α, Standard Free Energy of Micellization, $\Delta G_M^\circ$, and the Effect of Ethylene Glycol on the Free Energy of Micellization, $\Delta G_{EG}^\circ$, for CTAB, TTAB, and DTAB Water−EG Micellar Solutions at $T = 298.2$ K**

| vol % EG | $10^3 \times$ cmc/ M | α | $-\Delta G_M^\circ/$ kJ mol$^{-1}$ | $\Delta G_{EG}^\circ/$ kJ mol$^{-1}$ |
|---|---|---|---|---|
| | | CTAB | | |
| 0 | 0.925 | 0.22 | 30.46 | |
| 12 | 1.15 | 0.23 | 29.68 | 0.78 |
| 25 | 1.60 | 0.25 | 27.91 | 2.55 |
| 35 | 2.85 | 0.26 | 25.26 | 5.20 |
| | | TTAB | | |
| 0 | 3.62 | 0.23 | 24.65 | |
| 12 | 4.00 | 0.24 | 24.07 | 0.58 |
| 25 | 5.10 | 0.25 | 22.88 | 1.77 |
| 35 | 7.00 | 0.27 | 21.17 | 3.38 |
| | | DTAB | | |
| 0 | 14.5 | 0.25 | 18.35 | |
| 12 | 16.0 | 0.27 | 17.72 | 0.63 |
| 25 | 19.5 | 0.29 | 16.68 | 1.67 |
| 35 | 24.5 | 0.33 | 15.35 | 3.00 |

the inflection are fitted to two equations of the form $\kappa = A[\text{surfactant}] + B$, and by solving simultanously the two equations the point of intersection is obtained. Least-squares analysis is employed. Subsequently, the micellar ionization degree is calculated from the ratios of the slopes of the plots of $\kappa$ against [surfactant] above and below the cmc. Criticisms have arisen about this method, particularly when a high micellar ionization degree is responsible for the conductivity not showing an abrupt change in going from the premicellar surfactant concentration range to the postmicellar surfactant concentration range.[16] Conductivity data in the water−EG cationic micellar solutions investigated have shown that an increase in the amount of EG results in an increase in the micellar ionization degree. This is in agreement with previous theoretical[11] and experimental[8] data obtained for CTAB micellar solutions. Taking this into account, in order to check the reliability of the cmc values (and therefore of the α values) obtained by the Williams method, the Phillips method was considered.[17] The Phillips method was applied through an integration by the Runge−Kutta method and a least-squares Levenberg−Maquardt fitting. The application of the Runge−Kutta method to the conductivity data is described in ref 18. Figure 4 shows an example of the Williams and Phillips methods applied to conductivity data. The two values are in good agreement. The same result was obtained in all the water−EG cationic micellar solutions studied, which means that the Williams method can be used with confidence. This gives reliability to the micellar ionization degrees listed in Table 1. There are discrepancies between the cmc and α values obtained in this work and those obtained by Bakshi et al.[8] for the CTAB water−EG micellar solutions. These authors purified the surfactant as well as the ethylene glycol before use, whereas in the present work the surfactants and the organic solvent were used as received. In our opinion, this could be the origin of the differences in the cmc and α values.

The data in Table 1 can be used to obtain information about the thermodynamics of micellization. To relate the
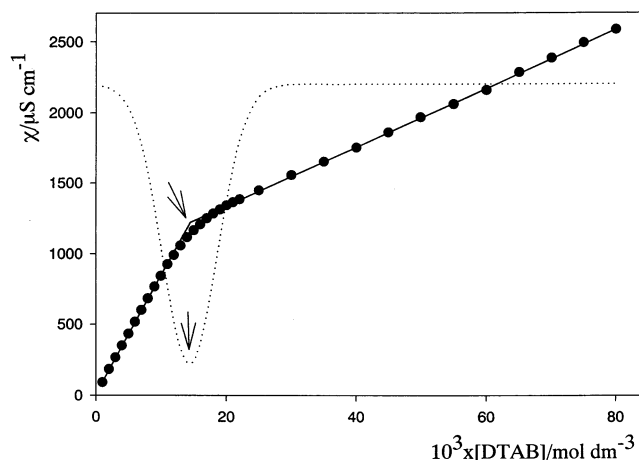
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**Figure 4.** Specific conductivity, $\kappa/\mu S$ cm$^{-1}$, of DTAB in water as a function of molar surfactant concentration. (●) Experimental points. Gaussian is the dotted line. Arrows denote the cmc obtained by the Williams and Phillips methods.

standard Gibbs free energy of micellization, $\Delta G_M^\circ$, to an equilibrium property such as the cmc, a pseudophase equilibrium model will be considered.[19] On this basis, the standard free energy of micelle formation of ionic surfactants is given by[19]

$$\Delta G_M^\circ = (2 - \alpha)RT \ln \text{cmc} \qquad (1)$$

where α is the micellar ionization degree. The $\Delta G_M^\circ$ values obtained by using eq 1 are listed in Table 1. Equation 1 is applicable when the aggregation number is large. Since a decrease in the aggregation number of the cationic micelles, as the amount of EG increases, is expected,[1,8] eq 1 may not be accurate for the higher concentrations of EG used, particularly in the case of DTAB.[13] Therefore, some of the $\Delta G_M^\circ$ values listed in Table 1 have to be viewed as an approximation. The dependence of the alkyltrimethylammonium bromide micellar aggregate characteristics on the amount of EG present in the mixture can be explained by considering the following solvent-dependent contributions to the free energy of micellization:[11] (i) the surfactant tail transfer free energy, (ii) the aggregate-core solvent interfacial free energy, and (iii) the headgroup interaction free energy. The large magnitude of the cmc originates mainly from the small magnitude of the tail transfer free energy from ethylene glycol−water mixtures compared to that from pure water. The (water−ethylene glycol)−hydrocarbon interfacial tension is lower than the pure water− hydrocarbon interfacial tension, and this results in a decrease in the aggregation number of the cationic micelles. On the other hand, the dielectric constant of EG (37.7 at 298.2 K[20]) is lower than that of water (78.39 at 298.2 K[20]). In the presence of 35 vol % of EG, the dielectric constant of the water−EG mixture at 298.2 K is 68.18.[21] Despite this, the ionic interactions at the micelle surface decrease rather than increase when the amount of EG in the mixture increases, this being due to the higher ionic strength present in the bulk solution because of the increase in the cmc. Therefore, the micellar ionization degree increases.

To calculate the effect of EG on the micelle aggregation process, eq 2 can be used:[10c]

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$$\Delta G^\circ_{EG} = \Delta G^\circ_{M(EG-water)} - \Delta G^\circ_{M(water)} \qquad (2)$$

The values of $\Delta G^\circ_{EG}$ are listed in Table 1 for the three surfactants studied. The EG effects on the micellization process are larger in CTAB than in TTAB and DTAB. If variations in the surfactant tail transfer free energy is the main factor controlling the cmc, one would expect the EG effects to follow the trend CTAB > TTAB > DTAB. However, no substantial differences are observed between TTAB and DTAB. This could be due to the assumptions involving eq 1 and, therefore, eq 2, which would affect particularly the DTAB micellar solutions.

With respect to the micellar ionization degrees, one can see that an increase in the volume percent of EG produces an increase in α for the three surfactants studied. As was mentioned above, this can be explained by a decrease in the interactions between the ionic headgroups at the micellar surface due to an increase in the ionic strength of the bulk phase. Apart from this, the micellar ionization degree follows the trend CTAB < TTAB < DTAB, although the values for CTAB and TTAB are closer than those for DTAB. This increase in the micellar dissociation with decreasing length of the alkyl group is in agreement with NMR data[22] and should be related to the headgroup spacing at the micellar surface.

Now, the kinetic data obtained in the water−EG micellar solutions will be considered. In this regard, it is necessary to take into account that the reaction of the organic substrate with water can make a contribution to the MBS + Br⁻ process investigated.[23] Besides, hydrolysis of the methyl 4-nitrobenzenesulfonate molecules can be affected by the presence of micelles[24] and by the composition of the water−EG bulk solution.[25] Brinchi et al.[24] found that the rate of the spontaneous hydrolysis of MBS molecules decreases by increasing the surfactant concentration in hexadecyltrimethylammonium mesylate, CTAOMs, micellar solutions. Besides, these authors considered that the micellar kinetic effects were similar for other hexadecyltrimethylammonium micellar solutions, with different counterions. With regard to the EG effects on the hydrolysis of MBS molecules, the reaction MBS + H$_2$O was studied in water and in water−EG homogeneous solutions. It was found that an increase in the amount of EG produces a decrease in the rate of the hydrolysis from $5.8 \times 10^{-5}$ s$^{-1}$ in pure water to $4.4 \times 10^{-5}$ s$^{-1}$ in water−EG, with 35 vol % of EG, at 298.2 K. That is, the effect of EG on the MBS + H$_2$O reaction is small. With this in mind, the authors assumed that the influence of changes in the surfactant concentration on the spontaneous hydrolysis of MBS molecules found in CTAOMs aqueous micellar solutions is similar to those in CTAB, TTAB, and CTAB micellar solutions, in the presence as well as in the absence of EG. The spontaneous hydrolysis is much slower than the reaction of methyl 4-nitrobenzenesulfonate molecules with bromide ions. Nonetheless, kinetic data shown in Figures 1−3 have been corrected, when necessary, for the spontaneous hydrolysis contribution. Similar Br⁻ + sulfonate ester reactions have also been studied in a variety of single surfactants as well as mixed surfactant micellar solutions.[26] However, no kinetic studies in water−cosolvent micellar solutions have been done.

**Table 2. Influence of the Amount of EG on the Reaction Methyl 4-Nitrobenzenesulfonate + Br⁻ in Water−EG Mixtures at $T$ = 298.2 K**

| | vol % EG | | | |
|---|---|---|---|---|
| | 0 | 12 | 25 | 35 |
| $10^4 \times k_2^{bulk}/M^{-1}\,s^{-1}$ | 4.50 | 4.63 | 5.35 | 6.27 |

To explain the kinetic data shown in Figures 1−3, taking into account pseudophase kinetic models, the observed rate for the reaction MBS + Br⁻ is equal to the sum of the processes occurring in each pseudophase. The differential expression is

$$-\frac{d[MBS_T]}{dt} = k_{obs}[MBS_T] = k_2^{bulk}[MBS_{bulk}][Br^-_{bulk}] + k_2^m[MBS_m][Br^-]_m \quad (3)$$

In this equation, square brackets indicate concentrations expressed in moles per liter of solution volume. The subscripts T, bulk, and m refer to the total, the water−EG bulk phase, and the micellar pseudophase, respectively. The observed rate of the reaction depends on the solution concentration of MBS and bromide ions. However, the rate of the reaction within the micellar pseudophase depends on the concentration of the bromide ions within the micelles in moles per liter of the reaction volume, $[Br^-]_m$, and not on its solution concentration, $[Br^-_m]$.[27] The relationship between the interfacial and solution concentrations of bromide ions is $[Br^-]_m = [Br^-_m]/(V_m[surfactant_m])$, $V_m$ being the molar reaction volume in units of dm$^3$ mol$^{-1}$. Taking this into account, the observed rate constant for the reaction MBS + Br⁻ can be written as

$$k_{obs} = \frac{k_2^{bulk}[Br^-_{bulk}] + (k_2^m/V_m)[Br^-_m]K_m}{1 + K_m[surfactant_m]} \quad (4)$$

In this equation, $(k_2^m/V_m) = k_{2m}$ (s$^{-1}$) is the second-order rate constant in the micellar pseudophase written with the concentrations as a molar ratio, $[Br^-_m]/[surfactant_m]$. $K_m$ is the equilibrium constant which describes the distribution of the MBS molecules between the water−EG bulk and micellar pseudophases. $k_2^{bulk}$ is the second-order rate constant in the water−EG bulk pseudophase. Therefore, to use eq 3 to discuss the kinetic data in water−EG micellar solutions, its value in the different homogeneous water−EG mixtures has to be obtained experimentally. Table 2 shows these values. One can see that an increase in the amount of EG present in the mixtures results in an increase in the second-order rate constant for the reaction MBS + Br⁻. This is in agreement with the expectations since an increase in the volume percent of EG originates a diminution of the polarity of the mixture[20,21] and this would favor reactions in which charge is dispersed in the transition state,[28] as is the case of the process investigated.[24]

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The distribution of the bromide ions between the bulk and micellar pseudophases was assumed to follow eq 5:[29]

$$K_{Br^-} = \frac{[Br_m^-]}{[Br_{bulk}^-]([surfactant_m] - [Br_m^-])} \quad (5)$$

Taking into account eq 5 and the mass balance, one can write

$$K_{Br^-}[Br_m^-]^2 -$$
$$(K_{Br^-}[surfactant_m] + K_{Br^-}[Br_T^-] + 1)[Br_m^-] +$$
$$K_{Br^-}[surfactant_m][Br_T^-] = 0 \quad (6)$$

For a given $K_{Br^-}$ value, eq 6 can be used to estimate the bromide ion concentration in the micellar pseudophase as a function of the micellized surfactant concentration (equal to $[surfactant_T] - cmc$) and total bromide ion concentration. Subsequently, by using eq 5 the bromide ion concentration in the bulk phase can be obtained. The authors considered a $K_{Br^-}$ value of 1000 mol$^{-1}$ dm$^3$ for aqueous CTAB micellar solutions. With regard to the other aqueous and water−EG micellar solutions, one would expect $K_{Br^-}$ to depend on the nature of the surfactant and on the amount of EG present in the bulk solution, since the micellar ionization degree depends on them (see Table 1) and the higher $\alpha$ is, the lower $K_{Br^-}$ is expected to be. To take the relation between $\alpha$ and $K_{Br^-}$ into account, the binding parameter can be expressed as

$$K_{Br^-} = \frac{1 - \alpha}{\alpha^2[surfactant_m]} \quad (7)$$

which indicates that a high micellar ionization degree corresponds to a low binding parameter. The change in $K_{Br^-}$ when the micellar ionization degree changes can be written as

$$\frac{K_{Br^-}(\alpha)}{K_{Br^-}(\alpha_0)} = \frac{(1 - \alpha)\alpha_0^2}{(1 - \alpha_0)\alpha^2} \quad (8)$$

where $\alpha_0$ is the micellar ionization degree of the aqueous CTAB micelles and $\alpha$ is the micellar ionization degree of any of the other water−EG alkyltrimethylammonium bromide micellar solutions. That is, the $K_{Br^-}$ values for the different micellar reaction media were calculated by using the $\alpha$ values listed in Table 1 and eq 8. From these binding parameters, using the cmc values listed in Table 1 and considering eqs 5 and 6, the bromide ion concentrations in the bulk and micellar pseudophases were calculated for each of the water−EG micellar reaction media. Once these concentrations were estimated, the kinetic data in Figures 1−3 were fitted by using eq 4. One can see that in all cases the agreement between the theoretical and the experimental data was good. However, before discussing the values of the adjustable parameters obtained it is interesting to make some comments about the fittings.

It is possible to find in the literature several $K_{Br^-}$ values for aqueous CTAB micellar solutions.[30] In this regard, the authors have checked how the consideration of one or another $K_{Br^-}$ value can affect the adjustable parameters obtained from the fitting of the kinetic data by using eq

**Table 3. Fitting Parameters for the Reaction Methyl 4-Nitrobenzenesulfoneto + Br$^-$ in Water−EG Alkyltrimethylammonium Bromide Micellar Solutions at $T = 298.2$ K**

| vol % EG | $K_m/$ mol$^{-1}$ dm$^3$ | $10^3 k_{2m}{}^a/$ s$^{-1}$ | vol % EG | $K_m/$ mol$^{-1}$ dm$^3$ | $10^3 k_{2m}{}^a/$ s$^{-1}$ |
|---|---|---|---|---|---|
| | | CTAB | | | |
| 0 | 76 | 5.87 | 25 | 42 | 4.38 |
| 12 | 62 | 5.10 | 35 | 27 | 3.80 |
| | | TTAB | | | |
| 0 | 71 | 4.13 | 25 | 30 | 3.79 |
| 12 | 42 | 4.05 | 35 | 13 | 3.60 |
| | | DTAB | | | |
| 0 | 39 | 3.92 | 25 | 17 | 3.36 |
| 12 | 27 | 3.58 | 35 | 10 | 3.30 |

$^a$ $k_{2m} = (k_2^m/V_m)$.

4. It was found that the $k_{2m}$ and $K_m$ values obtained by using different $K_{Br^-}$ values given in the literature for aqueous CTAB micellar solutions are similar. This point has also been investigated in a previous work.[31] Some authors have pointed out the problem concerning the possible lack of meaning of the kinetic constants estimated from fittings of kinetic data,[25,32] since more than one set of parameters are able to give good fittings. In this regard, the authors found that only one set of $k_{2m}$ and $K_m$ values gave the best fitting for each of the micellar solutions used as reaction media. However, for this to happen it is important to work within a wide surfactant concentration range. That is, one has to monitor the reaction at surfactant concentrations from just above the cmc (which, therefore, has to be obtained previously) to high enough [surfactant] to see the kinetic profiles go to saturation. Taking this into account, the kinetic experiments in TTAB were done at surfactant concentrations up to 0.15 M, whereas in DTAB micellar solutions the experiments were done up to 0.2 M. The authors found that, for instance, in water−EG DTAB micellar solutions if the fittings were done with experimental kinetic data corresponding to [DTAB] up to 0.1 M, the convergence was no good and more than one set of parameters gave similar results. When the surfactant concentration range was wide enough, using experimental data for $k_2^{bulk}$ and cmc, only one set of parameters gave the best fittings. Apart from this, only substantial changes in the adjustable parameters obtained from the fittings are worth discussing because of the simplicity of the model used for explaining the experimental kinetic data.

Table 3 shows the adjustable parameters obtained by the fitting of the kinetic data in Figures 1−3 by using eq 4. As was mentioned above, all the fittings are good, which points out that the pseudophase model used was adequate for discussing the kinetic data in water−EG micellar solutions. The authors found in the literature only one work on the applicability of the pseudophase ion exchange model for rationalizing kinetic micellar effects in water−glycerol mixtures,[33] where the equilibrium ion exchange constant, $K_{OH/Br}$, was assumed to be equal to that in water and independent of the amount of glycerol present in the bulk solution. Given the scarce studies on kinetic micellar effects in water−cosolvent micellar solutions, the conclusion that a simple pseudophase model is adequate to explain kinetic micellar effects in those media is helpful for future works.

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Table 3 shows that the equilibrium binding constants describing the distribution of the MBS molecules between the bulk and micellar pseudophases are small, in agreement with previous results.[24,31] Besides, $K_m$ values follow the trend $K_m(\text{CTAB}) > K_m(\text{TTAB}) < K_m(\text{DTAB})$ and it decreases as the volume percent of EG increases. In regard to the influence of the amount of EG present in the bulk phase, an increase in the volume percent of EG produces a decrease in the polarity of the bulk solution. A decrease in the dielectric constant, in the Reichardt parameter, $E_T$, in the Gutman donor number, DN, and in the $\pi^*$ polarity index[20,21,34] would result in the water−EG solutions being a better solvent for the organic substrate as the volume percent of EG increases. Therefore, the affinity of the MBS molecules for the bulk phase increases and, thus, $K_m$ is expected to decrease, as was found.

The interpretation of the influence of the surfactant nature on $K_m$ is similar, and it can be done by considering that the methyl 4-nitrobenzenesulfonate molecules are expected to be located at the micellar surface.[35] In a previous work,[1] the polarity of the micellar surface region of the CTAB, TTAB, and DTAB micelles in various water−EG solutions was investigated by using various methods. The pyrene 1:3 ratio method,[36] the solvent-dependent fluorescence of pyrene-3-carboxaldehyde,[37] and the Reichardt $E_T$ parameter[38] were considered. All of them give the same information. In water−EG solutions, with weight percent of EG up to 50%, the polarity of the surface micellar region follows the trend CTAB < TTAB < DTAB, although the polarities of the CTAB and TTAB interfacial regions are much more similar than those of DTAB, for any water−EG solutions studied. Besides, an increase in the amount of EG present in the bulk solution produces an increase in the polarity of the micellar surface in the three cationic micellar solutions studied. These results were explained by considering that the aggregation number of the CTAB, TTAB, and DTAB micelles decreases as the amount of EG increases. This would mean a less packed micelle, which would make the penetration of solvent molecules, water as well as ethylene glycol, in the palisade layer easier, resulting in a more polar environment for the probes used to get information about the interfacial region. On this basis, $K_m$ values are expected to follow the trend $K_m(\text{CTAB}) > K_m(\text{TTAB}) > K_m(\text{DTAB})$, in agreement with the observations (see Table 3). Besides, an increase in the polarity of the surface micellar region as the volume percent of EG increases would influence $K_m$, diminishing it. That is, the dependence of $K_m$ on EG content is due to a decrease in the polarity of the bulk phase as well as to an increase in the polarity of the surface micellar region when the volume percent of EG increases.

Table 3 shows that the relation $(k_m{}^2/V_m)$ follows the trend $k_{2m}(\text{CTAB}) > k_{2m}(\text{TTAB}) > k_{2m}(\text{DTAB})$ for all the water−EG micellar solutions studied and decreases as EG content increases for the three cationic micellar solutions studied. First, in order to compare reactivity in water and in micelles, the values corresponding to pure water will be considered. One can find in the literature $V_m$ values for aqueous CTAB, TTAB, and DTAB micellar solutions, and this will permit us to compare the results obtained for the

three surfactants. Using the data given in ref 39 and assuming spherical aggregates, one can estimate $V_m = 0.37$ dm$^3$ mol$^{-1}$ for CTAB, $V_m = 0.33$ dm$^3$ mol$^{-1}$ for TTAB, and $V_m = 0.30$ dm$^3$ mol$^{-1}$ for DTAB. From these values, one obtains the second-order rate constants at the micellar pseudophase, $k_2^m$, for the reaction MBS + Br$^-$ as equal to $2.17 \times 10^{-3}$, $1.36 \times 10^{-3}$, and $1.17 \times 10^{-3}$ M$^{-1}$ s$^{-1}$ for CTAB, TTAB, and DTAB, respectively. In all cases, the reaction is faster in the micellar pseudophase than in water ($k_2^w = 4.5 \times 10^{-4}$ M$^{-1}$ s$^{-1}$). The main factors involved in the catalysis of the reaction by the cationic micellar aggregates would be the electrophilic interaction of the ammonium headgroups and the forming nitrobenzene-sulfonate ion and disruption of the hydration shell of the bromide ion. As has been said previously,[40] the second factor is probably more important because reactions of nucleophilic anions are strongly inhibited by anionic solvation, and disruption of this solvation is a major part of the energy barrier to reaction. With respect to the influence of the surfactant nature on $k_2^m$, the reaction seems to follow the trend CTAB > TTAB > DTAB. Nonetheless, the differences are not large, particularly between TTAB and DTAB, and to discuss them would be rather speculative. They could be related to the differences in the polarity of the surface micellar regions (the reaction is favored by a decrease in the polarity of the reaction medium).

The discussion of the EG content effects on $k_2^m$ is difficult because no information about changes in $V_m$ upon changing the amount of EG in the bulk solution has been found in the literature and these values are needed in order to calculate $k_2^m$ from $k_{2m}$. The authors found some information about the influence of EG content on the aggregation number and the hydrodynamic radius of Triton X-100 micelles in water−EG solutions.[10] In this particular case, the two of them decrease as the weight percent of EG increases and, assuming spherical micelles, this results in a small decrease in $V_m$ for a weight percent of EG up to 40%. Nagarajan et al.[11] calculated the variation in the aggregation number of CTAB micelles in water−EG solutions when the amount of EG in the solution increases, $N_{agg}$ decreasing as EG content increases. No data about the hydrodynamic radius are given. Since the variations in $k_{2m}$ are not large, no discussion about them will be done here. Nevertheless, at first, since an increase in polarity is unfavorable for the reaction, an increase in the EG content is expected to retard the reaction occurring at the micellar surface, as is found.

In conclusion, a simple pseudophase model is useful for rationalizing the kinetic micellar effects observed on the reaction methyl 4-nitrobenzenesulfonate + Br$^-$ in water−ethylene glycol cationic micellar solutions, the surfactants being CTAB, TTAB, and DTAB. The reaction is accelerated by cationic micelles, as compared to the bulk phase, in any of the water−EG micellar solutions studied. For a given [surfactant], $k_{obs}$ decreases as the volume percent of EG increases. This is due to (i) a decrease in the equilibrium binding constant, which results in a decrease of the contribution of the reaction occurring in the micellar interfacial region, and (ii) a decrease in the bromide ion concentration in the interfacial region. Changes in $k_{2m}$

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are not large, and their discussion, since the variations in $V_m$ with the volume percent of EG are not known, would be speculative. Nonetheless, its changes seem to be related to changes in the polarity of the water−micelle interface.

Kinetic micellar effects of the addition of alcohols, such as 1-butanol, 1-pentanol, and 1-hexanol, on Br⁻ + sulfonate ester reactions in cationic micellar solutions, at a given [surfactant], are similar to those found by the

addition of EG in this work.[41] Factors i and ii can also account for them. However, alcohol molecules incorporate into the micelles, whereas EG molecules seem to remain in the bulk phase.

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