Study of the reaction 1-methoxy-4-(methylthio)benzene + IO_4^-: importance of micellar medium effects

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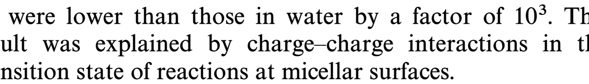
The oxidation of 1-methoxy-4-(methylthio)benzene by IO_4^-, rendering the corresponding sulfoxide and IO_3^-, was studied in zwitterionic (SB3-16) and nonionic ($Brij_{35}$, Tween 20, Tween 40, Tween 60 and Tween 80) aqueous micellar solutions. The association equilibrium constants of the sulfide molecules to the micellar aggregates present in the different media were obtained by spectroscopic measurements. In the case of the sulfobetaine micellar solutions, the equilibrium constant for the incorporation of periodate anions in the zwitterionic micellar aggregates was obtained through conductivity measurements. Taking into account literature data on this reaction in cationic and anionic micellar solutions, a comparison of the second order rate constants in the micellar pseudophases of nonionic, anionic, cationic and zwitterionic micellar solutions was undertaken. This comparison, together with kinetic data obtained in water–cosolvent mixtures, as well as in aqueous electrolyte solutions, shows that charge–charge interactions and the low polarity of the micellar pseudophases account for the large differences between the second order rate constants in pure water and those in micellar solutions.

Aqueous micelles and other association colloids can influence reaction rates and equilibria, and the concentration or depletion of reactants in the interfacial region has a major effect on the rates of bimolecular reactions.[1] Together with this *concentration effect*, micelles also exert a *medium effect* that influences reactivity. This effect depends on the transfer of substrate from water to micelles, on the reaction mechanism, and on the properties of the interfacial region, such as local charge, polarity and water content. For most of the bimolecular processes studied in micellar solutions, after the estimation of local concentrations in the micellar pseudophase (either experimentally or in terms of theoretical treatments), second order rate constants in water were found to be similar to those in micelles,[2] the kinetic micellar effects observed being mainly due to the concentration of one or both reactants in the small volume of the micelles. However, there are processes for which large kinetic micellar effects, not connected to concentration effects, are operative, as for example in aromatic substitution by azide ions.[2] Another example is the oxidation of organic sulfides to sulfoxides by anionic oxidants. The latter were investigated by Bunton *et al.* in anionic, cationic and zwitterionic micellar solutions.[3] These authors found that in anionic micellar solutions the second order rate constants were lower than those in water by factors of 2–6, but for reactions of some sulfides [such as 1-methoxy-4-(methylthio)benzene] the second order rate constants in cationic and zwitterionic micelles were lower than those in water by a factor of 10^3. This result was explained by charge–charge interactions in the transition state of reactions at micellar surfaces.

In order to complete the study carried out by Bunton *et al.*, the reaction between 1-methoxy-4-(methylthio)benzene, ArSMe and periodate anion, IO_4^- (Scheme 1), was studied in several nonionic micellar solutions (nonionic surfactants used were dodecyl tricosaoxyethylene glycol ether, $Brij_{35}$, and the esters of long-chain fatty acids and sorbitan polyethylene glycol: Tween 20, Tween 40, Tween 60 and Tween 80). The head groups of the nonionic surfactants have no charge and, therefore, no charge–charge interactions will be operative. This means that polarity and water content at the micellar surfaces of nonionic micelles will mainly determine the differences between the second order rate constants in water and in the micellar pseudophases of nonionic micellar solutions. This allows us, initially, to estimate the contribution of charge–charge interactions in ionic micellar solutions independent of the polarity and water content effect on the reaction rate.



$$\mathrm{Ar{-}S{-}Me + O{=}IO_3^- \rightarrow [Ar{-}\underset{\displaystyle Me}{\underset{|}{S^{\bullet+}}}\,O^-{-}IO_3^{\bullet-}]^{\neq} \rightarrow Ar{-}SO{-}Me + IO_3^-}$$

Scheme 1 Ar = 4-Methylbenzyl.

The reaction has also been studied in zwitterionic micellar solutions of *N*-hexadecyl-*N*,*N*-dimethyl-3-ammonio-1-propanesulfonate, SB3-16. Conductivity measurements have permitted the distribution equilibrium constant of periodate anion in SB3-16 micellar solutions to be obtained. The use of this equilibrium constant allows us to calculate the second order rate constant in the micellar pseudophase of these zwitterionic micellar systems.

The goal of this work is to estimate, if possible, the effect of the local charge of the interfacial region on the oxidation of the sulfide 1-methoxy-4-(methylthio)benzene by periodate, independent of other micellar medium effects. With this in mind, kinetic micellar effects on this reaction in cationic, anionic, zwitterionic and nonionic micellar solutions will be considered.

Experimental

Materials

1-Methoxy-4-(methylthio)benzene, ArSMe and sodium periodate were obtained from Aldrich. *N*-Hexadecyl-*N*,*N*-dimethyl-3-ammonio-1-propanesulfonate, SB3-16, Tween 20, Tween 40, Tween 60 and Tween 80 were from Fluka and used as received. Reichardt's dye, $E_T(30)$, and methyl orange were

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obtained from Aldrich, as were sodium dodecyl sulfate, SDS, and hexadecyltrimethylammonium chloride, CTAC. All the background electrolytes used were from Fluka. Water was obtained from a Millipore Milli-Q water system, its conductivity being less than 10^{-6} S cm^{-1}.

Measurements

Conductivity measurements. Conductivity was measured with a Crison MicroCM 2201 conductometer connected to a water-flow thermostat maintained at 298.2 ± 0.1 K.

Determination of the critical micellar concentration. The CMC of the SB3-16 aqueous solutions in the presence and in the absence of 2×10^{-3} mol dm^{-3} $NaIO_4$ was obtained by registering the spectrum of methyl orange as a function of surfactant concentration. The CMC obtained at 298.2 K for pure SB3-16 aqueous solutions, 2.7×10^{-5} mol dm^{-3}, agrees with that in the literature.[4]

E_T values. Spectra of the assay solutions containing the $E_T(30)$ dye were recorded in a Unicam UV-2 spectrophotometer at 298.2 K. These spectra were recorded against a blank consisting of an aqueous micellar solution of identical concentration to the assay solution. Five spectra were recorded for each assay solution.

Equilibrium binding constants. The equilibrium binding constants of ArSMe to the micellar aggregates present in the zwitterionic and nonionic micellar solutions used as reaction media can be written as:

$$K_m = \frac{[\mathrm{ArSMe_m}]}{[\mathrm{ArSME_w}][\mathrm{Surfactant_m}]} \qquad (1)$$

where the subscripts w and m denote the aqueous and micellar pseudophases, respectively, and $[\mathrm{Surfactant_m}]$ is the concentration of micellized surfactant, equal to the surfactant concentration minus the CMC. Assuming that Beer's law is obeyed, one can write:[5]

$$K_m = \frac{A_m - A_w}{A_m - A}\,\frac{1}{[\mathrm{Surfactant_m}]} \qquad (2)$$

where A is the observed absorbance and A_w and A_m are the absorbances in water and of fully micellar-bound sulfide, respectively. In the case of ArSMe we could not measure A_m directly because of the relatively low binding of this organic substrate to the micellar aggregates present in the different micellar reaction media, as indicated previously by Bunton *et al.*[3] To estimate K_m without the measurement of A_m the following equation was considered:[6]

$$A = A_m - \frac{A_m - A_w}{K_m[\mathrm{Surfactant_m}] + 1} \qquad (3)$$

The experimentally accessible terms of eqn. (3) are A, A_w and $[\mathrm{Surfactant_m}]$. Eqn. (3) was used to estimate the equilibrium association constant of 1-methoxy-4-(methylthio)benzene by registering the changes in absorbance at 260, 265 and 270 nm. From the fittings of the absorbance data, at the three different wavelengths, the same K_m was obtained, within experimental errors. The absorbance data in the case of the Tween surfactants were corrected for the contribution of the surfactant absorbance. This contribution was practically negligible in the case of Tween 20 and Tween 40. However, for Tween 60 and particularly for Tween 80, the contribution is large. In these cases, although the absorbance values were corrected from the contribution of the surfactant, the equilibrium binding constants obtained for Tween 60 and Tween 80 are subject to larger experimental errors than in the case of Tween 20 and Tween 40.

Kinetics. Rates of the reaction ArSMe + IO_4^- were followed in an excess of periodate ion at 260 nm. The rate measurements were performed using Unicam UV-2 and Unicam Helios γ spectrophotometers. In all cases the sulfide concentration was 1.5×10^{-5} mol dm^{-3} and the periodate concentration was 2×10^{-3} mol dm^{-3}. The low solubility of 1-methoxy-4-(methylthio)benzene in water made it necessary to prepare its solutions in acetonitrile. The percentage of acetonitrile in the reaction mixture was always 1 vol.%. Previous works[4,7] found that the presence of this percentage of acetonitrile does not affect the CMC of aqueous solutions of sulfobetaine and nonionic surfactants.

The temperature for the kinetic runs was maintained at 298.2 ± 0.1 K by using a water-jacketed cell compartment. Rate constants were reproducible within a precision of better than 4%.

To test our data the observed rate constant value obtained in water at 298.2 K, $k_{2w} = 1.51$ dm^3 mol^{-1} s^{-1}, was compared to that in the literature, $k_{2w} = 1.55$ dm^3 mol^{-1} s^{-1},[3] the agreement being good. Some kinetic runs were carried out in SB3-14 micellar solutions, the observed rate constant values also being in agreement with literature data.

The kinetics were not carried out at high concentrations of Tween 80 because of experimental problems.

Results and discussion

Fig. 1 to 6 show the dependence of the observed rate constant on changes in surfactant concentration for several of the micellar solutions used as reaction media. In all cases, the

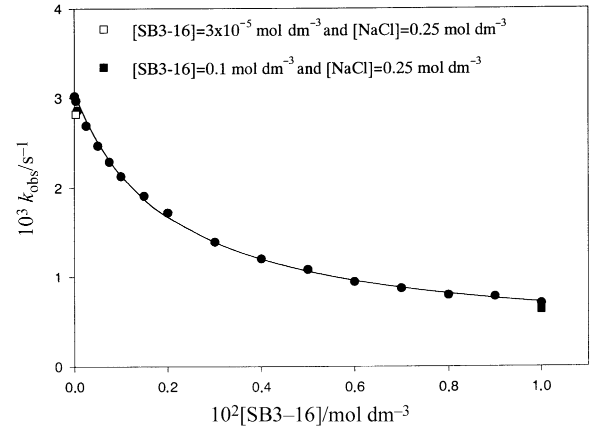

Fig. 1 Dependence of the observed rate constant, k_{obs}/s^{-1}, for the reaction 1-methoxy-4-(methylthio)benzene + IO_4^- on surfactant concentration in SB3-16 aqueous micellar solutions at 298.2 K.

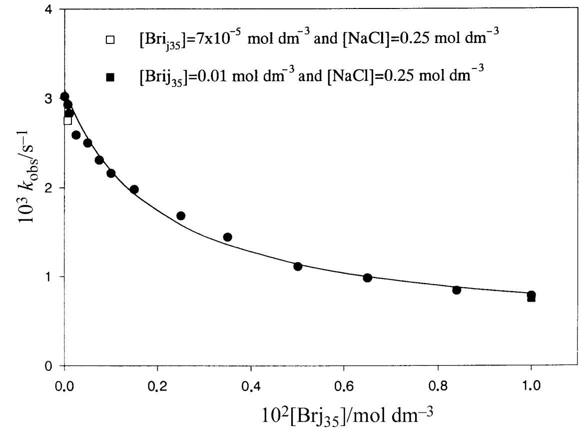

Fig. 2 Dependence of the observed rate constant, k_{obs}/s^{-1}, for the reaction 1-methoxy-4-(methylthio)benzene + IO_4^- on surfactant concentration in $Brij_{35}$ aqueous micellar solutions at 298.2 K.

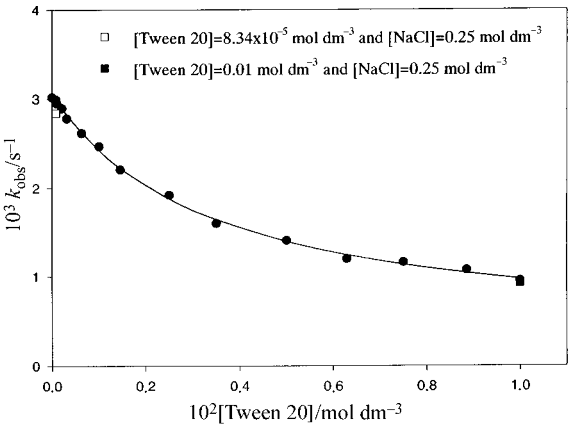

Fig. 3 Dependence of the observed rate constant, k_{obs}/s^{-1}, for the reaction 1-methoxy-4-(methylthio)benzene + IO_4^- on surfactant concentration in Tween 20 aqueous micellar solutions at 298.2 K.

same behavior is found, k_{obs} decreases as the surfactant concentration increases, this decrease being larger at low than at high surfactant concentrations. The reaction rate seems to reach a plateau for high surfactant concentrations. This behavior is described by the treatment of first order reactions based on pseudophase models:[7]

$$k_{OBS} = \frac{k_w + k_m K_m[\text{Surfactant}_m]}{1 + K_m[\text{Surfactant}_m]} \quad (4)$$

where k_w and k_m are pseudo-first order rate constants in the aqueous and micellar pseudophases, respectively. K_m is the equilibrium binding constant [described in eqn. (1)] of the 1-methoxy-4-(methylthio)benzene molecules to the micelles present in the reaction medium, and [Surfactant$_m$] is the concentration of micellized surfactant. The solid lines in Fig. 1 to 6 were obtained from the fittings of the kinetic data by using eqn. (4). The association equilibrium constants were obtained from spectroscopic measurements except in the case of the nonionic micellar solutions of Tween 60 and Tween 80, for which experimental problems (see Experimental) made K_m more reliable as an adjustable parameter. The CMC values considered for the fittings were those corresponding to the pure aqueous surfactant solutions in the case of the nonionic surfactants. The low concentration of sodium periodate present in the reaction medium is not expected to affect substantially the CMC of these surfactant solutions. The value of the CMC of SB3-16 aqueous solutions in the presence of 2×10^{-3} mol dm^{-3} of $NaIO_4$ was obtained from spectroscopic measurements by using methyl orange and was equal to 2.4×10^{-5} mol dm^{-3}. This value is reasonable in view of the variations of the CMC of SB3-14 aqueous solutions found in the presence of various amounts of $NaIO_4$. Table 1 shows the values of K_m and k_m obtained for the different micellar solutions used.

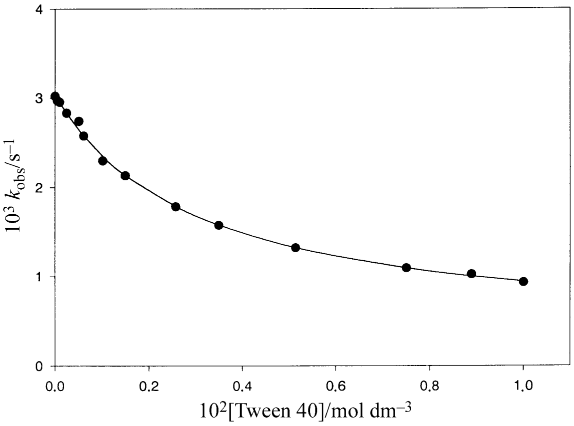

Fig. 4 Dependence of the observed rate constant, k_{obs}/s^{-1}, for the reaction 1-methoxy-4-(methylthio)benzene + IO_4^- on surfactant concentration in Tween 40 aqueous micellar solutions at 298.2 K.

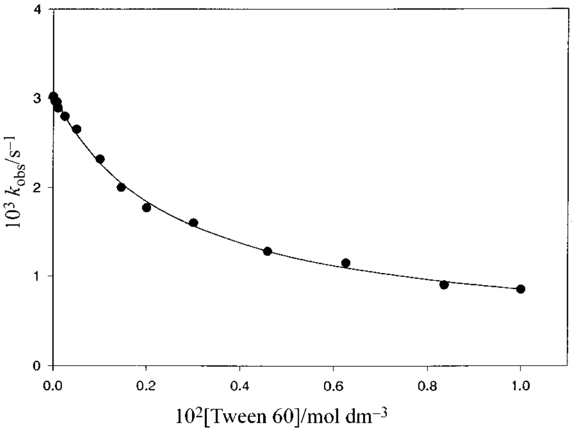

Fig. 5 Dependence of the observed rate constant, k_{obs}/s^{-1}, for the reaction 1-methoxy-4-(methylthio)benzene + IO_4^- on surfactant concentration in Tween 60 aqueous micellar solutions at 298.2 K.

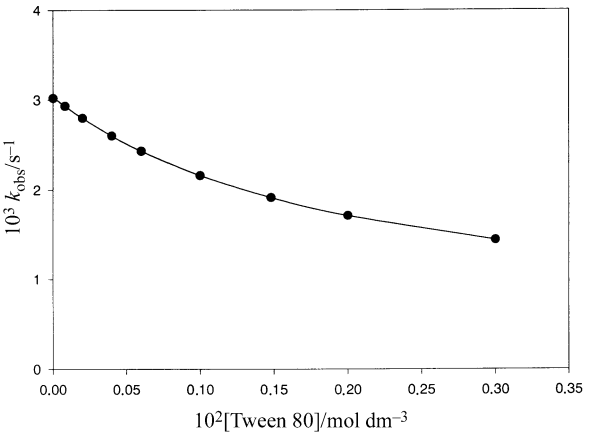

Fig. 6 Dependence of the observed rate constant, k_{obs}/s^{-1}, for the reaction 1-methoxy-4-(methylthio)benzene + IO_4^- on surfactant concentration in Tween 80 aqueous micellar solutions at 298.2 K.

To investigate the influence of the kinetic micellar medium effects on the reaction rate it is neccesary to obtain the second order rate constant of the reaction in the micellar surface. In order to do this, the following equation should be considered:

$$k_{obs} = \frac{k_{2w}[IO_4{}^-{}_w] + k_{2m}K_m[IO_4{}^-{}_m]}{1 + K_m[\text{Surfactant}_m]} \quad (5)$$

In this equation, the concentrations were referred to the total solution volume, k_{2w} is the second order rate constant in the aqueous phase (being equal to 1.51 dm^3 mol^{-1} s^{-1}), and k_{2m} (s^{-1}) is the second order rate constant in the micellar pseudophase written with concentration as a molar ratio, $[IO_4{}^-{}_m]$/[Surfactant$_m$]. To estimate k_{2m}, $[IO_4{}^-{}_m]$, and therefore $[IO_4{}^-{}_w]$, has to be calculated at the different surfactant concentrations. In this regard, and taking into account that the micellar surface of nonionic micelles has no charge as well as the hydrophilic character of the IO_4^- anion, the periodate ion concentration will be the same in the aqueous and micellar pseudophases of nonionic micellar solutions.[8] In the case of SB3-16 micellar solutions, the incorporation of periodate ions into the sulfobetaine micelles can be described by:[9]

$$K_{IO_4} = \frac{[IO_4{}^-{}_m]}{[IO_4{}^-{}_w]([\text{SB3-16}_m] - [IO_4{}^-{}_m])} \quad (6)$$

In this equation all concentrations are expressed as mol per liter of the total solution volume, $[IO_4{}^-{}_w]$ and $[IO_4{}^-{}_m]$ being

Table 1 Equilibrium association constants and pseudo-first order and second order rate constants for the reaction ArSMe + IO_4^- in several micellar solutions at 298.2 K with $k_{2w} = 1.51$ dm^3 mol^{-1} s^{-1}

Surfactant	K_m/M^{-1}	$10^4 \times k_m$/s^{-1}	k_{2m}/dm^3 mol^{-1} s^{-1}	k_{2m}/k_{2w}
SB3-14	300[a]	—	1×10^{-3}	0.00066
SB3-16	320 ± 13[b]	2.3 ± 0.4	$(1.2 \pm 0.1) \times 10^{-3}$	0.00079
Brij$_{35}$	300 ± 15[b]	3.3 ± 0.9	0.16 ± 0.04	0.106
Tween 20	287 ± 16[b]	2.7 ± 0.6	0.13 ± 0.04	0.090
Tween 40	325 ± 15[b]	3.0 ± 0.5	0.14 ± 0.04	0.100
Tween 60	381 ± 24[c]	2.8 ± 0.6	0.14 ± 0.04	0.093
Tween 80	470 ± 30[c]	3.1 ± 0.4	0.15 ± 0.05	0.102
SDS[d]	220	—	0.6	0.397
CTAC[d]	340	—	1.3×10^{-3}	0.00086

[a] Ref. 3(*c*); [b] Obtained from spectroscopic measurements in this work. [c] Obtained as an adjustable parameter from the kinetic data. [d] Values from ref. 3(*b*).

the concentrations of periodate ions in the aqueous and micellar pseudophases, respectively. This equation was shown to fit conductivity data well for added salts in zwitterionic micelles[10] and has permitted the estimation of K_X values for different anions.

Fig. 7 shows the variation of the conductivity of a 5×10^{-3} mol dm^{-3} $NaIO_4$ aqueous solution when different concentrations of SB3-16, up to 0.1 mol dm^{-3}, are added to the medium, at 298.2 K. To fit the conductivity data shown in Fig. 7, ion–ion and ion–micelle interactions were neglected as well as excluded volume effects (which become important for [SB3-16] > 0.1 mol dm^{-3}). The conductivity of the aqueous sodium periodate solutions in the presence of SB3-16 micelles can be expressed as:[11]

$$\kappa = \frac{qF\alpha[\text{SB3-16}_m]}{9.11 \times 10^{14}\rho} + 10^{-3}[IO_4{}^-{}_w]\Lambda_{IO_4^-} + 10^{-3}[Na^+{}_w]\Lambda_{Na^+} \tag{7}$$

Here F is the Faraday constant (esu mol^{-1}), q is the elementary charge (4.8×10^{10} esu), α is the fractional charge of the micelle equal to $([IO_4{}^-{}_m] - [Na^+{}_m])/[\text{SB3-16}_m]$. ρ is the friction coefficient given by the Stokes approximation $\rho = 6\pi\eta R_h$, η being the macroscopic viscosity of the dilute sodium periodate solution, which can be approximated to that of water (0.89 cP at 298.2 K), and R_h the micellar hydrodynamic radius equal to 27 Å[12] for SB3-16 micelles. $[IO_4{}^-{}_w] = [IO_4{}^-{}_T] - [IO_4{}^-{}_m]$ and $[Na^+{}_w] = [Na^+{}_T] - [Na^+{}_m]$. Λ is the equivalent conductance at infinite dilution. The numerical factors in eqn. (7) are introduced to express the specific conductance in the CGS system. The first term on the right hand side of eqn. (7) takes into account that, in spite of SB3-16 being neutral, in the presence of a salt a fraction of the ions bind to the micelles and, since the anion binding is stronger than that of the cations, the resulting micelles are negatively charged. Therefore, this term accounts for the micelles' contribution.[13,14] The solid line in Fig. 7 was fitted to the experimental conductivity data by including the binding of Na^+ ions with $K_{Na^+} = 1.5$ dm^3 mol^{-1}[10,11,15,16] and by considering $K_{IO_4^-} = 27$ dm^3 mol^{-1}. This value can be compared with those obtained by other authors for various anions in sulfobetaine micelles using the same method: $K_{Br^-} = 4.3$ dm^3 mol^{-1},[4,11] $K_I = 21$ dm^3 mol^{-1},[4] *etc.*

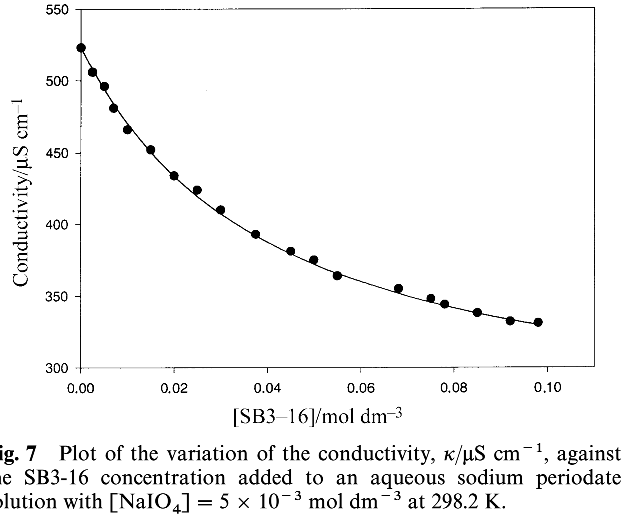

Fig. 7 Plot of the variation of the conductivity, κ/μS cm^{-1}, against the SB3-16 concentration added to an aqueous sodium periodate solution with $[NaIO_4] = 5 \times 10^{-3}$ mol dm^{-3} at 298.2 K.

Kinetic data shown in Fig. 1 were fitted using eqn. (5). Periodate ion concentrations in the aqueous and micellar pseudophases were calculated by using eqn. (6) with $K_{IO_4^-} = 27$ dm^3 mol^{-1}. A value for the second order rate constant of $k_{2m} = 8.9 \times 10^{-3}$ s^{-1} was obtained. To compare the reactivity in water and at the micellar surface it is useful to consider a second order rate constant written with concentration as local molarity, k_{2m} (dm^3 mol^{-1} s^{-1}), as:

$$k_{2m} = k_{2m} V_m \tag{8}$$

where V_m is the molar volume of the reaction region at the micellar surface, being equal to 0.14 dm^3 mol^{-1} in the case of SB3-16 micelles.[17] The values of k_{2m} rate constants for all the micellar media studied are listed in Table 1. This table also shows the values of K_m and k_{2m} obtained for the reaction under study in SDS, CTAC and SB3-14 by Bunton *et al.*[3a,b] One can see that the K_m and k_{2m} values obtained for SB3-14 and SB3-16 micellar solutions are similar, as expected. One can also see in Table 1 the value of the relation k_{2m}/k_{2w} obtained for anionic, cationic, zwitterionic and nonionic micellar solutions, which shows the difference in reactivity between the micellar and the aqueous phases due to the micellar medium effects.

We will consider first the results obtained in nonionic micellar solutions, for which charge–charge interactions are not operative since their micellar surfaces have no charge. Therefore, one would expect the polarity of the micellar pseudophase to be the main factor controlling reactivity. To investigate how changes in the relative permittivity of the reaction medium affects the reaction rate, the process was studied in various water–organic solvent mixtures and the second order rate constant values, k_{2S}, are listed in Table 2. Organic solvents that do not absorb at 260 nm were chosen. The relative permittivity of all the mixtures was 50.[18] One can see that the reaction is slower in the mixtures than in water by a factor close to 10^{-2}; that is, a diminution in the relative permittivity of the medium from 78.5 (pure water) to 50 strongly inhibited the reaction. This was also found by Ruff and Kuesman[19] in a study of the reaction in water–ethanol mixtures, the reaction rate being slower the higher the percentage organic solvent present in the mixture. The experimentally observed solvent effects are in agreement with the transition state being more polarized than the two reactants together in the initial state. The sulfide suffers electrophilic

Table 2 Kinetic data for the reaction 1-methoxy-4-(methylthio)benzene + IO_4^- in water–cosolvent mixtures and polarity indexes for these mixtures as well as for various micellar solutions at 298.2 K

Mixture[a]	$10^2 \times k_{2S}$/dm^3 mol^{-1} s^{-1}	ε[b]	E_T[c]	k_{2S}/k_{2w}[d]
Water–^{t}butyl alcohol 76.5 : 24.5	2.0	50	55.84	0.013
Water–methanol 40 : 60	5.0	50	57.3	0.036
Water–ethanol 49 : 51	4.2	50	55.4	0.028
Water–propanol 57.8 : 42.2	2.0	50	55.8	0.013
CTAC		31	53.2	
SB3-16		25	52	
SB3-14		25	52	
Brij$_{35}$		28	52.8	
SDS		36(51)[e]	57.5	

[a] Percentage by weight. [b] ε (pure water) = 78.4 at 298.2 K. [c] E_T (pure water) = 63.1 at 298.2 K. [d] k_{2w} = 1.51 dm^3 mol^{-1} s^{-1} at 298.2 K. [e] See text.

attack by the periodate anion, which results in a positive polarization of the sulfur atom and in an increase of the negative charge in the periodate moiety, both promoted by an increase in the relative permittivity of the reaction medium. Table 2 shows that the relative permittivity alone cannot explain the kinetic results found in the mixtures, since the second order rate constant is different for the different mixtures.

Another parameter frequently used as a polarity index is the Reichardt and Dimroth E_T parameter.[20] This parameter is equal to the lowest energy transition of the indicator *N*-phenol betaine, $E_T(30)$, dissolved in a given solvent, expressed in kcal mol^{-1}. Zachariasse *et al.*[21] have obtained the E_T parameter for various surfactants, as well as their effective relative permittivities. These values are listed in Table 2 together with the E_T values corresponding to the different water–cosolvent mixtures.[22] We obtained the E_T values as well as the effective relative permittivities for SB3-14, SB3-16 and Brij$_{35}$ as in ref. 21. To check our method the E_T values for SDS and CTAC were obtained and compared to those given by Zachariasse *et al.*, the agreement being good. In the case of the Tweens, experimental problems do not permit these values to be obtained. NMR studies have shown that the $E_T(30)$ molecules are predominantly solubilized in the micellar surface region and, therefore, from this parameter one obtains information about the surroundings of the $E_T(30)$ molecules at the micellar surface. The E_T values seem to indicate that the micellar surface of SDS micelles ($E_T = 51$) is substantially more polar than the surfaces of the rest of the micellar aggregates investigated. However, it is interesting to point out that whereas the effective relative permittivity values obtained by Zachariasse *et al.* coincide with those obtained by other authors by using different methods for cationic and nonionic micellar solutions,[23] the value corresponding to SDS micellar solutions is higher than that obtained by using other probe molecules. This has been explained by considering that the average solubilization site of the $E_T(30)$ molecule in the anionic micelles is further away from the micellar core than in cationic and nonionic micelles. In this case, its direct environment will contain a larger percentage of water molecules, its polarity being higher. We consider a value of 36[23] for the effective relative permittivity of the micellar surface of SDS micelles for comparison with the rest of the micellar solutions.

Table 1 shows that the k_{2m} values corresponding to the nonionic micellar solutions of Tween 20, Tween 40, Tween 80 and Brij$_{35}$ are similar. This indicates that the reaction site at the micellar surface of the nonionic micellar aggregates is similar in all these reaction media.

When the reactivity in nonionic micelles and that in water is compared, a decrease in the second order rate constant close to ten times is observed. Ruff *et al.*[19] found a decrease in the second order rate constant from 1.51 dm^3 mol^{-1} s^{-1} in water ($\varepsilon = 78.4$) to 7.98×10^{-3} dm^3 mol^{-1} s^{-1} in 30 : 70 (v/v) water–ethanol ($\varepsilon = 40.8$); that is, a decrease of close to two hundred fold. On this basis, and taking into account the effective relative permittivity values listed in Table 2, one would have expected a greater decrease in the second order rate constant in nonionic micellar solutions. However, there are some other points to consider. The first is that the effective relative permittivity obtained through the use of $E_T(30)$ or other probes responds to the environment sorrounding these molecules in the micellar pseudophase. The sulfide molecules, in spite of being incorporated into the micelles, can be localized in a different region from the $E_T(30)$ dye and their surroundings could be more polar and, consequently, the reaction will be less strongly inhibited. At this point it is worth noting that $E_T(30)$ molecules, as well as hydroxicoumarine molecules, are both located at the micellar surfaces of SDS micelles.[21,23] However, $E_T(30)$ dye molecules seem to be further away from the micellar core than the hydroxicoumarine ones and this gives two different effective relative permittivities, 36 and 51. Therefore, in the case of the reaction under study, which is strongly dependent on the polarity of the reaction site, the location of the reagents and of the transition state in the micellar pseudophase is quite important in determining the micellar medium effects. Another point is that the effective relative permittivities in Table 2 refer to alcohol–water mixtures or dioxane–water mixtures, that is, they are obtained from a direct comparison between homogeneous and heterogeneous solutions.

Now we will discuss the influence of the charge–charge interactions. Taking the nonionic micelles as reference for the micellar medium effects due to changes in the polarity from water to the micellar pseudophase, the charge–charge interaction would be responsible for an inhibition close to one hundred times in cationic and zwitterionic micelles and an acceleration of four times in anionic micelles. Oxidation of sulfide to sulfoxide involves build-up of positive charge on sulfur in the transition state (see Scheme 1) because there is a formal transfer of an electron to the oxidant, therefore, the process should be disfavored by interaction with cationic micellar head groups and favored by interaction with anionic head groups. In this regard, the interfacial electrical potential is 148 mV in CTAC micelles, 30 mV in the sulfobetaine micelles and −128 mV in SDS micelles.[10,23c] On this basis, one would expect a smaller inhibition in SB3-14 and SB3-16 micelles with respect to the reaction rate found in CTAC micelles. Meanwhile, an acceleration of four times in the reaction rate compared to that in nonionic, uncharged micelles seems small. At this point some comments are necessary. We are comparing second order rate constants calculated after the estimation of local concentrations of periodate ions in the micellar pseudophases, which involves uncertainties. On the other hand, a high ionic concentration is present in cationic and anionic micellar surfaces, and the possible influence of this high ionic concentration on the reaction rate has not been considered. To investigate this point, the influence of background electrolytes on the reaction rate was studied in the presence and in the absence of micelles.

Fig. 1 shows the influence of the addition of 0.25 mol dm^{-3} NaCl in SB3-16 micellar solutions. Fig. 2 and 3 show the same for $Brij_{35}$ and Tween 20. One can see that for low surfactant concentrations the observed rate constant is a little lower in the presence of the background electrolyte than in its absence. For high surfactant concentrations the observed rate constant remains unchanged by the addition of salts. At first, the presence of 0.25 mol dm^{-3} of NaCl could influence reactivity through the competition between chloride and periodate anions for the micellar surface of SB3-16 micelles. However, the fact that at [SB3-16] = 0.01 mol dm^{-3} the observed rate constant value is not influenced by the presence of the NaCl indicates that this effect, if operative, is not important. It is interesting to note that the affinity of the periodate anions for the sulfobetaine micelles is much stronger than that of the chloride anions.[6] These results can be explained by considering the changes in the equilibrium association constant provoked by the presence of the salt. Table 3 shows the K_m values obtained in SB3-16, $Brij_{35}$ and Tween 20 micellar solutions in the presence of 0.25 mol dm^{-3} of NaCl through spectroscopic measurements. One can see a small increase in the association equilibrium constants, which can account for the decrease in the observed rate constant at low surfactant concentrations. A stronger binding to the micellar aggregates results in a smaller k_{obs} since the reaction rate is much slower in the micellar pseudophase than in the aqueous phase. At high surfactant concentrations the sulfide molecules are practically incorporated into the micellar aggregates and this increase does not result in substantial changes in k_{obs}. Bunton *et al.* also found an increase in K_m when 0.25 mol dm^{-3} NaCl was added to SDS micellar solutions.[3a]

Table 4 shows the variation of k_2 when various amounts of NaCl and $NaClO_4$ were added to the reaction medium. At low or moderately concentrated salt solutions, the reaction rate does not change substantially. At high NaCl concentrations, the second order rate constant is higher than in pure water (1.51 dm^3 mol^{-1} s^{-1}). This result is in agreement with a more polarizable transition state with respect to the initial state. The presence of a high ionic concentration will stabilize the transition state, more than the initial state resulting in an acceleration of the process. This would mean that in ionic micellar solutions, the presence of a high ionic concentration at the micellar surface would provoke a small increase in the second order rate constant in the micellar pseudophase in ionic micellar solutions with respect to nonionic or zwitterionic micellar solutions. Nonetheless, taking as a reference the homogeneous aqueous solutions, this increase is small and it cannot account for the differences found in CTAC, SB3-14 and SB3-16, and SDS micellar solutions. That is, charge–charge interactions alone cannot explain the experimental results.

Table 3 Association equilibrium constants for 1-methoxy-4-(methylthio)benzene in various micellar solutions in the presence of 0.25 mol dm^{-3} NaCl at 298.2 K

Surfactant	$k_m/dm^3\ mol^{-1}$
SB3-16	350 ± 20
$Brij_{35}$	320 ± 20
Tween 20	320 ± 22

Table 4 Second order rate constants for the reaction 1-methoxy-4-(methylthio)benzene + IO_4^- in aqueous salt solutions with $[IO_4^-] = 2 \times 10^{-3}$ mol dm^{-3} at 298.2 K

Salt/mol dm^{-3}	$k_2/dm^3\ mol^{-1}\ s^{-1}$
0.1 NaCl	1.4
0.25 NaCl	1.4
1 NaCl	2.2
2 NaCl	2.3
0.1 $NaClO_4$	1.45
0.25 $NaClO_4$	1.42

If the nonionic micellar solutions are taken as a reference for the influence of the low polarity of the micellar surfaces on the reaction rate, k_{2m} should be substantially smaller in CTAC than in sulfobetaine micelles and its value in SDS micellar solutions should be higher than that found. All this leads us to the conclusion that maybe, at least for the reaction under study, the comparison between the kinetic data obtained in anionic and cationic micellar solutions does not inform us solely about the influence of charge–charge interactions in the transition state. In this particular case differences in the localization of the reagents as well as of the transition state in the micellar surface could be important.

NMR measurements show that in CTAC micelles the sulfide is located close to the micellar surface with the aromatic residue closer to the first three methylene groups of the chain than to the *N*-methyl group.[3b] The periodate anions will be strongly bound to the positively charged surfaces of CTAC micelles. In the case of SDS, the chemical shifts corresponding to the first three methylene groups of the chain are practically unaffected by the presence of the anionic micelles, thus suggesting that the sulfide interacts very little with them and stays adjacent to the sulfate head groups. In this position the sulfide molecules react with the periodate ions approaching the surface, the concentration of these anions being low in this negatively charged region. With this picture in mind, one would expect that the polarity of the reaction sites in cationic and anionic micellar solutions are not comparable, the reaction site being less polar in CTAC than in SDS micellar solutions and, therefore, one would expect a stronger decrease in the reaction rate for the former, independently of charge–charge interactions.

In the case of sulfobetaine micelles NMR measurements show that the average location of the sulfide molecules is close to the cationic center of the surfactant molecules. These measurements also show that periodate ions are surrounded by alkyl groups adjacent to the cationic center, with the two CH_2 groups between the cationic and anionic head groups residing at the micellar surface, rather than extending into the water. That is, the two reagents are localized in the same region of expected low polarity (see Table 2). Therefore, this could explain the small second order rate constant found in SB3-14 and SB3-16 micellar solutions with respect to that in CTAC micellar solutions. Taking this into account, the polarity of the reaction site in nonionic micellar solutions can also be different to those in cationic, anionic and zwitterionic micelles. Therefore, to take the micellar medium effects in nonionic micellar solutions as a reference for estimating charge–charge interactions alone would not be valid.

Summarizing, comparison of the kinetic data for the reaction between 1-methoxy-4-(methylthio)benzene + IO_4^- in cationic, anionic, zwitterionic and nonionic micellar solutions shows that the values of the observed rate constants are controlled by concentration and micellar medium effects. Once the micellar concentration effects are estimated by obtaining the second order rate constants, the differences in reactivity are mainly due to the polarity of the micellar pseudophase and charge–charge interactions. Taking the nonionic micellar solutions as reference for the polarity micellar medium effects and assuming a similar polarity for the reaction sites in all the micellar solutions studied, comparison between cationic, zwitterionic and anionic micelles shows that charge–charge interactions cannot account for the differences in reactivities found. It is neccesary to consider that the reaction sites at the micellar surfaces do not have similar polarities in the three types of micellar solutions. NMR measurements seem to indicate that the reaction site in SDS micelles is farther away from the micellar core than in CTAC micelles. On the other hand, the reaction site in sulfobetaine micelles seems to be the least polar. Another point to consider, and which can play a significant role in reactivity, is that periodate anions are mostly excluded from the SDS Stern layer due to their electrostatic interactions with the negatively charged head groups, whereas in cationic and sulfobetaine micelles, due to their positive interfacial electrical potential, periodate anions are strongly bound to the micelle surfaces. The results obtained show that it is neccesary to be careful when comparing reactivities, through the $k_{2\mathrm{m}}$ values, in various micellar solutions when the process studied is strongly dependent on the polarity of the reaction medium, as shown for the reaction studied in this work.

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