

Study of the bromide ion reaction with methyl naphthalene-2-sulfonate in water–DMSO TTAB micellar solutions

María Luisa Moyá,* Amalia Rodríguez, María Muñoz, María del Mar Graciani and Gaspar Fernández

Departamento de Química Física, Universidad de Sevilla, C/Profesor García González 2, 41012 Sevilla, Spain

Received 13 March 2006; revised 5 July 2006; accepted 7 July 2006

ABSTRACT: The reaction of bromide ions with methyl naphthalene-2-sulfonate (MeNS) has been investigated in water–dimethyl sulfoxide, DMSO, tetradecyltrimethylammonium bromide, TTAB, micellar solutions, with the weight percentage of DMSO up to 50%. In order to quantitatively rationalize the micellar kinetic effects observed, conductivity, surface tension, and steady-state fluorescence measurements were used to get information about the micellar reaction media. Results showed that changes caused by the addition of different amounts of DMSO to TTAB aqueous micellar solutions are made evident from the kinetic micellar effects, these being a helpful tool to obtain information on the micellar reaction media in the presence of the added organic solvent. Copyright © 2006 John Wiley & Sons, Ltd.

KEYWORDS: TTAB; micelles; DMSO; kinetics; thermodynamics; structure

INTRODUCTION

Dimethyl sulfoxide (DMSO) is a common organic solvent that has been used widely in biological studies and as a drug carrier across cell membranes.^{1–3} Due to two lone pairs on its oxygen atom, DMSO can interact with water forming strong hydrogen bonds. A single DMSO molecule is thought to form hydrogen bonds with as many as four water molecules simultaneously.⁴ In addition, the two methyl groups provide a non-polar attribute to the molecule causing effects of hydrophobic hydration and hydrophobic association of DMSO molecules. This combination of polar and non-polar characteristics makes DMSO and its aqueous solutions an important solvent in organic chemistry and fine chemical technology.^{2,5} The ability of a solvent to bring about the self-association of conventional amphiphiles can be characterized by its Gordon parameter,⁶ $G = \gamma_o/\bar{V}^{1/3}$, where γ_o is the solvent surface tension and \bar{V} its molar volume. For pure DMSO, the Gordon parameter is 1.02 J m^{-3} . Since G values equal or higher than 1.0 – 1.2 J m^{-3} seem to be required for self-association of the micellar type, micellization is expected to occur in pure

DMSO and, more so in water–DMSO mixtures. On this basis, DMSO seems to be an appropriate organic solvent in order to investigate how the addition of an organic solvent to an aqueous micellar solution affects the rate of a micelle-modified reaction. The chemical process chosen was the well known S_N2 substitution reaction methyl naphthalene-2-sulfonate (MeNS) + Br^- . In order to quantitatively rationalize kinetic micellar effects, it is necessary to obtain information about the micellar reaction media used. Conductivity, surface tension, and steady-state measurements were used to this purpose.

All measurements were done at 298.2 K.

EXPERIMENTAL

Materials

Tetradecyltrimethylammonium bromide (TTAB) was from Aldrich as were NaBr and DMSO. The surfactant was used without further purification and its cmc in water was in agreement with literature data (see Table 2).⁷ Hexadecylpyridinium chloride was from Fluka. Pyrene was from Aldrich and was purified before use. MeNS was synthesized following the method in the literature.⁸

Conductivity measurements

Conductivity was measured with a Crison microCM 2201 conductimeter connected to a water flow thermostat

*Correspondence to: M. L. Moyá, Departamento de Química Física, Universidad de Sevilla, C/Professor García González 2, 41012 Sevilla, Spain.

E-mail: moya@us.es

Contract/grant sponsors: DGICYTBQU2002-00691; Consejería de Educación y Ciencia de la Junta de Andalucía; contract/grant number: FQM-274.

maintained at 298.2 ± 0.1 K. The conductimeter was calibrated with KCl solutions of the appropriate concentration range.

Surface tension measurements

The surface tensions were measured by a du Noüy ring method using a KSV 703 digital tensiometer (Finland) equipped with an automatic device to set the time between two consecutive measurements and to select the rising velocity of the platinum ring. A water-jacketed sample beaker connected to a cryostat was used to control the sample temperature. Prior to each measurement, the ring was rinsed with ethanol and then heated briefly by holding it above a Bunsen burner until glowing. The vessel was cleaned by using chromic sulfuric acid, boiled in distilled water, and then flamed with a Bunsen burner before use. The precision in the measurements was $\pm 1 \text{ mN m}^{-1}$. Care has to be taken in using the du Noüy ring method to deduce surfactant properties, because the surfactant adsorption kinetics can influence the results.⁹ In our experiments, the ring rising velocity was chosen low enough to allow the surfactant adsorption to reach equilibrium.

Fluorescence measurements

Fluorescence measurements were made by using a Hitachi F-2500 fluorescence spectrophotometer. The temperature was kept at 298.2 ± 0.1 K by a water flow thermostat connected to the cell compartment.

A study of the fluorescence quenching of pyrene by *N*-hexadecylpyridinium chloride, CePyCl, was carried out. The introduction of pyrene in the water–DMSO micellar solutions was done as in Ref. [10]. The pair pyrene/CePyCl ensures that the residence time of the quencher in the micelles is much longer than the fluorescence lifetime of the probe.¹¹ The probe concentration was kept low enough ($2 \times 10^{-6} \text{ mol dm}^{-3}$) to avoid excimer formation, and the quencher concentration was varied from 5×10^{-5} to $25 \times 10^{-5} \text{ mol dm}^{-3}$. These values give [pyrene]/[micelles] and [quencher]/[micelles] ratios low enough to ensure a Poisson distribution.¹² Some comments about the aggregation numbers obtained will be made below.

Kinetics

The reaction between $\text{MeNS} + \text{Br}^-$ was recorded at 326 nm in a Unicam Helios- γ spectrophotometer in the presence of NaBr 0.1 M. Sodium bromide was added to the reaction media because in its presence, the reproducibility of the kinetics in water–DMSO TTAB micellar solutions was better than in its absence. MeNS

was added in $10 \mu\text{l}$ of acetonitrile to 1 ml of the reaction solution at 298.2 K, so that the organic substrate concentration in the reaction medium was 10^{-4} M. The kinetics were followed for more than five half-lives in all the water–DMSO micellar media. The observed rate constants were obtained from the slopes of the $\ln(A_t - A_\infty)$ against time plots, A_t and A_∞ being the absorbances at time t and at the end of the reaction, respectively. Each experiment was repeated at least twice, and the observed rate constants were reproducible within precision of better than 5%. The temperature was maintained at 298.2 ± 0.1 K using a water-jacketed cell compartment connected to a water flow thermostat.

In order to check the reliability of our kinetic data, the reaction was followed in hexadecyltrimethylammonium bromide micellar solutions, at [surfactant] = 0.04 M, in the presence and in the absence of NaBr 0.02 M. The observed rate constants obtained were 8.3×10^{-4} and $7.4 \times 10^{-4} \text{ s}^{-1}$,⁸ respectively, in good agreement with literature data.

RESULTS

Figure 1 shows the dependence of the observed rate constant for the $\text{S}_{\text{N}}2$ reaction $\text{MeNS} + \text{Br}^-$ on TTAB concentration in various water–DMSO TTAB micellar solutions, in the presence of NaBr 0.1 M.

The cmc of the water–DMSO TTAB solutions, in the presence of NaBr 0.1 M, were determined by using surface tension measurements (see Fig. 2). These data are summarized in Table 1. Surface tension measurements also provide information about the adsorption of surfactants at the air–liquid interfaces. The surface excess concentration, Γ_{max} , and the minimum area per surfactant molecule, A_{min} , at the air–solvent interface

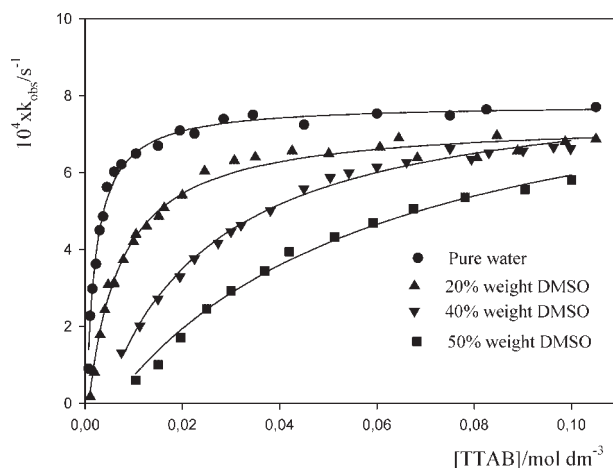


Figure 1. Influence of the TTAB, on the observed rate constant, $k_{\text{obs}}(\text{s}^{-1})$, for the reaction $\text{MeNS} + \text{Br}^-$ in various water–DMSO TTAB micellar solutions ($T = 298.2$ K)

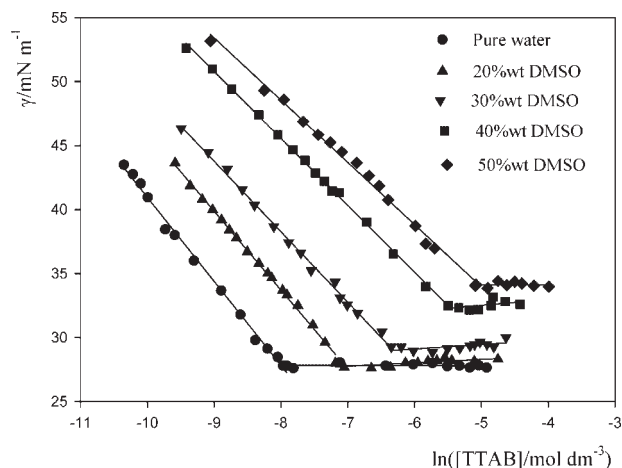


Figure 2. Dependence of the surface tension, γ (mN m^{-1}), of various water–DMSO TTAB solutions on $\ln([\text{Surfactant}])$ ($T = 298.2 \text{ K}$)

were obtained by using the following equations:

$$\Gamma_{\max} = -\frac{1}{qRT} \left[\frac{\partial \gamma}{\partial \ln C} \right]_{T,P} \quad (1)$$

$$A_{\min} = \frac{1}{\Gamma_{\max} N_A} \quad (2)$$

Here R is the gas constant, N_A is Avogadro's number, γ is the surface tension, and C is the concentration of surfactant in solution. The quantity q is the number of solute species whose concentration at the interface changes with change in the value of C . q is 1 for non-ionic and zwitterionic surfactants and 2 for ionic surfactants. In the water–DMSO surfactant solutions studied, NaBr 0.1 M was present. Therefore, the ionic strength of the solutions can be considered constant for the surfactant solutions in the premicellar region and, as a consequence, the value of the coefficient q is unity.¹³ The values of Γ_{\max} and A_{\min} are listed in Table 1. These values correspond to water–DMSO TTAB solutions in the presence of NaBr 0.1 M. Nonetheless, the presence of this moderate concentration of salt is not expected to affect the surface tension data strongly¹⁴ and the values of the Γ_{\max} and A_{\min} corresponding to the TTAB solutions in the absence of salt are expected to be similar to those summarized in Table 1. The minimum area per surfactant

Table 1. Critical micelle concentration, cmc, surface excess concentration, Γ_{\max} , and minimum area per surfactant molecule, A_{\min} , for TTAB in water–DMSO mixtures in the presence of NaBr 0.1 M ($T = 298.2 \text{ K}$)

DMSO (wt%)	cmc ($\times 10^4 \text{ mol dm}^{-3}$)	Γ_{\max} ($\times 10^6 \text{ mol m}^{-2}$)	A_{\min} ($\times 10^{20} \text{ m}^2$)
0	3.4 ± 0.2	2.6 ± 0.1	64 ± 2
20	8.6 ± 0.4	2.4 ± 0.1	69 ± 3
30	17.4 ± 0.8	2.3 ± 0.1	72 ± 4
40	41 ± 2	2.1 ± 0.1	79 ± 4
50	61 ± 3	2.0 ± 0.2	85 ± 4

molecule corresponding to pure water obtained in this work is in agreement with previous results,¹⁵ although it is smaller than that obtained through neutron reflection measurements.¹⁶

Table 2 shows the values of the critical micelle concentration and of the micellar ionization degree, α , of the water–DMSO TTAB solutions investigated in the absence of NaBr 0.1 M. The authors determined these cmc and α values from inflections in plots of conductivity, κ , against the surfactant concentration (Williams method¹⁷), as described in Ref. [18] (see Fig. 3). Nonetheless, since this method has been criticized,¹⁹ the authors also used the Phillips method²⁰ in order to estimate the cmc values. This method was applied through an integration by the Runge-Kutta method and a least-square Levenberg–Marquardt fitting, as described in Ref. [21]. The cmc values obtained by the two methods were in good agreement, thus giving reliability to the cmc and α values listed in Table 2. It is worth noting that the cmc and α values corresponding to pure aqueous solutions are in agreement with literature values.⁸

The aggregation number, N_{agg} , of the micelles present in the micellar solutions studied are also listed in Table 2. These values were obtained from the quenching of pyrene fluorescence by hexadecylpyridinium chloride (see Fig. 4). The N_{agg} value in TTAB aqueous micellar solution is small as compared with the literature value.²² This could be due to the quenching processes not being particularly effective in the large TTAB micelles.²³ There is another point that could also be responsible for the small aggregation numbers obtained: bromide ions can quench the pyrene excited state.²³ With this in mind, attention will be paid to how the presence of the organic solvent influences the aggregation numbers of TTAB micelles and it seems reasonable to conclude that N_{agg} decreases as the percentage by weight of DMSO in the mixture increases.

Table 4 shows solvent surface tension, γ_0 , the molar volume, \bar{V} , and the Gordon parameter, $G = \gamma_0/\bar{V}^{1/3}$, for the water–DMSO mixtures used as bulk phase in the cationic micellar solutions investigated. The molar volume of the mixtures were estimated from $\bar{V} = \bar{V}_{\text{DMSO}}X_{\text{DMSO}} + \bar{V}_{\text{water}}(1 - X_{\text{DMSO}})$.

DISCUSSION

The dependence of the observed rate constant on surfactant concentration for the reaction of bromide with MeNS + Br[−] (Scheme 1) in various water–DMSO TTAB micellar solutions are shown in Fig. 1. This Figure shows that k_{obs} increases upon increasing surfactant concentration in all the water–DMSO mixtures investigated, which can be explained by considering that an increase in [TTAB] causes a further incorporation of MeNS into the cationic micelles, where the interfacial bromide ion concentration is large. On the other hand, for a given

Table 2. Cmc, micellar ionization degree, α , aggregation number, N_{agg} , and standard Gibbs energy of micelle formation, $\Delta G_{\text{M}}^{\circ}$, values for water–DMSO TTAB micellar solutions ($T = 298.2 \text{ K}$)

DMSO(wt%)	cmc ($\times 10^4 \text{ mol dm}^{-3}$)	α	$N_{\text{agg}}^{\text{a}}$	$-\Delta G_{\text{M}}^{\circ} (\text{kJ mol}^{-1})$
0	3.6 ± 0.1	0.23 ± 0.01	58 ± 3	24.6
20	7.3 ± 0.2	0.28 ± 0.01	48 ± 5	20.9
30	10 ± 0.2	0.31 ± 0.01	35 ± 4	19.2
40	15.1 ± 0.5	0.36 ± 0.02	23 ± 4	17.0
50	22.4 ± 0.7	0.39 ± 0.02	19 ± 3	15.1

^a These aggregation numbers are approximated (see the text).

surfactant concentration, the observed rate constant is smaller when the weight percentage of the organic solvent is higher. If pseudophase kinetic models are considered, k_{obs} can be written as:²⁴

$$k_{\text{obs}} = \frac{k_2^{\text{bulk}} [\text{Br}_{\text{bulk}}^-] + (k_2^{\text{m}}/V_{\text{m}}) [\text{Br}_{\text{m}}^-] K_{\text{m}}}{1 + K_{\text{m}} [\text{TTAB}_{\text{m}}]} \quad (3)$$

Here $[\text{Br}_{\text{bulk}}^-]$ and $[\text{Br}_{\text{m}}^-]$ are the bromide ion concentrations in the bulk and micellar pseudophases referred to the total solution volume. V_{m} is the molar volume of the reactive region at the micellar surface and K_{m} is the equilibrium binding constant which describes the distribution of the organic substrate between the bulk and micellar pseudophases. $[\text{TTAB}_{\text{m}}]$ is the micellized surfactant concentration, equal to the total surfactant concentration minus the cmc. $(k_2^{\text{m}}/V_{\text{m}}) = k_{2\text{m}} (\text{s}^{-1})$ is the second order rate constant in the micellar pseudophase written with concentrations expressed as molar ratios, $[\text{Br}_{\text{m}}^-]/[\text{TTAB}]$, and k_2^{bulk} is the second order rate constant of the reaction in the bulk phase. k_2^{bulk} values were obtained experimentally, they being equal to 7.7×10^{-5} , 8.3×10^{-5} , 9.5×10^{-5} , $10.7 \times 10^{-5} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$ for 0, 20, 30, and 50% weight percentage of DMSO, respectively. At this point, it is worth noting that the reaction of MeNS with water can make a contribution to the reaction $\text{MeNS} + \text{Br}^-$,^{9,25} although this contribution

is not significant except at low surfactant concentrations. Kinetic data have been corrected, when necessary, from the spontaneous hydrolysis contribution as in Ref. 26].

The bromide ion concentrations $[\text{Br}_{\text{bulk}}^-]$ and $[\text{Br}_{\text{m}}^-]$ can be estimated by considering that the incorporation of the bromide anions into the TTAB micelles can be described by Eqn (4):²⁷

$$K_{\text{Br}^-} = \frac{[\text{Br}_{\text{m}}^-]}{[\text{Br}_{\text{bulk}}^-]([\text{TTAB}_{\text{m}}] - [\text{Br}_{\text{m}}^-])} \quad (4)$$

Considering Eqn (4) and the mass balance, one can write:

$$K_{\text{Br}^-} [\text{Br}_{\text{m}}^-]^2 - (K_{\text{Br}^-} [\text{TTAB}_{\text{m}}] + K_{\text{Br}^-} [\text{Br}_{\text{T}}^-] + 1) \times [\text{Br}_{\text{m}}^-] + K_{\text{Br}^-} [\text{TTAB}_{\text{m}}] [\text{Br}_{\text{T}}^-] = 0 \quad (5)$$

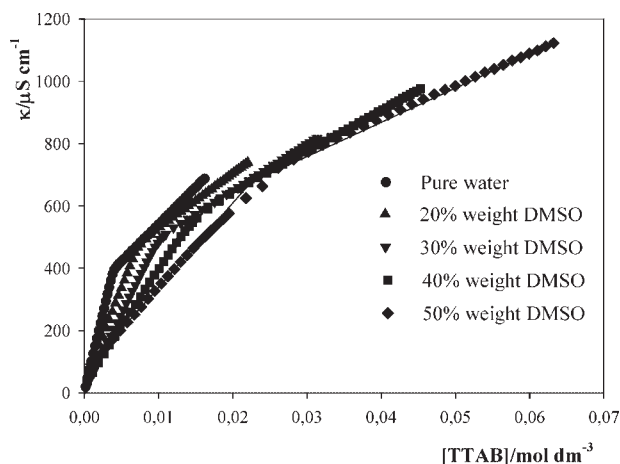
where bromide ions come from the surfactant and from the NaBr present in the reaction media. The authors considered a K_{Br^-} value of $900 \text{ dm}^3 \text{ mol}^{-1}$ in TTAB aqueous micellar solutions.²⁶ For the other micellar reaction media, K_{Br^-} was estimated from its dependence on α (Eqn (6)). In this way, for any water–DMSO TTAB

$$K_{\text{Br}^-} = \frac{1 - \alpha}{\alpha^2 [\text{TTAB}_{\text{m}}]} \quad (6)$$

micellar solution with an ionization degree equal to α , K_{Br^-} can be calculated by:

$$\frac{K_{\text{Br}^-}}{900} = \frac{(1 - \alpha) 0.23^2}{(1 - 0.23) \alpha^2} \quad (7)$$

where 0.23 is the micellar ionization degree of the aqueous TTAB micelles and 900 their corresponding K_{Br^-} value. The kinetic measurements were carried out in the presence of NaBr 0.1 M, whereas the micellar

**Figure 3.** Dependence of the specific conductivity, κ , in $\mu\text{S cm}^{-1}$, on surfactant concentration for water–DMSO TTAB solutions ($T = 298.2 \text{ K}$)**Table 3.** Fitting parameters for the reaction $\text{MeNS} + \text{Br}^-$ in DMSO–water TTAB bromide micellar solutions at 298.2 K

DMSO (wt%)	$K_{\text{m}} (\text{mol}^{-1} \text{ dm}^3)$	$10^4 \times k_{2\text{m}} = (k_2^{\text{m}}/V_{\text{m}}) (\text{s}^{-1})$
0	505 ± 12	9.41 ± 0.08
20	150 ± 4	8.8 ± 0.1
40	43 ± 3	8.7 ± 0.2
50	20 ± 2	9.3 ± 0.3

Table 4. Solvent surface tension, γ_o , solvent molar volume, \bar{V} , and Gordon parameter, G , for various water–DMSO mixtures. $T = 298.2\text{ K}$

DMSO (wt%)	$\gamma_o(\text{mN m}^{-1})$	$\bar{V}(\text{dm}^3 \text{mol}^{-1})$	$G = \gamma_o \bar{V}^{1/3}(\text{J m}^{-3})$
0	71.8 ^a	18.07 ^a	2.74
20	69 ± 1	28.7	2.2
30	64 ± 1	34.0	2.0
40	57 ± 1	39.4	1.7
50	53 ± 1	44.7	1.5
100	42.8 ^a	71.3 ^a	1.03

$$\bar{V} = \bar{V}_{\text{DMSO}}X_{\text{DMSO}} + \bar{V}_{\text{water}}(1 - X_{\text{DMSO}})$$

^aTaken from CRC Handbook of Chemistry and Physics, 8th ed., 2004–2005.

ionization degrees listed in Table 2 correspond to the micellar solutions in the absence of salt. However, previous work has shown that TTAB micelles remain spherical in water and in NaBr aqueous solutions at salt concentrations up to 0.1 M ^{28,29} and no substantial changes in the micellar ionization degree were considered within that salt concentration range. Besides, both theory and experiment indicate that ionization of the micelles for ions that are not extremely hydrophilic, such as Br^- , are not particularly sensitive to the concentration of added salt.³⁰ On this basis, the K_{Br^-} values corresponding to the different micellar reaction media were calculated by using the micellar ionization degrees listed in Table 2 and Eqn (7). K_{Br^-} values equal 900, 691, 478, and $420\text{ dm}^3\text{ mol}^{-1}$ for water–DMSO TTAB micellar solutions with 0, 20, 40, and 50% weight percentage of DMSO in the mixture, respectively.

Solid lines in Fig. 1 are the results of fitting the experimental kinetic data by using Eqn (3). One can see that the agreement between the experimental and the theoretical data was good. The use of cmc, α , and k_2^{bulk} experimental data has reduced as much as possible the number of adjustable parameters and only one set of ($k_2^{\text{m}}/$

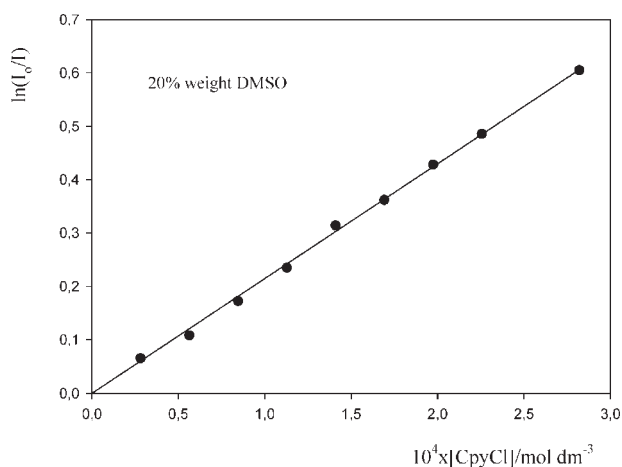
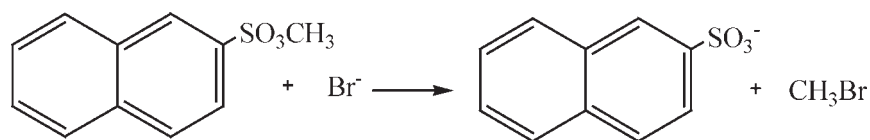


Figure 4. Influence of the quencher (*N*-hexadecylpyridinium chloride) concentration on the intensity of the pyrene fluorescence in water–DMSO TTAB micellar solutions with 20 wt% DMSO ($T = 298.2\text{ K}$)

V_m) and K_m values gives the best fitting for each of the micellar solutions investigated. Nonetheless, given the simplicity of the model used to rationalize the kinetic data, only substantial changes in the adjustable parameters are worth discussing.

The (k_2^{m}/V_m) and K_m values obtained from the fittings are listed in Table 3. This Table shows that k_{2m} seems to be independent of the weight percentage of DMSO present in the micellar reaction media. On the other hand, the equilibrium binding constant, K_m , of the MeNS molecules to the TTAB micelles decreases strongly when the amount of DMSO increases. In regard to the latter, an increase in the amount of DMSO results in a decrease in the polarity of the bulk phase (the dielectric constant is 78.39 and 46.68 for pure water and pure DMSO at 298.2 K ³¹). This means that the water–DMSO bulk phase is a better solvent for the organic substrate at higher weight percentages of DMSO. Consequently, the affinity of MeNS for the micellar pseudophase decreases when wt% DMSO increases, also decreasing K_m .

In order to compare the reactivity in water and in micelles, the second order rate constant in the micellar pseudophase expressed in $\text{mol}^{-1}\text{ dm}^3\text{ s}^{-1}$, k_2^{m} , has to be calculated (one cannot compare k_{2m} , a second order rate constant expressed in s^{-1} , to k_2^{bulk} , a second order rate constant expressed in $\text{mol}^{-1}\text{ dm}^3\text{ s}^{-1}$). Since $k_2^{\text{m}} = k_{2m} V_m$, from the k_{2m} values listed in Table 3 and the V_m values, k_2^{m} can be estimated. From the data in Ref.,[26] the molar reaction volume in TTAB aqueous micellar solutions was estimated to be $0.33\text{ dm}^3\text{ mol}^{-1}$. Therefore, the k_2^{m} value calculated for the reaction $\text{MeNS} + \text{Br}^-$ in TTAB aqueous micelles was $3.1 \times 10^{-4}\text{ dm}^3\text{ mol}^{-1}\text{ s}^{-1}$, to be compared to $k_2^{\text{bulk}} = 7.7 \times 10^{-5}\text{ dm}^3\text{ mol}^{-1}\text{ s}^{-1}$. That is, the presence of cationic TTAB micelles in pure water increases the rate constant. The main factors involved in this increase would be the electrophilic interaction of the ammonium head groups and the forming naphthalene-2-sulfonate ion and the disruption of the hydration shell of the bromide ion.³² The k_2^{m} values in water–DMSO micellar solutions could not be estimated because the corresponding V_m values are not known. Taking into account the decrease in the aggregation number found in the micellar solutions investigated by increasing the %wt of DMSO in the solutions, a reasonable assumption would be that V_m decreases upon increasing the amount of DMSO, or at least, a substantial increase in the molar reaction volume is not expected by increasing wt% of DMSO. Therefore, taking the $k_{2m} = (k_2^{\text{m}}/V_m)$ and k_2^{bulk} values into account, one can conclude that the rate constants of the reaction $\text{MeNS} + \text{Br}^-$ are larger in the micellar pseudophases than in the bulk phase not only in pure water, but also in the water–DMSO mixtures studied. Table 3 shows that k_{2m} is not practically affected by changes in the weight percentage of DMSO. Therefore, the diminution observed in k_{obs} when wt% of DMSO increases is mainly due to two factors: (i) A large decrease in K_m , which results in an increase of the contribution of



Scheme 1

the reaction taking place in the bulk phase. Since the reaction is slower in the bulk phase than in the micellar pseudophase, the observed rate constant diminishes. (ii) The increase in the micellar ionisation degree upon increasing the amount of DMSO present in the mixture. This increase will produce a diminution of the bromide ion concentration at the micellar surface, the reaction site, retarding the reaction.

From the data listed in Tables 1 and 2, additional information about the micellar solutions used as reaction media can be obtained. The Gibbs energy of micellization, ΔG_M^0 , can be calculated by:³³

$$\Delta G_M^0 = (2 - \alpha) RT \ln cmc \quad (8)$$

where α is the micellar ionization degree. This equation applies when the aggregation number is large. Therefore, taking into account the N_{agg} values listed in Table 2, ΔG_M^0 values obtained by using Eqn (8) for the higher weight percentages of DMSO have to be considered as approximated. ΔG_M^0 values in Table 2 shows that the TTAB aggregation process is less spontaneous when the wt% DMSO is larger. In this regard, the dependence of the ability of water–DMSO mixtures to bring about the self-association of conventional amphiphiles on the weight percentage of DMSO can be related to its cohesive energy density,⁶ which can be characterized by the Gordon parameter, $G = \gamma_o / \bar{V}^{1/3}$, where γ_o is the solvent surface tension and \bar{V} its molar volume. Table 4 shows the Gordon parameter values for the different mixtures used as bulk phases in the micellar solutions studied. The G parameter points out that an increase in the weight percentage of DMSO results in a decrease in the solvent cohesiveness, thereby improving the solvation of the hydrocarbon tails in the bulk phase and decreasing the solvophobic effect. In relation to this, the increase in the cmc by increasing wt%, EG can be explained by taking into account that the transfer of the surfactant tail from the water + DMSO bulk phase into the micellar core is less spontaneous when the amount of DMSO in the mixture increases.^{33–35} This is due to the water-polar organic solvent mixtures being better solvents for the surfactant molecules than pure water.³¹ There is also a dependence of the cmc on the interfacial energy contribution to ΔG_M^0 ,³⁴ but it is always much weaker when compared to the dependence on the solvophobic Gibbs energy contribution. As a consequence, cmc increases upon increasing wt% DMSO. This increase is

responsible for the increase in the micellar ionization degree observed when the weight percentage of DMSO increases. An increase in the ionic strength due to the increase in the monomer surfactant concentration (accompanying the substantial increase in the cmc) results in a diminution of the ionic interactions at the micellar surface (screening effects) and, consequently, the ionization degree increases upon increasing the weight percentage of DMSO. With respect to the decrease in the micellar aggregation numbers upon increasing the amount of DMSO present in the mixture, it can be explained by taking into account the decrease in the interfacial energy contribution to ΔG_M^0 due to a decrease in the solution–hydrocarbon interfacial tension when the amount of DMSO in the mixture increases (see the dependence of γ_o on wt% DMSO in Table 4).³⁴

Table 1 shows that Γ decreases, and A increases, when the amount of DMSO present in the mixture increases. This result can be related to changes in the water structure due to the presence of DMSO, interactions between DMSO and surfactant molecules, and the presence of DMSO at the air–solution interface. In regard to the solvent–surfactant interactions, an increase in the wt% DMSO causes a decrease in the dielectric constant, in the Reichardt parameter, E_T , in the Gutman donor number, DN, or in the π^+ polarity index³¹ of the mixture, this meaning that the surfactant molecules will be solubilized more easily and their tendency to be adsorbed at the air–solution interface will decrease. As a consequence, the surface excess concentration decreases and A increases when wt% EG increases.

Summarizing, the thermodynamic and structural changes caused by the presence of different amounts of DMSO in aqueous TTAB micellar solutions control the micellar effects observed on the reaction $MeNS + Br^-$ taking place in these micellar solutions. The decrease in k_{obs} originated by the addition of DMSO is mainly the result of two factors: (i) the decrease in the bromide ion concentration at the micellar surface, where the reaction takes place, due to an increase in the micellar ionization degree, and (ii) the decrease in the equilibrium binding constant due to the water–DMSO mixtures being a better solvent for the organic substrate molecules than pure water. The second-order rate constant in the micellar pseudophase in any of the water–DMSO micellar solutions studied is faster than in the bulk phase, although it shows no dependence on changes in the wt% of DMSO. The addition of DMSO, up to a percentage by weight of

50, to TTAB aqueous micellar solutions results in an increase in the critical micelle concentration and in the micellar ionization degree, whereas the micellar aggregation number decreases.

Acknowledgements

This work was financed by DGICYT (grant BQU2006-00597) and Consejería de Innovación, Ciencia y Empresa de la Junta de Andalucía. The authors thank Professor Victor Mosquera, from the University of Santiago de Compostela, Spain, for helping us in the application of the Phillips method for obtaining the cmc values. The authors also thank Professor Ana Troncoso, from the University of Seville, Spain, for helping us in the fluorescence measurements.

REFERENCES

- Ashwood-Smith MJ. In *Cryobiology*. Merymor HT (ed.). Academic Press: New York, 1966.
- Martin D, Hauthal HG. *Dimethyl Sulfoxide*. Wiley: New York, 1975.
- Anchordoguy TJ, Mancini CA, Crowe JN, Crowe LM. *Cryobiology* 1991; **28**: 467.
- Vieceli J, Benjamin I. *Langmuir* 2003; **19**: 5383.
- Martin D, Weise A, Niclas HT. *Angew.Chem.* 1967; **6**: 318.
- Ramadan M, Evans DF, Lumry R, Philson S. *J. Phys. Chem.* 1985; **89**: 3405.
- Van Os NM, Haak JR, Rupert LA. *Physicochemical Properties of Selected Anionic, Cationic and Nonionic Surfactants*. Elsevier: New York, 1993.
- Bacaloglu R, Bunton CA, Ortega F. *J. Phys. Chem.* 1989; **93**: 1497.
- Deleu M, Paquet M, Blecker C. In *Encyclopedia of Surface and Colloid Science*, Hubbard AT (ed). Dekker: New York, 2002, 5119.
- Velazquez MM, Costa MB. *J. Chem. Soc., Faraday Trans.* 1990; **86**: 4043.
- Malliaris A, Lang J, Zana R. *J. Colloid Interface Sci.* 1986; **110**: 237.
- (a) Tachiya M. *Chem. Phys. Lett.* 1975; **33**: 289; (b) Infelta PP, Gratzel MJ. *J. Phys. Chem.* 1970; **70**: 179; (c) Infelta PP. *Chem. Phys. Lett.* 1980; **61**: 88.
- Rosen MJ. *Surfactants, Interfacial Phenomena* (3rd edn). Wiley: New York, 2004.
- Graciani MM, Rodríguez A, Muñoz M, Moyá ML. *Langmuir* 2005; **21**: 7161.
- Venable RL, Nauman RV. *J. Phys. Chem.* 1964; **68**: 3498.
- Simister EA, Thomas RK, Penfold J, Aveyard J, Binks BP, Cooper P, Fletcher PDI, Lu JR, Sokolowski A. *J. Phys. Chem.* 1992; **96**: 1383.
- Williams RJ, Phillips JN, Mysels KJ. *Trans. Faraday Soc.* 1955; **51**: 728.
- Rodríguez A, Graciani MM, Muñoz M, Moyá ML. *Langmuir* 2003; **19**: 7206.
- Sarmiento F, del Río JM, Prieto G, Atwood D, Jones MN, Mosquera V. *J. Phys. Chem.* 1995; **99**: 17628.
- Phillips JN. *Trans. Faraday Soc.* 1955; **51**: 561.
- Mosquera V, García M, Varela LM. In *Handbook of Surfaces and Interfaces of Materials*, vol. 3, Nalwa HS (ed). Academic Press: New York, 2001; 401.
- Berr S, Jones RRM, Johnson JS. *J. Phys. Chem.* 1992; **96**: 5611.
- Van Stam J, Depaemelaere S, De Schryver FC. *J. Chem. Edu.* 1998; **75q**: 93.
- (a) Bunton CA, Nome F, Quina F, Romsted LS. *Acc. Chem. Res.* 1991; **24**: 357; (b) Savelli G, Germani R, Brinchi L. In *Reactions and Synthesis in Surfactants Systems*, Texter J (ed.). Surfactant Science Series/100, Marcel Dekker: New York, 2001, Ch. 8, p. 175 and references therein.
- (a) Bunton CA, Moffatt JR. *J. Phys. Chem.* 1988; **92**: 2896; (b) Bunton CA, Moffatt JR. *Ann. Chim. (Rome)* 1987; **77**: 117; (c) Bacaloglu R, Bunton CA, Cerichelli G, Ortega F. *J. Phys. Chem.* 1989; **93**: 1490.
- Graciani MM, Rodríguez A, Muñoz A, Moyá ML. *Langmuir* 2003; **19**: 8685.
- Bunton CA, Gan JH, Moffatt JR, Romsted LS, Savelli G. *J. Phys. Chem.* 1981; **85**: 4118.
- Imae T, Ikeda S. *J. Phys. Chem.* 1986; **90**: 5216.
- Eckold G, Gorski N. *Colloid Surf. A* 2001; **183–185**: 361.
- Keiper J, Romsted LS, Yao J. *Colloid Surf. A* 2001; **176**: 3.
- Marcus Y. *Ion Solvation*. Wiley: London, 1985.
- (a) Bohme KD, Young LB. *J. Am. Chem. Soc.* 1970; **72**: 7354; (b) Bohme K, Mackay GI, Pay JD. *J. Am. Chem. Soc.* 1974; **96**: 4027; (c) Tanaka T, Mackay GI, Payzant JD, Bohme DK. *Can. J. Chem.* 1976; **74**: 1643; (d) Olmsted WE, Braumen JI. *J. Am. Chem. Soc.* 1977; **99**: 4219; (e) Henschman M, Paulson JF, Hiel PM. *J. Am. Chem. Soc.* 1983; **105**: 5509; (f) Dewar MJ, Storch DM. *J. Chem. Soc., Chem. Comm.* 1985; 94.
- Desnoyers JE, Perron G. *Langmuir* 1996; **12**: 4044.
- Nagarajan R, Wang Ch-Ch. *Langmuir* 2000; **16**: 5242.
- Rodríguez A, Muñoz M, Graciani MM, Moyá ML. *Langmuir* 2004; **20**: 9945.