Catatanonic Reverse Micelles as an Optimal Microenvironment To Alter the Water Electron Donor Capacity in a $S_N2$ Reaction

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Supporting Information

ABSTRACT: The effect of interfacial water entrapped in two types of catanionic reverse micelles (RMs) on the kinetic parameters of the $S_N2$ reaction between dimethyl-4-nitrophenylsulfonium trifluoromethanesulfonate ($S^+$) and $n$-butylamine ($BuNH_2$) was explored. Two catanionic surfactants, composed of a mixture of oppositely charged ionic surfactants without their original counterions, were used to create the RMs. Thus, benzyl-$n$-hexadecyltrimethylammonium 1,4-bis(2-ethylhexyl) sulfosuccinate (BHD-AOT) and cetyltrimethylammonium 1,4-bis(2-ethylhexyl) sulfosuccinate (CTA-AOT) were formed. Also, the well-known anionic surfactant sodium 1,4-bis(2-ethylhexyl) sulfosuccinate (Na-AOT) was employed as a comparison. Our results showed an important catalytic-like effect of all RMs investigated in comparison with a water–benzene mixture, and the rate constant values depend on the type of surfactant used. Faster reaction in BHD-AOT RMs than in CTA-AOT and Na-AOT RMs was observed. This behavior was attributed to the strong interaction (by hydrogen bonding with AOT anion and ion-dipole interaction with BHD$^-$) between the entrapped water and the BHD-AOT interface, which reduces the solvation capacity of water on $S^+$. In CTA-AOT (and Na-AOT) RMs, the water–interface interaction is weaker and the electron pairs of water can solvate $S^+$ ions. In summary, the chemical structure of the counterion on the catanionic surfactant alters the interfacial region, allowing the progress of a reaction inside the RMs to be controlled.

1. INTRODUCTION

Reverse micelles (RMs) are supramolecular aggregates formed by surfactant molecules dispersed in nonpolar solvents. RMs are organized so that the surfactant head groups point inward to the center containing the polar solvent and the hydrophobic tails extend outward into the organic nonpolar continuous phase, allowing them to encapsulate water or other polar solvents in their polar heart.1,2 Taking into account their composition, RMs have shown a wide array of applications,3–12 demonstrating that these new surfactants form spherical RMs in different nonpolar solvents and that the magnitude of the water–catanionic surfactant interaction at the interface is different in both systems.21 In BHD-AOT RMs a strong water–surfactant interaction was detected while for CTA-AOT this interaction seems to be weaker. These results are interesting because a simple change in the catanionic composition of the catanionic surfactant promotes remarkable changes in the RM interface, particularly in the water–surfactant interaction. For example, BHD-AOT RMs offer a less electron donating environment than CTA-AOT.21

The differences in the physicochemical properties of the RMs systems can have a great impact on the kinetic parameters of chemical7,23 and enzymatic reactions.9,24–26 Nevertheless, to the best our knowledge, the effect of a catanionic interface on the kinetic parameters of a chemical reaction has not yet been assessed. In this work, we studied the kinetics of the reaction between dimethyl-4-nitrophenylsulfonium trifluoromethanesulfonate ($S^+$) and $n$-butylamine ($BuNH_2$) as an $S_N2$ model (Scheme 2) to fully understand the microenvironment of the catanionic micellar interface.

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2. RESULTS AND DISCUSSION

To fully understand the effect of the catanionic micellar media on the SN2 reaction, first we studied the behavior of this reaction in homogeneous media and later in different RMs: Na-AOT, BHD-AOT, and CTA-AOT. At this point, it is necessary to denote that the kinetic data in BHDC RMs are not included as a comparison because the counterion chloride of the surfactant acts as a strong nucleophile for the reaction, competing with BuNH2 for S+.

2.1. Studies in Homogeneous Media. The observed spectra of the mixture of S+ with BuNH2 at different times are shown in Figure S1A. In Figure S1B is shown the absorbance changes at \( \lambda = 342 \) nm as a function of time. The reaction of S+ with BuNH2 is a bimolecular reaction, which follows the rate law described in eq S1 and, as mentioned previously that \([\text{BuNH}_2] \gg [\text{S+}]\), the system presents a typical pseudo-first-order behavior. Thus, the \( k_{\text{obs}} \) values obtained in this media as a function of the \([\text{BuNH}_2]\) are plotted in Figure 1. The procedure to obtain the \( k_{\text{obs}} \) values from the absorbance changes is fully described in Supporting Information.

As observed, there is a linear dependence of \( k_{\text{obs}} \) values on the BuNH2 concentration. From the linear fit (eq S2), the second-order rate constant \( k_2 \) value is obtained ((2.2 ± 0.1) \( \times 10^{-1} \) M\(^{-1}\) s\(^{-1}\), Table 1). A similar value in toluene was reported by Ranieri et al.\(^{27} \) As our goal was to study the kinetics of this reaction in RMs systems without \((W_0 = 0)\) and with water \((W_0 > 0)\), it was interesting to study the effect of water on the kinetic parameters of this reaction in homogeneous media. Thus, the reaction was investigated in benzene saturated with water, where the water solubility is around 0.03 M\(^{28} \) and the \( k_{\text{obs}} \) values obtained are plotted in Figure S2. As shown, there is also a linear dependence of \( k_{\text{obs}} \) on BuNH2 concentration in benzene saturated by water. The \( k_2 \) value calculated for benzene saturated with water is (7.8 ± 1.0) \( \times 10^{-5} \) M\(^{-1}\) s\(^{-1}\), and it is three-fold smaller than in neat benzene, indicating a much slower reaction (Table 1). It should be noted that no reaction was detected in neat water. Ranieri et al.\(^{27} \) observed that \( k_2 \) values for this reaction depend strongly on the Kamlet-Taft hydrogen-bond accepting ability (\( \beta^2 \)) of the reaction media. In solvents with low \( \beta^2 \) values the

Table 1. Second-Order Rate Constant Values for the Reaction of S+ and BuNH2 in Different Solvents and RM Media at 30 °C\(^a\)

| media         | \( W_0 \) | \( k_2 \) (M\(^{-1}\) s\(^{-1}\)) | \( k_i \) (M\(^{-1}\) s\(^{-1}\)) |
|---------------|----------|-------------------------------|-------------------------------|
| neat benzene  | 0        | (3.2 ± 0.1) \( \times 10^{-1} \) |                                |
| benzene:water | 1.5      | (8.4 ± 0.2) \( \times 10^{-1} \) | (1.3 ± 0.1) \( \times 10^{-1} \) |
| benzene:water | 10       | (1.2 ± 0.1) \( \times 10^{-1} \) | (7.6 ± 0.1) \( \times 10^{-1} \) |
| Na-AOT        | 0        | (3.2 ± 0.1) \( \times 10^{-1} \) | (8.4 ± 0.2) \( \times 10^{-1} \) |
| BHD-AOT       | 0        | (1.20 ± 0.02) \( \times 10^{-4} \) | (7.6 ± 0.1) \( \times 10^{-1} \) |
| BHD-AOT       | 1.5      | (7.6 ± 0.1) \( \times 10^{-1} \) | (9.6 ± 0.1) \( \times 10^{-4} \) |
| CTA-AOT       | 0        | (5.8 ± 0.2) \( \times 10^{-1} \) |                                |
| CTA-AOT       | 1.5      | (9.6 ± 0.1) \( \times 10^{-1} \) |                                |

\( a_{k_2} \) is the second-order rate constant in homogeneous media, and \( k_i \) is the second-order rate constant for the reaction in the RMs. \([\text{BuNH}_2]\) = 0.03 M.

Scheme 1. Molecular Structures of CTA-AOT and BHD-AOT

Scheme 2. SN2 Reaction of Dimethyl-4-nitrophenylsulfonium (S+) with n-Butylamine (BuNH2) To Produce Methyl 4-Nitrophenyl Sulfide (P) and N-Methybutylammonium
reaction tends to be faster than in solvents with high $\beta$ values. This behavior was attributed to the solvent capability to form hydrogen bonds with highly acidic methyl groups, diminishing the electrophilicity of the $S^+$ ion and reducing the reaction rate. Water has a $\beta$ value much higher than that of benzene, and the rate reaction is null in neat water and even negligible in a high OH$^-$ concentration and temperature. Furthermore, it is known that the amine nucleophilicity is reduced in hydrogen bond donor solvents, due to the hydrogen bond interaction between the solvent molecules and the electron pair of the amine. This interaction leads to a high degree of amine solvation and consequently reduces its availability as a nucleophile. These facts explain why the reaction rate in benzene saturated with water is slower than in neat benzene. It is important to notice that, in blends such as benzene:water, water is dispersed without a defined organization/structure which leads to the formation of water microdomains (with a water molecule arrangement similar to that in bulk) where the reaction is slower than in neat benzene.

**2.2. Studies in Reverse Micellar Media.** Figure 2 shows the $k_{\text{obs}}$ values obtained for the reaction between BuNH$_2$ and the surfactant concentration (BHD-AOT, CTA-AOT, and Na-AOT) has on the kinetics profiles at $W_0 = 0$ and [BuNH$_2$] = 0.03 M. Figure 3 shows the kinetic results ($k_{\text{obs}}$) for the BHD-AOT/benzene RM system.

As observed, $k_{\text{obs}}$ decreased sharply as BHD-AOT concentration is increased from 0 to 0.01 M, reaching an almost constant value after that concentration. Similar behaviors were observed for both CTA-AOT and Na-AOT RMs, as shown in Figures S3 and S4, respectively. To explain these behaviors when varying the [surfactant], some considerations must be taken into account. Correa et al. studied the reaction between 4-fluoro-3-nitrobenzoate and piperidine in both BHDC and Na-AOT RMs. They observed, as in our case, that as the surfactant concentration was increased, $k_{\text{obs}}$ decreased, reaching a constant value with surfactant concentrations above 0.05 M. This behavior was attributed to the partition of piperidine between the organic solvent and the micellar interface, while 4-fluoro-3-nitrobenzoate resides completely in the micellar interface.

Taking into consideration the backgrounds described above and the results shown in Figure 2, we can consider that the reaction takes place mainly in the RM pseudophase. Apparently, $S^+$ molecules are located in the micellar interior favored by the presence of the negatively charged headgroup of the AOT, an interaction that seems to anchor the molecule at the interface. On the other hand, BuNH$_2$ molecules can be distributed between the organic phase and the micellar interface, as previously shown in Na-AOT RMs. In Scheme 3 is summarized the probable location of the reactants in the RMs.

As mentioned previously, the $k_{\text{obs}}$ values decreased sharply with the increment of the surfactant concentrations between 0 and 0.01 M (Figures 3, S3, and S4). These tendencies at low surfactant concentrations are typical for reactions that take place in the nonpolar/surfactant solutions but not in an organized media. To simplify our investigations, we decide to consider for the analysis only the reaction data when the RMs are formed ([surfactant] > critical micellar concentration, CMC). Although, for benzene/Na-AOT RMs, the CMC value is around $10^{-3}$ M, and for benzene/BHD-AOT and

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**Figure 2.** Dependence of $k_{\text{obs}}$ values with BuNH$_2$ concentration for the reaction between $S^+$ and BuNH$_2$ in Na-AOT RMs at $W_0 = 0$. Straight lines were plotted to guide the eye. [Na-AOT]/M = (■) 0.01; (▲) 0.1; (●) 0.2. [S$^+$] = 5 x $10^{-3}$ M; $T$ = 30 °C.

**Figure 3.** Dependence of $k_{\text{obs}}$ values with the BHD-AOT concentration for the reaction between $S^+$ and BuNH$_2$ in the BHD-AOT/benzene RMs in the absence of water added ($W_0 = 0$). [S$^+$] = 5 x $10^{-3}$ M; [BuNH$_2$] = 0.03 M; $T$ = 30 °C.
benzene/CTA-AOT RMs, both values are around 10⁻² M, as inferred from previous studies. Thus, to ensure that all S⁺ molecules are incorporated in the micellar interface, as proposed in Scheme 3, we worked only with [surfactant] > 0.01 M. Thus, the BuNH₂ partition process can be expressed according to eq 1:

$$K_p = \frac{[\text{BuNH}_2]_{\text{RMs}}}{[\text{BuNH}_2]_{\text{a}}[\text{Surf}]_{\text{RMs}}}$$

where BuNH₂ₐ and BuNH₂ₚₐₐ represent the BuNH₂ molecules in the organic phase and the RM system, respectively. Surfₚₐₐ represents the surfactant that forms RMs. It is conventional for micellar aggregates to consider the concentration of micellized surfactant ([Surf]ₚₐₐ) as [Surf]ₚₐₐ = [Surf]ₚₐₐ – CMC. Also, the mass balance for BuNH₂ can be considered as BuNH₂ₜₐₐ = BuNH₂ₐ + BuNH₂ₚₐₐ. Thus, the partition constant ($K_p$) of BuNH₂ can be defined by eq 2.

$$k_{\text{obs}} = \frac{k_i[BuNH_2]_{\text{total}}}{(1 + K_p[Surf]_{\text{RMs}})}$$

where $k_i$ is the second-order rate constant for the reaction in the RMs. $K_p$ values were calculated by using the Encinas–Liss method (see Supporting Information), and they are shown in Table S1. These values are quite similar and expected for BuNH₂ in RMs media.

Using the corresponding $K_p$ value for each RM system, $k_i$ was calculated by fitting eq 3 at [surfactant] > 0.01 M. Figure 4 shows the fitting of data obtained in the BHD-AOT/benzene RM system at $W_o = 0$, while in Figures S5 and S6 are plotted the data for CTA-AOT and Na-AOT RMs, respectively. All $k_i$ values are summarized in Table 1.

Table 1 shows that there are significant differences in the kinetic parameters of all RM systems studied. First, at $W_o = 0$, $k_i$ values are larger in BHD-AOT RMs than in the other two systems. We have recently reported that the BHD-AOT interface has low polarity and especially a lower electron donor capability environment than CTA-AOT and Na-AOT, which allows faster reaction rates. Table 1 also shows that the reaction is slightly faster in CTA-AOT RMs than in Na-AOT RMs. This behavior can be explained by considering that the presence of CTA⁺ cation at the micellar interface (more amphiphilic than Na⁺) reduces its electron donor capability with respect to the Na-AOT interface; hence, the interaction with S⁺ is diminished and the reaction rate is faster.

A similar approach was used for the RM systems with water added ($W_o = 1.5$), which are shown in Figures S7, S8, and S9 for the benzene/BHD-AOT/water, benzene/CTA-AOT/water, and benzene/Na-AOT/water RM systems, respectively. Particularly, in the BHD-AOT system, $k_i$ values are eight times larger than for CTA-AOT and almost 50 times larger than for Na-AOT. The water entrapped in RM systems has physicochemical properties different from that in bulk due to its interaction with the RM interface. In Na-AOT RMs, the entrapped water forms hydrogen bonds with the micellar interface, disrupting its neat structure. This interaction allows the electron pairs of water to be available to interact with S⁺, reducing its availability to react with BuNH₂. A similar behavior can be invoked in CTA-AOT RMs; thus, the water molecules interact through hydrogen bonds with the AOT anion (and also solvate the S⁺ molecules with their free electron pairs), as represented in Scheme 4. Finally, in the BHD-AOT RMs, the water–interface interaction occurs through electron pairs of water with the BHD cation. This water–interface interaction is stronger than in the other two RMs studied, freeing the S⁺ molecules and allowing faster reaction rates (Scheme 4). As suggested from previous works, in BHD-AOT RMs a stronger water–surfactant interaction can be invoked while for CTA-AOT this interaction seems to be weaker. This leads to more water molecules interacting with the interface in BHD-AOT RMs, with its hydrogen bond network completely disrupted. On the other hand, for CTA-AOT RMs a weaker water–cationic surfactant interaction allows the water molecules to hydrogen bond with each other. We hypothesize that the benzyl group present in the BHD⁺ moiety in BHD-AOT has notable impact on the behavior of the cationic interface in comparison with the interface created in CTA-AOT. As a consequence, in BHD-AOT RMs the interfacial water appears to be less electron donating than in CTA-AOT RMs.

Even though the reaction inside RMs is slower than in pure benzene (Table 1), an important catalytic-like effect is observed in the RM systems containing entrapped water in comparison with the kinetic parameters of benzene saturated by water. For example, $k_i$ values for BHD-AOT RMs ($W_o = 0$).
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Scheme 4. Location of S+ and BuNH2 and the Effect of the Water Entrapped in (A) BHD-AOT and (B) CTA-AOT RMs

1.5) are four-fold larger than the k_i value in the benzene saturated by water (Table 1). This catalytic-like effect is even noticeable in RM systems with a high water content; for example, the k_i value for Na-AOT RMs at W_0 = 10 is still larger than in the benzene saturated by water. Interestingly, the data show that, in RM media, water does not solvate BuNH2 molecules as strongly as in homogeneous media, because the rate constant values are very much larger than that observed in water and benzene:water mixtures (Table 1). It is important to notice that in all micellar media studied at W_0 > 0, the final water concentration was larger than in benzene:water solution (0.03 M). For example, at W_0 = 1.5 and [surfactant] = 0.05 M, the [water] is 0.075 M. Consequently, the amount of water around S+ and BuNH2 is not the key to explain the results observed in the present work. If the amount of water was the reason for the solvation of S+, the reaction rate values in all the RMs would be smaller than in homogeneous media, opposite to our results shown in Table 1. These results demonstrate that due to interaction with the surfactant polar head, the water molecules entrapped in RM systems have different physicochemical properties and arrangement than in bulk solution. Thus, it seems that when water is entrapped inside RMs, particularly in BHD-AOT RMs, it can solvate an electrophile without deactivating it for S+2 reaction. This property of the RMs can be very useful for reactions where one or both reactants are soluble in a nonpolar organic solvent.

3. CONCLUSIONS

In this work, the effect of interfacial water entrapped in catanionic RMs composed of BHD-AOT and CTA-AOT surfactants on the kinetic parameters of the reaction between S+ and BuNH2 (following an S+2 model) was explored. This S+2 reaction was chosen due to its high dependency on the electron donor capacity of the environment. Our results show a catalytic-like effect in both RMs investigated in comparison with the reaction in benzene:water solution. Thus, when the polar solvent is entrapped in both catanionic RMs, the novel interface changes the water electron donor ability. On the other hand, we observed the difference in the kinetic parameters obtained for both catanionic RMs, with faster reactions in the BHD-AOT than in the CTA-AOT RMs. This behavior can be attributed to the strong interaction between the entrapped water and the BHD-AOT interface, which is hydrogen bonding with the AOT anion and ion-dipole interaction with the BHD+ cation. The last interaction notably reduces the electron donor capacity of the interface water for the solvation of S+, thus accelerating the reaction. In the CTA-AOT case, water interacts with the RM interface only through hydrogen bonding with the AOT anion, allowing the electron pairs of the water molecules to interact with the S+ molecules, slowing the reaction. The catalytic-like effect of water entrapped in the RMs, particularly for BHD-AOT, has potential application for nanoreactors.

4. EXPERIMENTAL SECTION

4.1. Materials. Both catanionic surfactants, benzyl-n-hexadecyldimethylammonium chloride (BHD-AOT) and cetyltrimethylammonium bromide (CTAB), and benzyl-n-hexadecyldimethylammonium chloride (BHDC) were obtained from Sigma (>99% purity). All surfactants were dried under vacuum prior to use. Ultrapure water was obtained from Labonco Equipment model 90901-01. Benzene and 2-propanol from Sigma (HPLC quality) were used without prior purification. n-Butylamine (BuNH2) from Riedel de Haeén was distilled from sodium under a nitrogen atmosphere prior to being used. K3(CN)6Fe from Mallinkrodt and tris(2,2-bipyridine)-ruthenium(II) chloride·5H2O (Ru(bpy)2+) from Sigma were used without further purification. 4-Nitrothioanisole and methyl trifluoromethanesulfonate were purchased from Sigma and used as received.

The synthesis of dimethyl-4-nitrophenylsulfonyl trifluoromethanesulfonate (S+) was carried out as reported by Ranieri et al. with some modifications. In brief, 3 × 10^-3 mol of methyl p-nitrobenzenesulfonylate was dissolved in 5 mL of dichloroethane and added dropwise to an appropriate volume of methyl trifluoromethanesulfonate (0.01 mol approx) at 4 °C. To achieve a complete reaction, the mixture was stirred for 1 h at 37 °C. The excess of methyl trifluoromethanesulfonate and dichloroethane was removed using vacuum evaporation, and the final product was crystallized and purified using small amounts of 2-propanol. The formation of S+ was confirmed using UV–vis spectroscopy, with the appearance of an absorption band at 242 nm, in accordance with the literature.

4.2. Methods. The stock solutions of Na-AOT, BHD-AOT, and CTA-AOT in benzene were prepared by weight and volumetric dilution. All solutions were sonicated for a few minutes until they were optically clear. Different amounts of water were added using a calibrated microsyringe. The W_0 (W_0 = [water]/[surfactant]) parameter was used to express the amount of water dissolved in the
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