

Nonlinear Response of a Batch BZ Oscillator to the Addition of the Anionic Surfactant Sodium Dodecyl Sulfate

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Received: October 27, 2006; In Final Form: November 29, 2006

The response of the Belousov–Zhabotinsky (BZ) system to the addition of increasing amounts of the anionic surfactant sodium dodecyl sulfate (SDS) was monitored at 25.0 °C in stirred batch conditions. The presence of SDS in the reaction mixture influences the oscillatory parameters, i.e., induction period and oscillation period, to an extent that depends on the surfactant concentration. The experimental results have shown that the induction period increases slightly on increasing surfactant concentration and, then, a further increase in the [SDS] leads to an enhancement while the oscillation period increases monotonously on increasing SDS concentration. It has been proposed that the response of the oscillatory BZ system to the addition of SDS is due to the peculiar capability of the organized surfactant assemblies to affect the reactivity by selectively sequestering some key reacting species. Indeed, explanations of the experimental results have been given on the basis of the role played by the micellar shape, which in turn dictates the hydrophobic nature. The suggested perturbation effects have been supported by performing viscosity measurements on the aqueous SDS solutions and by the spectrophotometric estimation of the binding constant of the bromine species to the micellar aggregates. This study has indirectly corroborated the existence of two kind of micelles and unambiguously revealed that the bromine species show a different affinity toward the spherical and rod-like micelles.

Introduction

Nonlinear Behavior. The biological systems are one of the most evident manifestations of self-organization phenomena that can be present in a system far from the equilibrium when it is governed by mechanisms whose equations imply nonlinear terms. Their complex biochemistry is subject to a multitude of such phenomena on both temporal and spatial scale, such as chemical oscillations, waves of concentration, or chaos. The phenomena seem to be determining in the regulation and signal transmission within all the biological systems, from the simple unicellular systems to the human. In this context, the compartmentalization due to the presence of several membranes (cellular, nuclear, etc.) plays a relevant role. In fact, the biological membranes not only represent the physical border of the cells but are the centers of important processes, i.e., biosynthesis, energy transduction, transmission of the genetic information, etc. The majority of the processes that occur in the membranes is characterized by very complex mechanisms of reaction, which nowadays are not very well elucidated. In order to bypass the difficulties present in the study of the complex dynamics in the biological systems, it is possible to employ a model system that even though exhibits a wide number of nonlinear phenomena turns out to be simpler to study. Among the model systems that have attracted the attention of researchers, the oscillating reaction of Belousov–Zhabotinsky (BZ) is one of the most extensively studied.^{1–7} In fact, the first study was undertaken in order to mimic the Krebs cycle. In its "classic" version, the BZ reaction consists of the bromination and oxidation of an organic substrate (the malonic acid) in strongly acidic medium, in the presence of a catalyst (one

electron redox couple, usually the system Ce(IV)/Ce(III) or Ferriin/Ferriin). Over the past decades, the numerous studies concerning the dynamical behavior of the BZ reaction have indicated a continuing interest in this system. Several models have been proposed,¹ and among them, the latest, Marbourg–Budapest–Missuola (MBM), is one² of the most reliable. The considerable interest is justified if we consider that the reaction mechanism is far to be completely elucidated and also the observed behavior is extremely sensitive to the experimental conditions applied. In addition, peculiar features have been detected^{8–12} by performing the BZ reaction in aggregated systems. It is worth remembering that in the BZ reaction there are several species, and among them radicals, the concentration of which (very low) oscillates with time. These peculiar species can be properly exploited to initiate radical polymerization reaction.^{13,14}

Surfactants. Some of the difficulties related to the use of biological membranes can be bypassed by employing aggregated systems based on surfactants,¹⁵ i.e., micelles, vesicle, and microemulsions. Surfactant molecules consist of a hydrophilic head which can be anionic, cationic, zwitterionic, or non-ionic and a hydrophobic tail which is usually linear or branched, with or without unsaturations. This dual nature is the origin of the capability of the molecule of self-organizing in aqueous solvents in thermodynamically stable aggregates called "micelles." The surfactant concentration at which the reversible association of a certain number of monomers leads to aggregates (micelles) is the "critical micellar concentration" (cmc). For ionic surfactants, in aqueous solution the cmc value is strongly dependent¹⁶ on the presence of added electrolytes, and in particular, it decreases on increasing electrolyte concentration. The presence of electrolyte dictates¹⁷ both the size and shape of the aggregated system; e.g., at low ionic strength the micelles assume a

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spherical shape while as the micelles grew in size with added electrolyte, packing considerations would force the aggregates to take a more elongated rod shape, whose interior possesses a more hydrophobic nature. In addition, both the shape and size of the micelles may vary on increasing surfactant concentration. In fact, analogous to the effect induced by electrolyte,¹⁷ the increase in the surfactant concentration forces the spherical aggregates to undergo to a sphere-to-rod transition.

A micelle is characterized by three preferential solubilization sites:¹⁵ the hydrophobic core, the palisade layer, with the polar portion in contact with the micellar surface and the hydrophobic portion directed toward the core, and the hydrophilic shell. Thus, sparingly water-soluble additives are hosted in the hydrophobic core; amphiphilic molecules prefer the palisade layer and are oriented with the polar part in contact with water and the hydrophobic part toward the core, while highly polar species interact with the hydrophilic shell. The chemical reactivity of the additive is markedly dependent on the solubilization site. For instance, the rate of a bimolecular chemical reaction¹⁸ is enhanced when both reactants are sharing the same solubilization sites, while it is inhibited when they are confined in different ones.

On the basis of the peculiar features above-described, the aggregated systems are very able to act as model systems, because they not only possess numerous structural characteristics of the membranes but above all have the advantage of being thermodynamically stable and easily reproducible. Therefore, they can be used to study a great variety of problems related to biological system, even because it is easier to exploit various techniques in solution than at the biological interfaces.

Surfactants in Nonlinear Chemistry. While quite a large amount of work dealing with the determination of the physicochemical properties of surfactant aggregates has been done, there exist a scant number of systematic studies on the behavior of oscillating chemical reactions in the presence of organized systems.^{8–12} It is worth remembering that a systematic kinetic study in the presence of aggregated systems offers the advantage of providing important information not only on both reactivity and reaction mechanisms in these media but also on the solubilization and location of the solute in the micellar structure. This way, by studying the behavior of the oscillating BZ systems in the presence of micelles, valuable information to elucidate the reaction mechanism and the nonlinear phenomena can be obtained.

Bearing in mind this information and aiming to obtain insights into the role played by an anionic surfactant in influencing the dynamical behavior of the BZ mixture, we have undertaken a systematic study on the response of the system, in stirred batch conditions, to the addition of increasing amount of the anionic surfactant sodium dodecylsulfate (SDS). This surfactant was chosen for two main reasons: it does not react with the components of the BZ systems and is able to form micelles¹⁶ which undergo to shape transitions depending on the experimental conditions used for the dynamical experiments. The SDS perturbation effects have been proposed on the basis of the nonlinear response of the BZ reaction upon addition of the anionic surfactant. Moreover, we have performed tensiometric measurements to estimate the critical micelle concentration of the surfactant under the same experimental conditions used for the dynamical experiments. Support for the explanation of the peculiar BZ response has been provided by the spectrophotometric determination of the binding constant of the bromine to the SDS micellar aggregates and by viscosity measurements on the aqueous SDS solutions.

The findings of this work allow for a broad insight into the driving forces that lead to the intriguing dynamical behavior of oscillating BZ reaction in the presence of aggregated system and, indeed, evidence the role played by the micellar shape.

Experimental Methods

Materials. Ce(SO₄)₂·4H₂O, malonic acid (MA), sodium bromate, sodium bromide, sodium sulfate, and sulfuric acid were of commercial analytical quality (Fluka) and were used without further purification. Sodium dodecyl sulfate (SDS) obtained from Fluka was purified by recrystallization from ethanol.

Stock solutions of all chemicals used were prepared by weight before use. Deionized water from reverse osmosis (Elga, model Option 3), having a resistivity higher than 1 MΩ·cm, was used to prepare all solutions. Stock solutions of sulfuric acid were standardized by acid–base titration.

Potentiometric Measurements. The oscillating mixtures for the kinetic runs were prepared by mixing freshly prepared aqueous stock solutions of NaBrO₃, SDS (at the desired concentration) with Ce(IV) in 1.80 mol dm⁻³ sulfuric acid, and MA in 1.80 mol dm⁻³ sulfuric acid. Appropriate aliquots of the stock solutions were mixed in a 100 mL double walled glass reactor in order to obtain the following initial concentrations of reactants: [MA] = 0.10 mol·dm⁻³, [NaBrO₃] = 7.50·10⁻² mol·dm⁻³, [Ce(IV)] = 6.32·10⁻³ mol·dm⁻³, [H₂SO₄] = 0.90 mol·dm⁻³, while the surfactant concentration was varied in the range 1.0·10⁻³–1.0·10⁻² mol dm⁻³. In all experiments the last reagent added was the Ce(IV).

The dynamics of the BZ system was followed under constant stirred batch condition by monitoring the redox potential of the solution as a function of time by means of home made platinum electrode in combination with a Hg/HgSO₄ and 0.9 mol dm⁻³ H₂SO₄ reference electrode. The electrical contact between the solution and reference electrode was established by means of a very small hole in the glass of the reference electrode, which has the function of the salt bridge. Diffusion of the solution was negligible, and no significant amount of mercury passed in the solution. This was verified by comparing oscillation parameters obtained with the potentiometric measurements and those obtained under the same experimental conditions following cerium(IV) absorbance spectrophotometrically. A Hewlett-Packard multimeter connected to a computer was used to collect the data. Induction period (IP) was measured as the time between start of the reaction and start of the first oscillation. Oscillation period (τ) was calculated as the time between two subsequent maxima in the oscillation. Inhibitory and autocatalytic phases τ_{inh} and τ_{aut} , respectively, were calculated as the time between a minimum and a subsequent maximum and a maximum and a subsequent minimum, respectively. All these values were calculated as the mean of five oscillation cycles. All the oscillatory parameters values reported in this work are the mean of five different experiments; moreover, the oscillation period and its components represent the means of the first five oscillatory cycles.

Surface Tension and Viscosity Measurements. Both the surface tension and the viscosity of surfactant aqueous solution were determined in the absence and presence of 0.9 mol dm⁻³ H₂SO₄ and 7.50·10⁻² mol·dm⁻³ NaBrO₃.

The surface tension measurements were carried out by means of a KSV-Sigma 70 automatic tensiometer by using the Wilhelmy plate method. The critical micelle concentrations (cmc) of the SDS in aqueous solution was estimated as the intersection point of the two linear plots, above and below the cmc, of the surface tension versus log of surfactant concentra-

tion. Either in the absence or in the presence of acidic bromate, the surface tension versus \log [SDS] plots do not show a minimum value. This clearly indicates that the surfactant does not contain impurities. The obtained cmc values of the SDS in the absence and in the presence of added electrolytes are $7.9 \cdot 10^{-3} \text{ mol dm}^{-3}$ and $3.2 \cdot 10^{-5} \text{ mol dm}^{-3}$, respectively. It has to be highlighted that the cmc value obtained in aqueous solution is in good accordance with that reported in the literature,¹⁶ while that in the presence of electrolytes is about 2 orders of magnitude lower. The lower cmc value can be attributed to the very high value of the ionic strength. In fact, it is well established¹⁷ that the presence of ionic additives strongly influence the micellization process leading to a lower cmc value.

The relative viscosity (η_r) of the aqueous surfactant solutions was calculated from the well-known relationship $\eta_r = \eta/\eta_0 = (t/t_0)(\rho/\rho_0)$. The solution flowing time (t) was measured with an Ostwald viscosimeter calibrated by measuring the viscosity (η_0) and density (ρ_0) of the solvent and its draining time (t_0).

Moreover, the density of the aqueous surfactant solutions (ρ) was measured. The density of the solvent and aqueous surfactant solutions was measured at $25.000 \pm 0.001 \text{ }^\circ\text{C}$ by using a vibrating tube flow densimeter (Model 03D, Sodev Inc.) sensitive to 3 ppm. The temperature was maintained constant within $0.001 \text{ }^\circ\text{C}$ by using a closed loop temperature controller (Model CT-L, Sodev Inc.). The calibration of the densimeter was made using a procedure reported in the literature.¹⁹

Spectrophotometric Measurements. The UV-vis spectra of the Ce(IV) acidic aqueous solutions in the absence and presence of the SDS were monitored with a computer-controlled Beckman spectrophotometer model DU-640, equipped with thermostated compartments for cuvettes. Quartz UV grade spectrophotometer cuvettes having a path length of 0.1 cm were used.

To verify that Ce(IV) species do not react with the SDS, we monitored the UV-visible spectra of the Ce(IV) acidic aqueous solution as a function of both the surfactant concentration and the time. It was found that, in all cases examined, the spectra do not show any significant change with respect to that obtained in aqueous acidic solution within 2 h observation.

The UV-vis spectra of the bromine-bromide acidic aqueous solutions in the absence and presence of the SDS were monitored as a function of time with an Analytic Jena S600 diode-array spectrophotometer. Quartz UV grade spectrophotometer cuvettes having a path length of 0.2 cm were used. All solutions contained $0.9 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$ and $2.5 \cdot 10^{-2} \text{ mol dm}^{-3} \text{ Na}_2\text{SO}_4$. The latter salt was used to keep the same ionic strength like in the BZ experiments, since the NaBrO₃ could not be applied here because it would react with the excess bromide.

It was found that preparing the bromine-bromide acidic aqueous solutions by adding the bromine solutions to the bromide one led to loss of bromine due to volatilization. Thus, we opted for the in situ preparation of bromine according to reactions R1–R3 (we follow the notations of the MBM model), whose sum gives:



Consequently, aqueous acidic solutions of known stoichiometric concentration in bromine and bromate ion were prepared by mixing in a manual Hi-Tech stopped-flow apparatus the aqueous acidic solutions of sodium bromate and bromide. The stopped-flow was directly connected to the quartz cuvette through a black tube. The bromate concentration was kept constant at $2.0 \cdot 10^{-4} \text{ mol dm}^{-3}$, while that of the bromide was always in excess and varied in the range $1.40 \cdot 10^{-3}$ – $2.25 \cdot 10^{-2} \text{ mol dm}^{-3}$. The

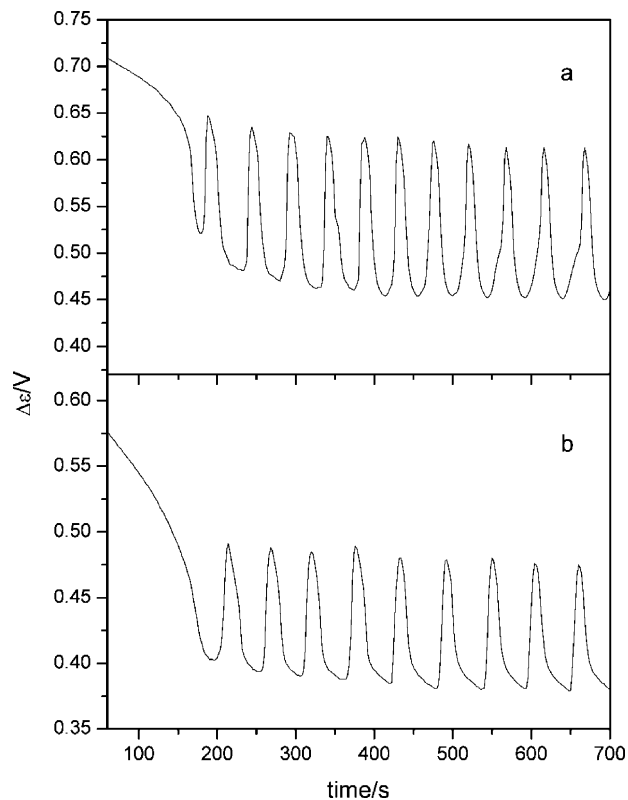


Figure 1. Potential of a Pt electrode in the course of the BZ reaction (a) in the absence of surfactant and (b) in the presence $0.008 \text{ mol dm}^{-3}$ of SDS. $[\text{MA}]_0 = 0.1 \text{ mol dm}^{-3}$; $[\text{BrO}_3^-]_0 = 7.50 \cdot 10^{-2} \text{ mol dm}^{-3}$; $[\text{Ce(IV)}]_0 = 6.32 \cdot 10^{-3} \text{ mol dm}^{-3}$; $[\text{H}_2\text{SO}_4]_0 = 0.90 \text{ mol dm}^{-3}$; $t = 25.0 \text{ }^\circ\text{C}$.

measurements were carried out in the presence of $4.50 \cdot 10^{-3}$ and $1.0 \cdot 10^{-2} \text{ mol dm}^{-3}$ SDS.

All equipment was interfaced to a computer for both data collection and analysis and the temperature of the experiments was regulated to $25.0 \pm 0.1 \text{ }^\circ\text{C}$ with a thermostat Heto model DT HetoTerm.

Results and Discussions

Figure 1a shows the potentiometric time series of the BZ system under stirred batch condition in the absence of the anionic surfactant SDS. Perusal of this Figure shows that the potential of the solution monotonically decreases and then, after the so-called induction period (IP), the system begins to oscillate with an oscillation period (τ) which is composed by two parts, i.e., the time corresponding to the inhibitory and autocatalytic phase, τ_{inh} and τ_{aut} , respectively. Addition of the anionic micelle-forming surfactant does not alter the qualitative profile of the solution potential as a function of time but influences the oscillatory parameters with exception of the amplitude. In fact, for all SDS concentration applied, the amplitude of the oscillations as a function of surfactant was found to be independent of the [SDS]. A typical plot is shown in Figure 1b. In particular, as it can be seen in Figure 2, the induction period slightly increases on increasing surfactant concentration, and then an augmentation can be noticed while the oscillation period always increases on increasing [SDS] (see Figure 3a). Different trends can be observed for both τ_{inh} and τ_{aut} as a function of surfactant concentration (Figure 3b,c). In fact, analogous to the IP trend, the presence of SDS first slightly increases the inhibitory phase and then an increase can be detected, while influences to a less extent the autocatalytic phase since only an initial increase can be noticed and then the τ_{aut} values are almost constant. It is

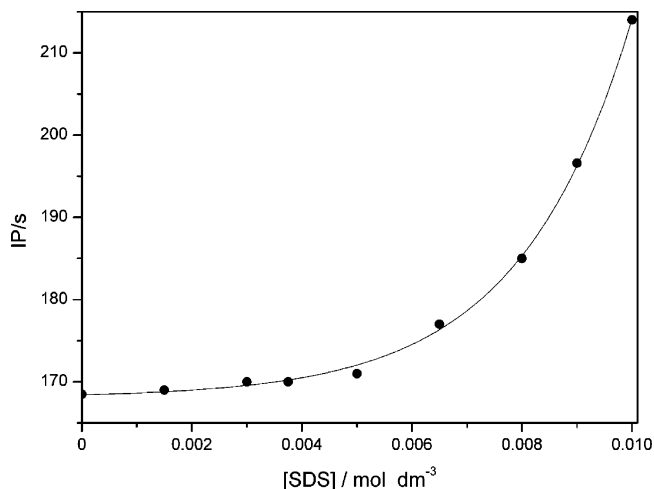


Figure 2. Induction period (IP) as a function of surfactant concentration for the BZ system.

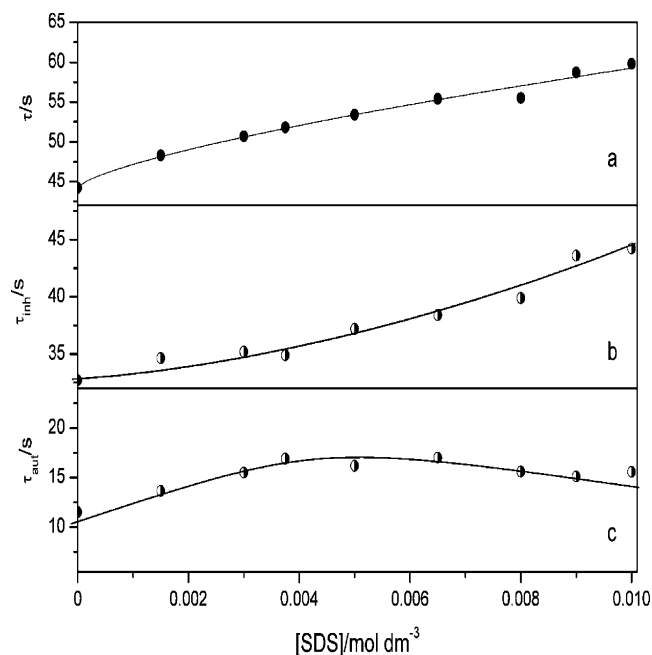


Figure 3. (a) Oscillation period (τ), (b) time of the inhibitory phase (τ_{inh}), and (c) time of the autocatalytic phase (τ_{aut}) as a function of surfactant concentration for the BZ system.

worth saying that the surfactant concentration at which there is a discontinuity point coincides in all trends of the oscillatory parameters and it is well above the cmc of the SDS obtained in the present work (see the experimental section).

Analogous effects on the oscillation period were previously¹² obtained for a modified BZ system, while the induction period was found to be independent of the SDS concentration. The differences with our system are due to the diverse experimental conditions used and above all to the nature of the catalyst used, i.e., a ruthenium(III) complex instead of cerium(IV).

The dynamic response of the oscillatory BZ system to the addition of SDS can be explained by taking into account the influence of the anionic micellar aggregates on some key steps of the mechanism of the BZ reaction. In fact, the peculiar feature of the micelles implying three different solubilization sites, namely, the hydrophilic head groups, the palisade layer, and the interior hydrophobic core, allows for selective interactions between the aggregated system and some crucial species. In

particular, we can reasonably assume that hydrophobic compounds, such as bromomalonic acid or bromine, are confined into either the palisade layer or the core of the micellar aggregate while the malonic acid is located in the aqueous pseudo-phase. Evidence on the organophilic and hydrophilic nature of the bromomalonic and malonic acid, respectively, has been recently²⁰ provided. In addition, the lack of partition of the malonic acid into non-ionic micellar aggregates has also been previously⁹ demonstrated.

Thus, bearing in mind all these considerations, the rate of the reaction R30 has to be inhibited by the presence of SDS micelles to an extent that depends on the surfactant concentration:



As the inhibition makes reaction R30 slower, it will require a longer time to accumulate a critical amount of BrMA which is able to “turn off” the autocatalytic reaction. Moreover, we have also to consider not only that the SDS micelles exert a rate-retarding effect on the bromomalonic acid formation but also that once the BrMA is formed they are able to incorporate it into the hydrophobic micellar interior, most likely in the palisade layer. This way to reach the higher $[\text{BrMA}]_{\text{CRIT}}$ requires even more time; i.e., the induction period becomes longer. Evidence of the solubilization of bromine species into aggregated systems has been previously²¹ reported for other reactions.

These justifications are also supported by the trends of the other oscillatory parameters; in fact, in the presence of SDS, the BZ system is forced to oscillate with a longer oscillation period since, for the same reasons, the autocatalytic phase requires a longer time to be turned on. However, at this stage we have provided explanations for the observed findings in the oscillatory parameters over the whole surfactant concentration investigated but we have not discussed that the trends evidence two regions of behavior. Thus, an additional discussion is needed. It is reasonable to propose that under our experimental conditions the SDS forms two different types of aggregated systems. One possibility is that, at low surfactant concentration, the micellar aggregates assume a spherical shape while on increasing surfactant concentration they become more elongate, i.e., rod-like micelles. As it is well-known,^{17m} spherical micelles are less hydrophobic in nature than the rod-like ones, so the solubilization capability of the latter ones toward the bromine and bromomalonic acid is higher. As a consequence, the rod-like SDS micelles are much more effective in influencing the oscillatory parameters. The shape transition of the SDS micelles induced by either high electrolyte concentration or augmentation of surfactant concentration are very well documented in the literature.¹⁶

We can highlight that the presence of SDS micelles in the BZ mixture plays a relevant role; i.e., the organized surfactant assemblies affect the reactivity by selectively sequestering the reacting species, and the influence extent depends on the shape of the micelles.

Therefore, to corroborate our explanations on the perturbation effects, we have performed systematic viscosimetric and spectrophotometric studies, whose results will be discussed in the following subsections.

Viscosimetric Data. To prove that, under the experimental conditions used in the present work, two kinds of micelles having different shapes exist, we have performed a systematic viscosimetric study.

The viscosity of the aqueous SDS solutions in the presence of $7.50 \cdot 10^{-2} \text{ mol dm}^{-3} \text{ NaBrO}_3$ and $0.9 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$ was

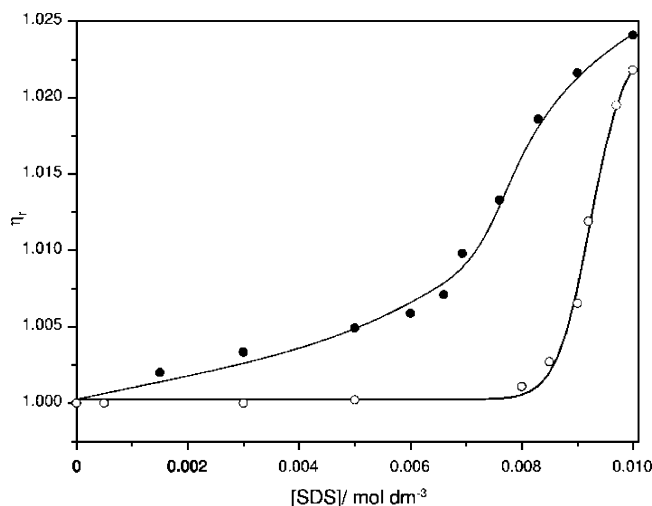


Figure 4. Relative viscosity (η_r) as a function of surfactant concentration of aqueous SDS surfactant solutions in the absence (●) and in the presence (○) of $0.075 \text{ mol dm}^{-3} \text{ NaBrO}_3$ and $0.9 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$, $t = 25.0 \text{ }^\circ\text{C}$.

measured as a function of surfactant concentration, and for comparison the measurements were been carried out in the absence of added electrolytes. The complete course of the relative viscosity (η_r) as a function of surfactant concentration is illustrated in Figure 4. In both cases two linear regions of behavior can be detected even though some significant differences have to be discussed. In particular, in the absence of added electrolytes the η_r trend shows the classical behavior; i.e., at low surfactant concentration, the relative viscosity values are almost constant and then after a discontinuity point increase. These trends are indicative of micelle formation, and the break point can be taken as the critical micelle concentration. The cmc value obtained in the present work in the absence of added electrolytes is in good agreement with that previously¹⁶ obtained and is very close to the value tensiometrically obtained in the present work (see the experimental section). In the presence of acidic bromate, the trends differ to some extent. In fact, at low SDS concentration, the η_r values slightly increases on increasing surfactant concentration and then after the inflection point, a further augmentation of the [SDS] leads to an increase in the relative viscosity values. It is worth saying that the surfactant concentration at which the η_r trend shows the discontinuity point coincides with that obtained in the IP trend. Thus, taking into account that the presence of electrolytes strongly influences both the micellization process and the shape of the aggregated system, we can ascribe the observed trends to the formation of two different types of aggregated systems. According to the tensiometric measurements, the cmc value under these experimental conditions is almost 2 orders of magnitude lower than the value obtained in the absence of additives. As a consequence, it is reasonable to rule out that the break point corresponds to the cmc of the surfactant and assume that most likely up to a surfactant concentration corresponding to the inflection point the SDS forms only spherical micelles, while at higher surfactant concentration these micelles undergo to a more elongated shape. This transition implies the formation of the more hydrophobic aggregated system which interacts to a larger extent with the reacting substrates and, in turn, reflects the observed effects on the oscillatory parameters.

Spectrophotometric Data. The spectrophotometric method based on the analysis of the alterations provoked by the presence of surfactant upon the reversible reaction (E1) between the bromine and bromide to give tribromide ions was employed to

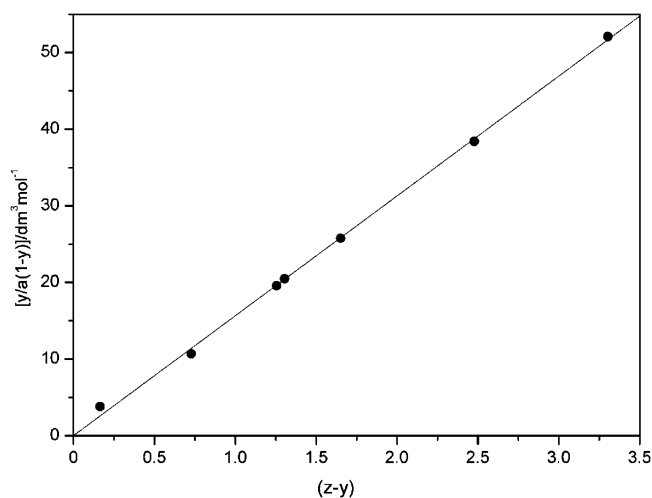


Figure 5. Results obtained for reaction (E1) plotted according to eq 2. $[\text{Br}_2]_0 = 6.0 \cdot 10^{-4} \text{ mol dm}^{-3}$; $2.0 \cdot 10^{-4} \leq [\text{Br}^-]_0 \leq 2.0 \cdot 10^{-3} \text{ mol dm}^{-3}$; $[\text{H}_2\text{SO}_4]_0 = 0.90 \text{ mol dm}^{-3}$; $[\text{Na}_2\text{SO}_4]_0 = 2.5 \cdot 10^{-2} \text{ mol dm}^{-3}$; $t = 25.0 \text{ }^\circ\text{C}$. (●) Experimental data and (—) curve calculated by a linear least-square fit of eq 2.

determine the binding constant (K_B) of the bromine to SDS micelles under the experimental conditions used for the dynamical experiments:



The procedure employed necessitate of the determination of the equilibrium constant (K) for reaction E1 under our experimental conditions:

$$K = \frac{[\text{Br}_3^-]}{[\text{Br}_2][\text{Br}^-]} \quad (1)$$

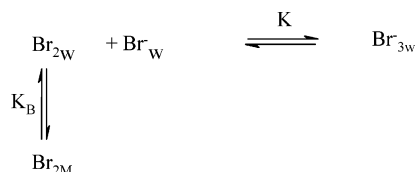
To further prove that two kinds of aggregated systems so far exist, i.e., spherical and rod-like micelles, and to get evidence for the different solubilization capability of the two types of aggregated systems, we have performed the spectrophotometric measurements at two SDS concentrations. In particular, we have chosen one concentration below and the other above the transition concentration.

Absorbance Data in the Absence of Surfactant. The UV-vis spectra of the Br_3^- species in aqueous acidic solutions over a wide bromide concentration range, obtained as described in the experimental section, were monitored as a function of time. It was found that, for each solution, the equilibrium absorbance values depend on the bromide concentration and, in particular, increases on increasing bromide concentration. These values were used to calculate the K value according to eq 2, previously²² used for an analogous system. Similarly, for our system we can assume that if activity coefficients are disregarded, the measurement of the maximum absorbance as a function of bromide concentration allows us for the evaluation of the equilibrium constant of reaction E1 through the use of the eq 2:

$$\frac{y}{a(1-y)} = K(z-y) \quad (2)$$

where a is the formal (analytical) concentration of bromine, $y = [\text{Br}_3^-]/a$, $z = [\text{Br}^-]/a$, ($[\text{Br}^-]$ is the formal analytical concentration of bromide), and K is the equilibrium constant, as defined above.

SCHEME 1



The value of y has been obtained as the ratio between the absorbance at 270 nm measured in the solution at the bromine and bromide concentrations considered, and that corresponding to a solution in which the bromine is completely converted into tribromide ion by addition of an excess of bromide, for the latter purpose the molar extinction coefficient reported in the literature²³ has been used.

The calculated values according to each terms of eq 2 are reported in Figure 5. The linear least-squares analysis of these data according to eq 2 enabled us to determine the equilibrium constant, whose value is $15.6 \pm 0.1 \text{ dm}^3 \text{ mol}^{-1}$. The linearity of the plot indicates that, under our experimental conditions, the activity coefficients of all the involved species can be considered as independent of the composition of the reaction mixture. The obtained K value is slightly lower with respect to that obtained in aqueous solution;²⁴ however, it is worth saying that this is in line²⁵ with the effects of salts on the equilibrium constant of such a kind of reaction.

Absorbance Data in the Presence of Surfactant. Analogous experiments to those described in the above section were performed in the presence of two particular concentrations of sodium dodecylsulfate, i.e., one below and the other above the sphere-to-rod transition concentration. However, some differences have to be discussed. First, at each bromide concentration, the equilibrium absorbance values are slightly lower with respect to those registered in the absence of surfactant, while no shift in the λ_{max} values could be detected. The observation that the tribromide absorbance is different in the absence and presence of surfactant suggests that partitioning of the Br_2 species into the micellar aggregates is altering the apparent Br_3^- formation constant. Since the anionic micelles repel the two anionic species while showing an higher affinity toward the bromine, a shift of the equilibrium constant in favor of the Br_2 will be observed. This way the production of tribromine conform to the Scheme 1, which implies that the bromine is solubilized in both the aqueous region (w) and the micellar pseudo-phase (M); thus, the concentration of bromine affecting the reaction in the aqueous pseudo-phase will depend on the partition equilibrium condition.

The binding constant K_{B} for the partition of bromine is given by the equation

$$K_{\text{B}} = \frac{[\text{Br}_2]_{\text{M}}}{[\text{Br}_2]_{\text{W}} \cdot C} \quad (3)$$

where $[\text{Br}_2]_{\text{M}}$ is the analytical concentration of the bromine associated to the micelles (in moles of bromine per liter of solution), $[\text{Br}_2]_{\text{W}}$ is the analytical concentration of the bromine confined in the aqueous pseudo-phase, and C is the micellized surfactant concentration ($[\text{SDS}] - \text{cmc}$). The concentration of Br_2 associated to the micelles is obtained by means of the following mass balance condition (in which the volume occupied by the micellar pseudo-phase can be neglected):

$$[\text{Br}_2]_{\text{M}} = [\text{Br}_2]_{\text{total}} - [\text{Br}_2]_{\text{W}} - [\text{Br}_3^-] \quad (4)$$

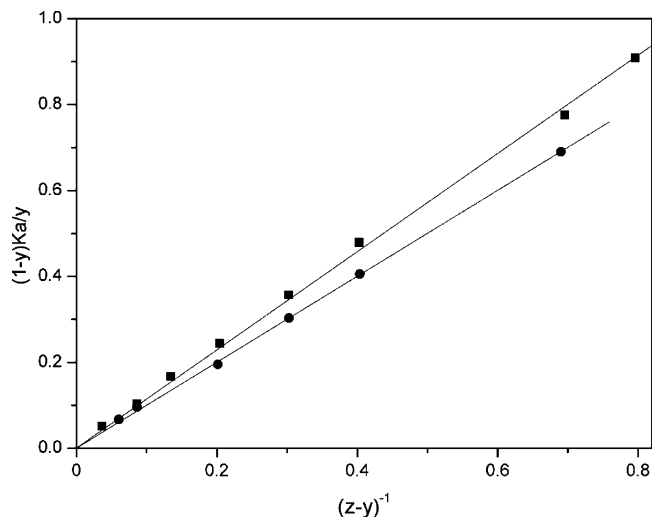


Figure 6. Results obtained for reaction (E1) plotted according to eq 5, in the presence of (●) $4.5 \cdot 10^{-3} \text{ mol dm}^{-3}$ and (■) $1.0 \cdot 10^{-2} \text{ mol dm}^{-3}$ SDS. $[\text{Br}_2]_0 = 6.0 \cdot 10^{-4} \text{ mol dm}^{-3}$; $7.0 \cdot 10^{-4} \leq [\text{Br}^-]_0 \leq 5.0 \cdot 10^{-2} \text{ mol dm}^{-3}$; $[\text{H}_2\text{SO}_4]_0 = 0.90 \text{ mol dm}^{-3}$; $[\text{Na}_2\text{SO}_4]_0 = 2.5 \cdot 10^{-2} \text{ mol dm}^{-3}$; $t = 25.0 \text{ }^\circ\text{C}$. (●, ■) Experimental data and (—) curve calculated by a linear least-square fit of eq 5.

By doing the proper combining of eq 2–4, we obtain the following relationship:

$$\frac{(1-y)Ka}{y} = \frac{1 + K_{\text{B}}C}{z-y} \quad (5)$$

Thus, for both SDS concentration, analogous to the treatment reported above, we calculated each term of eq 5, whose values are shown in Figure 6. The linear least-squares analysis of these data according to eq 5 allowed us to calculate only the binding constant at the higher $[\text{SDS}]$ ($K_{\text{B}} = 10.0 \pm 0.1 \text{ dm}^3 \text{ mol}^{-1}$). As for the lower surfactant concentration, it was not possible to calculate the K_{B} value because the slope was close to the unit. The above-discussed meaning of the linearity of the plot holds also in the presence of SDS. Moreover, the obtained K_{B} value is lower than that obtained previously²² for the iodine in the same aggregated system but at lower ionic strength. If allowance is made for the different nature of the solubilized species and experimental condition used, this result is the logical consequence of micelles having higher hydrophobic nature.

From the obtained binding constant value, we can reasonable suggest that the bromine species are located in the palisade layer of the micelles.

The spectrophotometric results indirectly demonstrate that two kind of aggregated systems so far exist depending on the SDS concentration used and unambiguously reveal that the bromine species show a different affinity toward the two kinds of micelles. Indeed, they give rise of the observed response of the BZ system to the addition of the SDS.

Summary

The cerium(IV) catalyzed Belousov–Zhabotinsky (BZ) oscillating system responds in a peculiar way to the addition of increasing amount of the anionic surfactant sodium dodecyl sulfate (SDS).

The values of the oscillatory parameters, i.e., induction period and oscillation period, depend on the surfactant concentration used, which dictates the shape of the aggregated systems.

Support for the proposed existence of two kind of aggregated systems was provided by performing viscosity measurements on the aqueous SDS solutions.

The perturbation mechanism of the oscillatory BZ system was corroborated by spectrophotometric investigations for the estimation of the binding constant of the bromine to the micellar aggregates. These studies have indirectly corroborated the existence of two kind of micelles and unambiguously revealed that the bromine species show a different affinity toward the spherical and rod-like micelles.

Acknowledgment. The authors thank the Università degli Studi di Palermo for financial support (Research Funds ex quota 60%).

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