Observations of the Effect of Anionic, Cationic, Neutral, and Zwitterionic Surfactants on the Belousov−Zhabotinsky Reaction

Anumita Paul*

Department of Chemistry, Indian Institute of Technology Guwahati, Guwahati 781 039 India

Received: December 2, 2004; In Final Form: February 11, 2005

In this paper we report the experimental observations of the effects of various surfactants on the oscillations of the ferroin-catalyzed Belousov−Zhabotinsky (BZ) reaction. The oscillations are followed by observing the change in absorbance at 510 nm due to ferroin in a well-stirred closed BZ reacting system. We have used sodium dodecyl sulfate (SDS) as the anionic surfactant, cetyl trimethylammonium bromide (CTAB) as the cationic surfactant, Triton X-100 as the neutral surfactant, and 3-[(3-cholamidopropyl)dimethylammonio)]-1-propanesulfonate (CHAPS) as the zwitterionic surfactant. In general, we observed that there is a change in the oscillation behavior in the presence of each of these surfactants above their critical micellar concentrations. For different surfactants, the time-dependent evolution of the oscillations is found to be characteristic of the surfactant. The results of our study suggest that the evolution of oscillations is most regular in the presence of micelles of SDS.

Introduction

An emerging area of recent experimental focus in nonlinear oscillatory chemical reaction is control over its dynamics.[1] This has important consequences in biological and chemical applications.[2−4] Control can be achieved externally by applications of electric field,[5] magnetic field,[6] and light[7] and internally by performing reactions in the presence of nonreacting chemical species such as micelles.[8−11] Micelles, vesicles, and microemulsions are known to significantly affect chemical reaction kinetics.[12,13] Recent studies of Belousov−Zhabotinsky (BZ) oscillatory reactions have shown that micelles may have effects on the induction period, oscillation time period and amplitudes, and reaction kinetics, or even initiate oscillations in a reaction that does not exhibit oscillations in the absence of micelles.[8−10,14]

Here we report experimental observations on the effects of micelles of anionic, cationic, neutral, and zwitterionic surfactants, in an attempt to determine the effect of ionic/polar headgroups on the kinetics of ferroin-catalyzed BZ reaction in a closed reaction system. We have used sodium dodecyl sulfate (SDS) as the anionic surfactant, cetyl trimethylammonium bromide (CTAB) as the cationic surfactant, 3-[(3-cholamidopropyl)dimethylammonio)]-1-propanesulfonate (CHAPS) as the zwitterionic surfactant, and Triton X-100 (TX-100) as the neutral surfactant. We probed the reaction kinetics by monitoring the time-dependent changes in the visible absorption due to ferroin at 510 nm. Our observations suggest that the presence of surfactants above critical micellar concentrations (cmc) affect the oscillations of the BZ reaction depending on the nature of the surfactants. We find that the time evolution of the oscillations and the amplitude are markedly different in the presence of different surfactants. Our results suggests that micelles of SDS are best able to the regulate the rate of oxidation and reduction reactions of the iron catalyst such that the BZ reaction approaches the steady state systematically.

* Email: anumita@iitg.ernet.in

Experimental Section

Stock solutions of reagents, KBrO$_3$ (SD Fine Chemicals), KBr (Aldrich, spectroscopic grade), malonic acid (Aldrich), ferroin (FeSO$_4$, E. Merck; and 1,10-phenanthroline, SD Fine Chemicals), SDS (Aldrich), CTAB (Aldrich), and H$_2$SO$_4$ (SD Fine Chemicals) were prepared in Millipore filtered water from which appropriate volumes of solutions were transferred to a 3 mL cuvette and stirred well. Ferroin was added in the end and the UV−visible spectra were recorded immediately after the addition of ferroin and closure of the sample compartment. This took typically between 20 and 30 s. For the study with CHAPS, 0.0262 g of the reagent (Sigma) was measured in the reaction cuvette and then dissolved in 715 μL of water with stirring. The other reagent solutions were added after dissolving the surfactant. Similarly for the study with TX-100, 0.0014 g of the reagent (Aldrich) was first dissolved in 715 μL of water with stirring and the other solutions were added after the surfactant was dissolved. The reagents were used as received. The final concentrations of the reagents, other than surfactants, were 0.12 M KBrO$_3$, 1×10^{-4} M KBr, 0.01M malonic acid, 0.3 M H$_2$SO$_4$, and 3.4×10^{-4} M ferroin. In the case of the BZ reaction in the presence of CTAB the [Br$^-$] was 2.2×10^{-3} M while the concentrations of all other reagents were unaltered. The reaction was monitored by visible absorption of ferroin ([Fe(phen)]$^{2+}$) at 510 nm by using a Hitachi U2001 UV−visible spectrophotometer. The reaction temperature was maintained at 30 ± 0.2 °C by a thermostated cell holder that uses a water circulating system to keep the temperature constant.

Results

Parts A, B, C, D, and E of Figure 1 show the results obtained for the time-dependent absorption at 510 nm of a typical BZ reaction mixture and BZ reaction in the presence of 1, 2, 8, and 16 mM sodium dodecyl sulfate (SDS), respectively. The sudden initial rise and fall in absorbance (off scale in Figure 1) were present in all the spectra and are probably due to the initial evolution of bromine.[10,15] Thereafter the oscillatory behavior

TABLE 1

reaction system	reaction time, s oscillation time period (average), s oscillation time period (range), s							
ordinary BZ	160−1680 76 70−80	1680−4090 80 70−80	4090−4880 78 80−70	4880−5630 75 80−70	5630−6240 65 70−60	6240−6950 58 60−50		
BZ in SDS	100−1330 62 60−70	1330−1970 64 60−70	1970−2640 67 60−70	2640−3350 71 60−80	3350−4110 76 70−80	4110−4890 78 70−80	4890−5580 69 70−50	
BZ in CTAB	410−1120 − 190−110	1120−1520 80 100−70	1520−1840 64 70−60	1840−2120 56 60−50	2120−2370 50 50	2370−2590 44 50−40	2590−2790 40 40	
BZ in TX-100	320−670 − 30−40	670−1120 45 40−50	1120−1640 52 50−60	1640−2200 56 50−60	2200−2780 58 50−60	2780−3370 59 50−60	3370−3970 60 60	3970−4560 59 60−50	4560−5120 51 60−50
BZ in CHAPS	110−350 48 40−50	350−610 52 50−60	610−890 56 50−60	890−1220 66 60−70	1220−1580 72 60−80	1580−2000 84 80−90	2000−2480 96 90−100	2480−3090 121 100−130	3090−4670 − 150−420

commenced without any induction period. As evident from Figure 1A, the variation of the absorbance minima in the oscillations was not very regular for the ordinary BZ reaction. However, the absorbance maxima increased marginally to a constant value between 1000 and 2200 s and then decreased nearly linearly as the reaction progressed to steady state. The oscillation time period is initially ∼80 s up to ∼3500 s into the reaction, and then reduces to 50 s in the last few oscillations.

With addition of SDS there were three notable changes in the time-dependent absorption spectra at 510 nm, as shown in Figure 1B−E. First, the values of absorption maxima increased considerably (note the scale in Figure 1A is amplified 3 times that in Figure 1E), and second, the absorbance minima are much better regulated and show near-constant values above 2 mM

concentration of SDS. Third, the absorbance maxima show significant initial increase and then exponential decrease with the progress of the BZ reaction in the presence of SDS above 2 mM. Addition of 16 mM SDS had an effect on the oscillation time period, which was 60 s initially and then increased up to 80 s with the progress of the reaction. In the last few oscillations the time period was found to reduce to 50 s; see Table 1. Separate surface tension measurements (inset, Figure 1C) show that the critical micelle concentration of SDS in the presence of BZ reactants was ∼2.2 mM.

The effect of a variety of micelle systems was investigated by following the BZ reaction in the presence of SDS, CTAB, CHAPS, and TX-100, above cmc.[15−17] The time-dependent absorption spectra at 510 nm are shown in Figure 2. Table 1
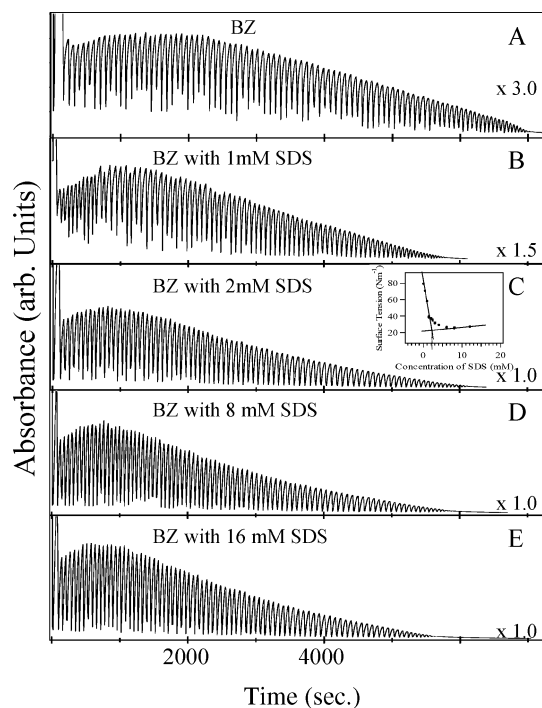
Figure 1. Time evolution of absorbance at 510 nm in a closed stirred BZ reaction system with initial concentration of reactants [KBrO$_3$] = 0.12 M, [KBr] = 1 × 10^{-4} M, [malonic acid] = 0.01 M, [H$_2$SO$_4$] = 0.3 M, and [ferroin] = 3.4 × 10^{-4} M. (A) In absence of sodium dodecyl sulfate (SDS). (B) In the presence of 1 mM SDS. (C) In the presence of 2 mM SDS. (D) In the presence of 8 mM SDS. (D) In the presence of 16 mM SDS. Inset in (C) shows the phase transition in surface tension of the BZ reaction occurs at ∼2.2 mM SDS.
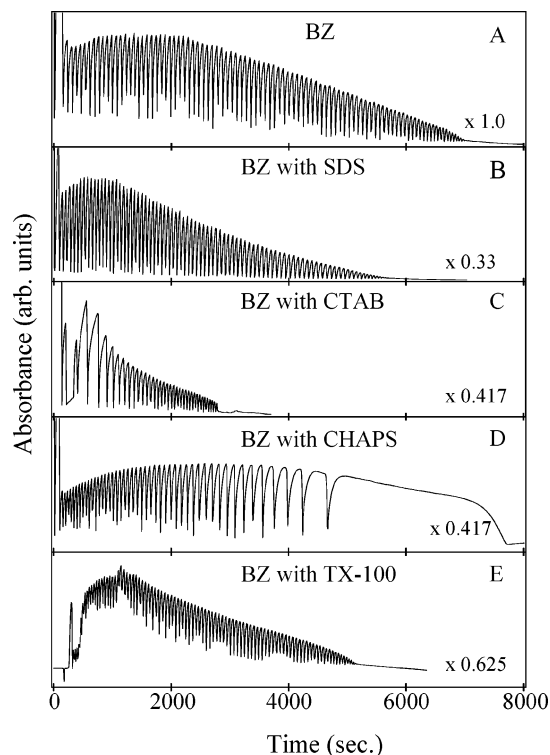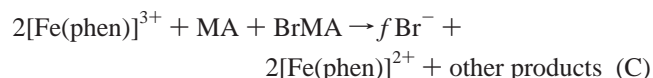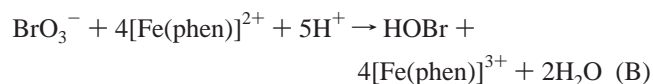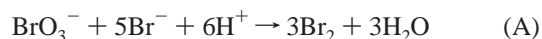

Figure 2. Time evolution of absorbance at 510 nm in a closed stirred (A) BZ reaction, (B) BZ in [SDS] = 16 mM, (C) BZ in [CTAB] = 2.2 mM, (D) BZ in [CHAPS] = 15.8 mM, and (E) BZ in [TX-100] = 0.8 mM. The initial concentrations were [KBrO$_3$] = 0.12 M, [malonic acid] = 0.01 M, [H$_2$SO$_4$] = 0.3 M, and [ferroin] = 3.4 × 10^{-4} M in each case. [KBr] = 1 × 10^{-4} M in the case of SDS, TX-100, and CHAPS; [Br$^-$] = 2.2 × 10^{-3} M in the case of CTAB.

Effect of Surfactants on the BZ Reaction

J. Phys. Chem. B, Vol. 109, No. 19, 2005 **9641**

lists the evolution of the time periods in each of these BZ systems. As evident from these, the exact course of the BZ reaction is characteristic of the surfactant used. Thus, while anionic SDS had a marginal effect, cationic CTAB, zwitterioninc CHAPS, and nonionic TX-100 showed marked changes in the amplitude and time period of oscillations for the BZ reaction. The presence of 2.2 mM cationic surfactant CTAB (Figure 2C) shortened the total oscillatory phase of the BZ reaction considerably. For example, with the same concentrations of reactants (except Br^-, whose concentration is the same as CTAB) the ordinary BZ reaction took more than 7000 s for oscillations to cease, whereas with CTAB the oscillations were over by 3000 s. The longer time period in the beginning (190 s) followed by a continuous reduction in time period down to 40 s toward the last few oscillations is very distinct for CTAB. The absorbance maxima decreased rapidly but smoothly while the absorbance minima were found to be more or less constant throughout the reaction. Also seen in Figure 2C is the presence of an induction period (<340 s) between the initial evolution of Br_2 and commencement of sustained oscillations. Interestingly, with zwitterionic CHAPS, shown in Figure 2D, the initial oscillation time period was faster (40 s) than the ordinary BZ reaction, and as the reaction progressed there was a steady decline in the rate of oscillations down to 150 s. Toward the end of the reaction, the oscillation time period increased rapidly to very long values of up to 420 s. In contrast, the addition of neutral TX-100 (Figure 2E) made the initial oscillations chaotic with time periods faster (30 s) than the addition of any other surfactant in this study. There was also an initial induction period of about 260 s, after which there was a peak due to Br_2 evolution. The rapid oscillations of small amplitude progressed to oscillations with larger amplitudes and nearly constant time period (60 s). Interestingly, TX-100 shows a distinct rise in absorbance maxima followed by smooth decay while the absorbance minima show large variations, paralleling the behavior of absorbance maxima but with marked irregularities. Zwitterionic CHAPS (Figure 2D) shows a gradual rise in absorbance maxima followed by their slow decrease above 3000 s, while the absorbance minima evolve irregularly.

Discussion

The mechanism of the BZ reaction has been extensively investigated, and although details of the mechanism are yet to be resolved, the overall features of the reaction are fairly well explained by the Field–Körös–Noyes (FKN) mechanism.[18] According to the FKN mechanism, species such as HOBr, $HBrO_2$, $BrO_2\bullet$, and Br_2 are proposed to be present in the reaction medium apart from the starting reactants. Three major processes that are important in understanding the oscillatory behavior of the BZ reaction are

$$BrO_3^- + 5Br^- + 6H^+ \rightarrow 3Br_2 + 3H_2O \qquad (A)$$

$$BrO_3^- + 4[Fe(phen)]^{2+} + 5H^+ \rightarrow HOBr +$$
$$4[Fe(phen)]^{3+} + 2H_2O \quad (B)$$

$$2[Fe(phen)]^{3+} + MA + BrMA \rightarrow f\,Br^- +$$
$$2[Fe(phen)]^{2+} + \text{other products} \quad (C)$$

Process A removes Br^- ions from the medium generating HOBr and $HBrO_2$ intermediates. Also, the $[Br^-]/[BrO_3^-]$ concentration ratio is known to play a critical role in controlling the start of the autocatalytic step in process B, during which ferrin ([Fe-(phen)]$^{2+}$) is oxidized to ferrin ([Fe(phen)]$^{3+}$). The autocatalytic step is initiated when the concentration of Br^- falls below a critical value given by $[Br^-]_{critical}/[BrO_3^-] \approx 10^{-5}$. Termination of process B occurs when the autocatalyst, $HBrO_2$, disproportionates to HOBr and BrO_3^- at high concentrations of $HBrO_2$. Malonic acid (MA) and its bromo derivatives reduce ferrin ([Fe-(phen)]$^{3+}$) back to ferroin ([Fe(phen)]$^{2+}$), releasing Br^- ions in the resetting process C.

Since the BZ reaction involves positive ions, negative ions, and neutral species present in the aqueous medium, it is expected that surfactants with varying charges would induce different effects depending on the charge of the surfactant in solution. Moreover, above critical micelle concentrations the hydrophobic core of the micelles may entrap nonpolar species, thus influencing the kinetics and the course of the BZ reaction. Other effects such as surface tension, viscosity, density, and ionic strength could also affect the course of the BZ reaction.[19]

Our observations in Figure 1 with varying concentration of SDS show that the effect is dramatic when the concentration of the surfactant is above its critical micelle concentration, suggesting the importance of micellar structures in determining the course of the BZ reaction, consistent with earlier literature reports.[14] It may be worth mentioning here that the critical micelle concentration (cmc) of SDS in pure water is 8.3 mM and, as the ionic strength increases, the value of cmc is known to go down.[15−17,20,21] In the present case, in Figure 1, the onset of smoother absorbance rise and decay characteristics begins to appear at an SDS concentration of 2 mM, which is ~1/4 cmc of SDS in pure water. Further, the apparent time evolution of the BZ reaction in the presence of 2, 8, and 16 mM SDS (~1/4, ~1, and ~2 cmc, respectively, in ordinary water) are very similar, indicating the presence of a considerable population of micelles well below 8.3 mM SDS (i.e., cmc in pure water). Independent surface tension measurement studies (Figure 1C, inset) confirm that for the BZ reaction mixture used in our studies the cmc of SDS occurs at ~2.2 mM. We further note that at 1 mM SDS (i.e., <1 cmc in BZ) the reaction clearly behaved neither like pure BZ nor like the BZ reaction in the presence of 16 mM SDS. The short time period at the initial stages is abruptly replaced by longer time periods in the case of 1 mM SDS. In addition, there is a sudden jump in absorbance maximum and minimum value ~700 s into the reaction. A closer look at the amplitudes of oscillations at 2 mM SDS also suggests that the reaction is not completely developed as at 16 mM SDS. The above results indicate that, at concentrations above ~2 mM, SDS molecules in micelle form regulate the concentration of reactive species in BZ reaction such that the oscillations are considerably altered.

The ordering of solvent molecules in the vicinity of the micelle interface is known to affect the local dielectric constant of the medium.[20] This in turn can affect the absorption coefficient of a chromophore.[10] Accordingly, the absorbance due to ferroin in the BZ reaction at 8 mM, at 16 mM, and to some extent at ~2 mM SDS is greater than that for the pure BZ reaction. It may be noted here that addition of a noninterfering salt such as $NaNO_3$ did not affect the absorption intensity or the oscillatory behavior of the BZ reaction, thus ruling out ionic strength variation as the reason for the above-mentioned observations. Further, although the addition of 1 mM SDS reduces the surface tension of the aqueous phase by nearly 30%, the evolutionary nature of the BZ reaction is not affected much, whereas when the surface tension of the solution is reduced further by a another 30% (at 8 mM SDS), the nature of the BZ

SCHEME 1
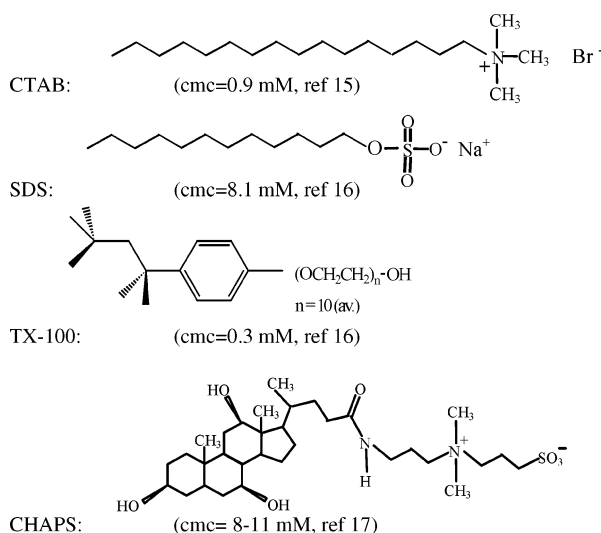
reaction is altered. Thus surface tension alone cannot account for the observed effects on the BZ reaction.

The above observations suggest that by controlling the environment of the BZ reaction with nonreactive aggregates, such as micelles, it is possible to change the course of the BZ reaction. The effect of micelles can be many-fold. It is conceivable that the ionic/polar headgroups of micelles may act as a surface where reactants and solvents are adsorbed in a characteristic manner, dramatically affecting the reaction events of the nonlinear BZ reaction.[20] Moreover, the hydrophobic core of the micelles may act as regions where nonpolar/nonionic reactants may preferentially partition, altering their effective concentration and hence the course of the BZ reaction. Such compartmentalization of reactants in microemulsions has been shown to markedly affect oscillations and pattern formation in BZ reactions.[22] Additionally, the BZ reaction can be affected in the presence of micelles by affecting transport properties of the reactants due to changes in diffusion coefficient of the reactants and/or changes in viscosity and density of the medium.[11,14,19]

Since the BZ reaction is, in essence, a reaction between various ionic and neutral species, it is important to study the effect of micelles with different charges, i.e., anionic, cationic, neutral, and zwitterionic, to delineate the effects of ionic/polar headgroups from the other effects of the micelles. The results of such a study (Figure 2) shows that the time-dependent evolution of the BZ reaction for the anionic SDS, cationic CTAB, neutral TX-100, and zwitterionic CHAPS (Scheme 1) is characteristic of the surfactant. This is expected, as surfactants with varying charges and micelle environment would have differing effects on the various reactive species, hence altering the kinetics of the multiple nonlinearly coupled steps in the BZ reaction. Further, the binding constants of various ions and neutral species to micelle would be different, depending on the charge on the surfactant, nature of the surfactant, nature of the ion/neutral species, and ionic strength of the medium. Also, the rates of dissociations of micelles into individual monomers would be different for different surfactants and ionic strengths of the medium.[21] All these factors would affect the oscillations in the BZ reaction, and different surfactants would have different effects of varying magnitudes as supported by our observations in Figure 2. It is, thus, difficult to determine the exact reason-(s) for the observed differences in the oscillation for the BZ system in the presence of micelles. However, the data in Figure 2 show significant changes in time period and amplitudes, whose

analysis may shed light on some of the major factors affecting the BZ reaction in the presence of various micelles. Since in our closed BZ systems no additional reactants are added, each oscillation starts with a slightly different concentration of reactants; hence the systems in our study evolve with time. Our BZ systems do not exhibit phases of period doubling, torus oscillations, or chaos as observed in other closed BZ systems.[23] Rather our systems exhibit varying degrees of irregularities in their evolution (Figure 1S). In particular, we note that the absorbance maxima and minima for the closed BZ reaction in the presence of micelles of SDS and CTAB evolve relatively smoothly while absorbance minima in the presence of TX-100, CHAPS, and ordinary BZ reaction show irregular evolution. An important observation from Figure 2 is that, while the formation of ferroin through successive oscillations is relatively slow and regular, in all the systems studied there are large irregularities in the onset and termination of fast autocatalytic process (also Figure 1S). Since the charges on the polar headgroup of SDS and CTAB are opposite, it is likely that the hydrophobic core of the micelle has a role to play in regularizing the reaction events such that the BZ reaction is able to evolve more systematically in these two micellar systems.

The nature of the evolution of a closed BZ system is reflected in its amplitude as well as in time period changes (Table 1). For the ordinary BZ reaction, the time period is found to first increase slightly ($70 \rightarrow 80$ s) and then decrease slightly ($80 \rightarrow 70 \rightarrow 60$ s). In presence of 16 mM SDS the oscillation time period continuously increases ($60 \rightarrow 80$ s), except for the last few oscillations. More dramatic behavior is observed for the case of CTAB, where the time period reduces rapidly from $190 \rightarrow 50$ s. In presence of CHAPS, the oscillations are initially fast, which steadily slow down from $40 \rightarrow 420$ s. The change in time period is dramatic with the last oscillation being more than 3000 s long. For TX-100 the reaction is initially very irregular. Clear and fast oscillations emerge later, whose time period increases, $45 \rightarrow 60$ s with the progress of the reaction. Since the trends in the oscillation time period (i.e., cationic CTAB decreases dramatically, anionic SDS increases gradually, neutral TX-100 increases more significantly, and zwitterioinc CHAPS increases dramatically, while ordinary BZ increases and then decreases slightly) are weakly correlated with the charge of the headgroup, this suggests that the electrostatic nature of the micelles does not have a dominant role to play.

It is clear from the behavior of oscillation amplitudes and time periods that the presence of micelles of surfactants SDS and CTAB induce systematic evolution in the closed BZ system. While SDS is able to regulate the rates of oxidation and reduction reactions of the BZ catalyst uniformly such that the oscillation amplitude and time period evolve slowly, CTAB does so with significant changes in oscillation time period and amplitudes. Since the charges of SDS and CTAB micelles are opposite, i.e., anionic vs cationic, the increased regularity observed in the evolution of the closed BZ reaction in these systems is probably due to the hydrophobic nature of the core of micelles. Note that this is consistent with our observations that surfactants below cmc and that noninterfering ions such as $NaNO_3$ did not affect the course of the plain BZ reaction, since micelles were absent in both these cases. Further, it appears that, apart from the hydrophobic core, the charge on the polar headgroup of the micelles and other hydrodynamic factors affect the reaction events such that oscillations of the BZ reaction are characteristic of the micellar system. This is not surprising, as surfactants with varying charges and micelle environment would
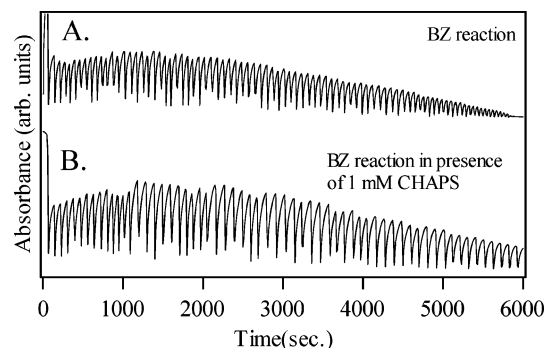
Figure 3. Time evolution of absorbance at 510 nm in a closed stirred (A) BZ reaction and (B) BZ in [CHAPS] = 1 mM, both at 32 °C.

affect the concentration of various reactive species and the kinetics of the multiple nonlinearly coupled steps in the BZ reaction.

The most nonpolar species in the BZ reaction is Br_2; hence this molecule would prefer to reside inside the hydrophobic core of the micelles. It is to be noted that the likelihood of ionic reactants and neutral polar intermediates residing inside the hydrophobic core of the micelles has been reported to be low for the ferroin-catalyzed BZ reaction involving malonic acid.[9−10] Preferential partitioning of Br_2 into the hydrophobic poly-(dimethylsiloxane) (PDMS) has also been shown to affect the temporal pattern formation in the BZ reaction by affecting the concentration of bromide ions in the aqueous phase, a key inhibiting species in the BZ reaction.[24] It is plausible that micellar environment changes the effective concentration of Br_2 characteristic of each surfactant. In this regard, it may be noted that that the irregularities observed at the onset and the termination of the autocatalytic step (Figure 1S) is linked to [Br^-] and [$HBrO_2$], respectively, both of which are related to the concentration of Br_2, through the reactions $2HBrO_2 = BrO_3^- + HOBr + H^+$ and $HOBr + H^+ + Br^- = Br_2 + H_2O$. Whether a BZ system is able to overcome the irregularity depends on the micelle system. We find that SDS does so most efficiently, followed by CTAB. Numerical simulations of a model BZ system also supports that oscillations are sensitive to effective [Br^-] and any related phenomenon/event, such as its loss or partitioning away from the reactive aqueous phase and changes in rate constants or kinetics associated with its concentration, can impart varying degrees of perturbation and irregularity to the BZ system (Figure 2S).

Interestingly, both CTAB and CHAPS show dramatic changes in time period not seen with ordinary BZ, TX-100, or SDS, indicating an intriguing possibility of major involvement of radicals in the BZ mechanism as both CTAB and CHAPS have N centers that can support such mechanisms (Scheme 1). Polymerization reactions of acrylonitrile and aniline driven by BZ systems are well-known and are believed to involve radical mechanisms.[25,26] A control experiment, Figure 3, with a BZ reaction in the presence of 1 mM CHAPS (which is much lower than its cmc) shows that the evolution of the oscillations is closer to the ordinary BZ reaction than to the 15.8 mM CHAPS (Figure 2). Thus the dramatic changes observed in CHAPS and CTAB systems of Figure 2 are probably not due to major radical involvement in the BZ reaction with the N centers of these micellar systems.

On careful examination of the structure of the surfactants (Scheme 1), one finds that the hydrocarbon tails in SDS and CTAB are quite hydrophobic with only C−C bonds. CTAB, containing a C16 chain, is expected to be more hydrophobic than SDS, which contains a C12 chain.[27] On the other hand,

TX-100 has a polar headgroup with a long tail containing ether linkages ending in an aromatic group. CHAPS, in contrast, has both positive and negative charges in the headgroup and a relatively short cyclic aliphatic tail containing hydroxyl groups. The order of hydrophobicity is expected to be CTAB > SDS > TX-100 > CHAPS. Accordingly we find that the more hydrophobic SDS and CTAB bring regularity in the BZ reaction. However, SDS is able to better regulate the overall rates of the reactions such that the reduction and oxidation cycles in BZ oscillations show minimal irregularity in their evolution toward steady state. We conclude therefore that the hydrophobic character of the micelles plays an important role along with charges of the polar headgroup and other hydrodynamic properties in affecting the concentrations of species and the rates of reactions in the closed, well-stirred, BZ system.

Conclusion

In conclusion, we would like to point out that the presence of surfactants above critical micelle concentrations alter the course of oscillations in a well-stirred closed BZ reaction, characteristic of the nature of the surfactant. Various processes, such as adsorption of reactants, preferential solubility in hydrophobic core, and hydrodynamic parameters, and their relative rates and dynamics presumably affect the kinetics of the multistepped nonlinear BZ reaction in a complex way, making the influence of each surfactant unique to the reaction. Anionic SDS is found to be most efficient in regulating the evolution of the BZ reaction followed by cationic CTAB. With progress of the reaction the oscillation time period increases marginally for anionic SDS, decreases dramatically for cationic CTAB, increases dramatically for zwitterionic CHAPS, and increases marginally for TX-100 compared to a marginal increase and decrease for the plain BZ reaction. We conclude therefore that hydrophobic character, charge of the headgroups, and other hydrodynamic processes of the micellar environment influence the overall course of the BZ reaction.

Supporting Information Available: Phase plots showing the transient nature of the oscillations and their varying degrees of irregular evolution for the BZ systems studied. Stochastic simulations of model BZ system showing various factors, including rate constants and additional equilibria, that could potentially influence the effective concentration of Br^- and hence the oscillations in a closed system. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) (a) Sakurai, T.; Mihaliuk, E.; Chirila, F.; Showalter, K. *Science* **2002**, *296* (5575), 2009. (b) Petrov, V.; Gaspar, V.; Masere, J.; Showalter, K. *Nature* **1993**, *361* (6409), 240. (c) Mihaliuk, E.; Sakurai, T.; Chirila, F.; Showalter, K. *Phys. Rev. E* **2002**, *65* (6, Pt 2), 065602.

(2) Epstein, I. R.; Showalter, K. *J. Phys. Chem.* **1996**, *100*, 13132.

(3) Larter, R. *Chem. Rev.* **1990**, *90*, 355.

(4) Demin, O. V.; Westerhoff, H. V.; Kholodenko, B. N. *J. Phys. Chem. B* **1999**, *103*, 10695.

(5) Astumanian, R. D.; Chovk, P. B.; Tsong, T. Y.; Westerhoff, H. V. *Phys. Rev. A* **1989**, *39*, 6416.

(6) Møller, A. C.; Olsen, L. F. *J. Phys. Chem. B* **2000**, *104*, 140.

(7) (a) Okazaki, N.; Mori, Y.; Hanazaki, I. *J. Phys. Chem.* **1996**, *100*, 14941. (b) Vanag, V. K.; Zhabotinsky, A. M.; Epstein, I. R. *Phys. Rev. Lett.* **2001**, *86* (3), 552.

(8) (a) Vanag, V. K.; Hanazaki, I. *J. Phys. Chem. A* **1997**, *101*, 2147. (b) Vanag, V. K.; Hanazaki, I. *J. Phys. Chem.* **1996**, *100*, 10609.

(9) Cavasino, F. P.; Cervellati, R.; Lombardo, R.; Liveri, M. L. T. *J. Phys. Chem. B* **1999**, *103*, 4285.

(10) Maritato, M.; Nikles, J.; Romsted, L. S.; Tramontin, M. *J. Phys. Chem.* **1985**, *89*, 1341.

(11) (a) Vanag, V. K.; Epstein, I. R. *Phys. Rev. Lett.* **2001**, *87* (22), 228301. (b) Epstein, I. R.; Vanag, V. K. *AIP Conf. Proc.* **2003**, *676* (Experimental Chaos), 265.

(12) Otto, S.; Engberts, J. B. F. N.; Kwak, J. C. T. *J. Am. Chem. Soc.* **1998**, *120*, 9517.

(13) Cavasino, F. P.; Sbriziolo, C.; Turco Liveri, M. L. *J. Phys. Chem. B* **1998**, *102*, 5050.

(14) Rustici, M.; Lombardo, R.; Mangone, M.; Sbriziolo, C.; Zambrano, V.; Turco Liveri, M. L. *Faraday Discuss.* **2002**, *120*, 39−51.

(15) Israelachvili, J. N. *Intermolecular and Surfaces Forces*, 2nd ed.; Academic Press: New York, 1995.

(16) (a) Stark, R. E.; Leff, P. D.; Milheim, S. G.; Kropf, A. *J. Phys. Chem.* **1984**, *88*, 6063. (b) Hjelmeland, L. J.; Nebert, D. W., Jr.; Osborne, J. C. *Anal. Biochem.* **1983**, *130*, 72.

(17) Moullik, S. P. *Curr. Sci.* **1996**, *71*, 368.

(18) Fields, R. J.; Körös, E.; Noyes, R. M. *J. Am. Chem. Soc.* **1972**, *94*, 8649.

(19) Yoshimoto, M.; Shirahama, H.; Kurosawa, S.; Naito, M. *J. Chem. Phys.* **2004**, *120* (15), 7067.

(20) Rawat, S. S.; Mukherjee, S.; Chattopadhyay, A. *J. Phys. Chem. B* **1997**, *101*, 1922.

(21) Adamson, A. W.; Gast, A. P. *Physical Chemistry of Surfaces*, 6th ed.; John Wiley & Sons: New York, 1997.

(22) Vanag, V. K.; Epstein, I. R. *Science* **2001**, *294*, 835.

(23) Wang, J.; Sørensen, P. G.; Hynne, F. *J. Phys. Chem.* **1994**, *98*, 725.

(24) Ginn, B. T.; Steinbock, B.; Kahveci, M.; Steinbock, O. *J. Phys. Chem. A* **2004**, *108*, 1325.

(25) Washington, R. P.; West, W. W.; Misra, G. P.; Pojman, J. A. *J. Am. Chem. Soc.* **1999**, *121* (32), 7373.

(26) Chowdhury, D.; Paul, A.; Chattopadhyay, A. *J. Colloid Interface Sci.* **2003**, *265* (1), 70.

(27) (a) *Handbook of Surface and Colloid Chemistry*, 2nd ed.; Birdi, K. S., Ed.; CRC Press: Boca Raton, FL, 2003. (b) Trapani, G.; Altomare, C.; Franco, M.; Latrofa, A.; Liso, G. *Int. J. Pharm.* **1995**, *116*, 95.