Belousov−Zhabotinsky Oscillations in Bromate−Oxalic Acid−$MnSO_4$−H_2SO_4−Acetone System in Nonionic Surfactant Medium. A Calorimetric Study

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Thermal oscillations in oxalic acid−bromate−$MnSO_4$−H_2SO_4−acetone system have been studied in aqueous solution of nonionic surfactants, TX-100, Tweens (20, 40, and 60), and Brijs (56, 58 and 76). It has been observed that significantly low concentration of the surfactants can inhibit the oscillatory reaction. In general, they have inhibitory effects on the frequency and enthalpy of oscillations. The inhibition has been found to have direct dependence on the length of the nonpolar tail of the surfactant molecule. There is a threshold concentration for a surfactant above which oscillation stops, and this threshold or critical concentration decreases with increasing length of the surfactant chain. The amphiphile *n*-heptanol has also shown significant inhibitory effect.

Introduction

After the publication of the sensational papers by Belousov[1] and Zhabotinsky[2] on the classical oscillatory reactions (B−Z reaction), numerous workers have undertaken the study of this reaction, where periodic changes or oscillations in the concentration of one or more components with time take place, from various points of view. Field, Körös, and Noyes[3] have elucidated the detailed mechanism of this complex reaction (FKN mechanism), and a number of mathematical models[4−8] have been developed to rationalize the mechanism. The study has since then been a subject of chemical, biological, and mathematical interest. The most commonly studied B−Z reaction, the metal ion catalyzed bromination of organic compounds in homogeneous media by strongly acidic aqueous solution of potassium bromate, involves the systems bromate/malonic acid/H_2SO_4/cerium ion and bromate/gallic acid/H_2SO_4/ferroin, although a variety of organic compounds and mixture of compounds[9−12] have been found to produce oscillation. Although most of the studies have employed potentiometry and spectrophotometry, reports on calorimetric measurements are rare in the literature. We had undertaken the study of the B−Z reaction by using calorimetric measurements[13−15] to generate useful thermochemical data.

Of the different aspects of the oscillatory reactions, their features in compartmentalized conditions (viz. micellar, reverse micellar, liquid crystalline[16−19] media), in enzyme catalyzed systems,[20,21] across membranes[22−24] and in polymer gels,[25] have drawn attention of many researchers and have become a subject matter of growing interest. Recently, a micellar solution of sodium lauryl sulfate (NaLS) has been used to promote oscillations in the fluorescence intensity from irradiated solutions,[26] and a cationic surfactant, cetyltrimethylammonium bromide (CTAB), has been used in generating spontaneous oscillations in the electrode potential across a liquid membrane.[27,28] The behavior of chemical oscillators in organized amphiphilic assemblies imparting spatial order on a temporarily ordered system has been reported.[29,30] The influence of cetyltrimethylammonium sulfate and NaLS on the B−Z reaction using ruthenium bipyridyl as catalyst has been studied.[31] Cavasino et al.[32] have studied the kinetics of oxidation of Ce(IV)-catalyzed B−Z reaction with methyl-, ethyl-, and benzylmalonic acid in the presence and absence of cetyltrimethylammonium nitrate (CTAN) and NaLS.

Noszticzius et al. and others[33−38] have studied oscillations in the oxalic acid/bromate/acetone/Ce^{3+} or Mn^{2+} (catalyst)/H_2SO_4 system with and without acetone. Thermal oscillations of this system have been previously studied by us.[39] We have chosen this B−Z oscillatory system for the present study thermometrically to understand the effect of some nonionic surfactants on the thermal oscillations. Instances of thermometric/calorimetric investigations on oscillatory reactions are limited, and studies of B−Z reactions in nonionic surfactant media are rarely found in the literature.[29] In the present paper, we have presented the findings on the study of B−Z oscillatory process of oxalic acid/bromate/acetone/$MnSO_4$/H_2SO_4 system in aqueous solutions of Triton X-100, Tween 20, 40, and 60, and Brij 56, 58, and 76, expecting to provide meaningful information and to generate useful data of chemical and biological interest.

Experimental Section

Materials. Potassium bromate, sulfuric acid, acetone, oxalic acid, and manganous sulfate used obtained from E. Merck (Germany). Among the surfactants, TX-100 was obtained from Spectrochem (India), Tweens (20, 40, and 60) were obtained from Sigma (USA), and Brijs (56, 58, and 76) were obtained from Aldrich (USA). *n*-Heptanol used was an A.R.-grade product from Lancaster (Germany). Doubly distilled conductivity water was used in all preparations.

Methods

Calorimetry. The reaction was studied in a TRONAC (458) (USA) isoperibol titration calorimeter. A mixture (18 mL) of

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TABLE 1: Trade Name, Chemical Name, and CMC Values of the Surfactants Used in This Study

trade name	chemical name	cmc/ m mol dm^{-3}
Triton X-100	(*p*-tert-octylphenoxy)polyoxyethylene(9.5) ether	0.24
Tween 20	polyoxyethylene(20) sorbitan monolaurate	0.05
Tween 40	polyoxyethylene(20) sorbitan monopalmitate	0.023
Tween 60	polyoxyethylene(20) sorbitan monostearate	0.021
Brij 56	polyoxyethylene(10) cetylether	0.002
Brij 58	polyoxyethylene (20) cetyl ether	0.007
Brij 76	polyoxyethylene (10) stearyl ether	0.003

0.155 mol dm^{-3} potassium bromate and 1.1 mol dm^{-3} acetone in 1.25 equiv dm^{-3} sulfuric acid was taken in the reaction vessel. A 2 mL sample of a mixture of 0.625 moldm^{-3} oxalic acid and 0.013 mol dm^{-3} manganous sulfate in 1.25 equiv dm^{-3} sulfuric acid was added from the buret. The heat change during the oscillation was recorded in a Houston Omniscribe Stripchart Recorder. The heat produced during the oscillation was calculated following the procedure described earlier.[13] To examine the effect of a surfactant on the oscillatory process, the required concentration of the material was maintained in the titrant solution.

Tensiometry. The cmc (critical micelle concentration) of the surfactant was determined in 1.25 equiv dm^{-3} sulfuric acid medium by measuring surface tension with a Krüss (du-Nüoy) Tensiometer (Germany) by the ring detachment method following the procedure described earlier.[40] All the measurements were taken at a constant temperature of 303K.

Results and Discussion

Cmc and Surfactant Structure. The cmc values of the surfactants, namely, (TX-100, Tween 20, 40, and 60, and Brij 56, 58, and 76), in aqueous medium are given in Table 1, and their structures are depicted in Figure 1. Tensiometric measurements were performed to check whether the cmc values of the surfactants used in the present study changed in the 1.25 equiv dm^{-3} H_2SO_4 medium. It has been found that these values remain more or less same as those in the aqueous medium. In some cases, slight variation has been observed. For example, the cmc of TX-100 is 0.24 mM in aqueous medium, and it is 0.21 mM in 1.25 equiv dm^{-3} H_2SO_4 (Figure 2).

Effect of Surfactants on the Oscillatory Process. Maritato et al.[31] have studied the effects of two ionic surfactants, cetyltrimethylammonium sulfate [$(CTA)_2SO_4$] (cationic) and sodium lauryl sulfate [NaLS] (anionic), on the malonic acid/bromate/Ru(II) (catalyst)/H_2SO_4 B−Z system. In the present study, we have chosen nonionic surfactants which are seldom employed[29] in the study of oscillatory reactions. All these surfactants have shown inhibitory effect on the B−Z reaction. The number of oscillations (*n*) and the total enthalpy of oscillation (ΔH_{osc}) have been found to decrease with the increase in concentration of the surfactants in each case up to a certain threshold concentration, above which no oscillation has been observed. This threshold concentration is different for different surfactants. It is strikingly seen that each of the added surfactants affects the reaction at a very low concentration. In Figure 3, the effects of Tween 40 of five different concentrations on the oscillatory process studied here is presented. The process has been systematically inhibited on increasing [Tween 40].

During the calorimetric measurements, a large exothermic stage was observed just after the start of the addition of the reactants (mixture of oxalic acid and manganous sulfate) from the buret, which continued for a short period of time (2−6 min). There was no overlay between the initial induction period and the subsequent oscillation, which started well after the complete

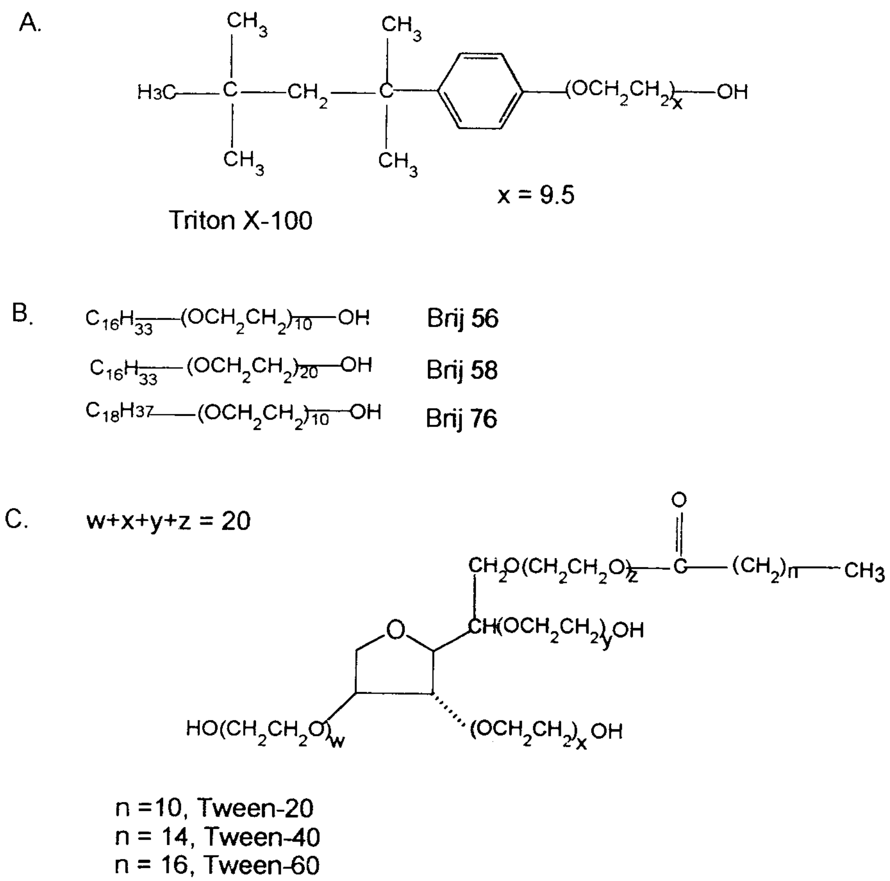

Figure 1. Structures of nonionic surfactants used in this study.

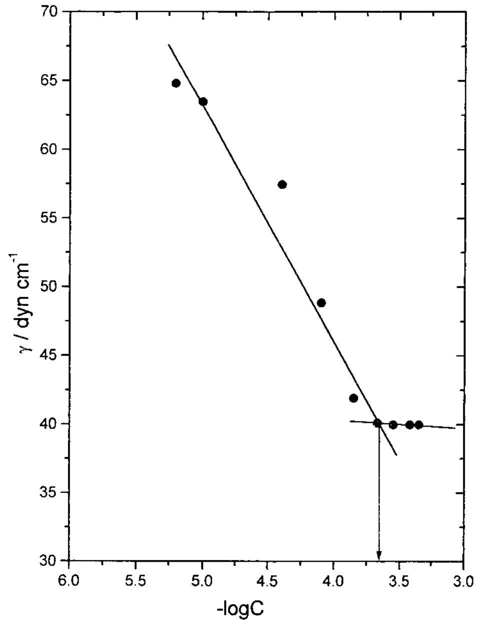

Figure 2. Tensiometric evaluation of cmc of TX-100 in 1.25 equiv dm^{-3} H$_2$SO$_4$ at 303 K.

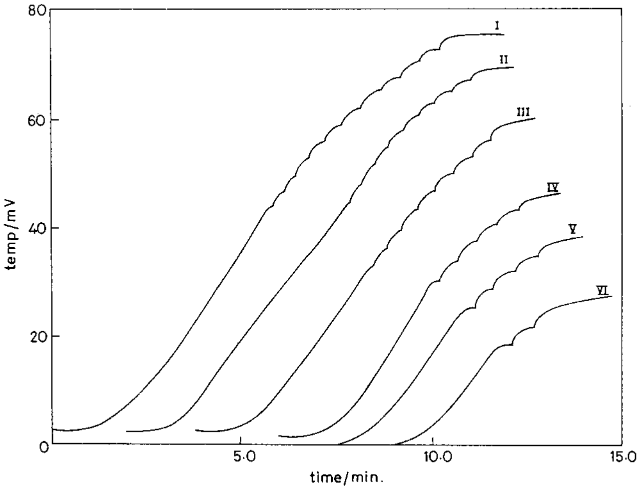

Figure 3. Effect of Tween 40 at five different concentrations on the oscillatory process of the bromate/oxalic acid/H$_2$SO$_4$/MnSO$_4$ system at 303 K. [O A] = 0.0625 mol dm^{-3}; [H$_2$SO$_4$] = 1.25 equiv dm^{-3}; [KBrO$_3$] = 0.14 mol dm^{-3}; [MnSO$_4$] = 0.0013 mol dm^{-3}; [acetone] = 1.0 mol dm^{-3}. I, without surfactants; II, [Tween 40] = 10^{-8} mol dm^{-3}; III, [Tween 40] = 10^{-7} mol dm^{-3}; IV, [Tween 40] = 10^{-6} mol dm^{-3}; V, [Tween 40] = 10^{-5} mol dm^{-3}; VI, [Tween 40] = 2 × 10^{-5} mol dm^{-3}. ([Tween 40] ≈ cmc)

addition of the reactants. This initial heat (I_h) decreased with increasing [surfactant], but in some cases, the I_h values became irregular with increasing [surfactant]. This is depicted in Figure 4, where the inhibitory effects of the surfactants at identical concentration of 10μM have been shown. For the Brijs, I_h follows the trend Brij 56 < Brij 76 < Brij 58. This trend for the Tweens is Tween 60 < Tween 40 < Tween 20.

It has been observed that with increasing [TX-100], both n and ΔH_{osc} decrease, and the oscillation stops at concentration $>2 \times 10^{-4}$ mol dm^{-3}. The initial heat I_h has decreased with increasing [Triton X-100]. An appreciable I_h was obtained even when the oscillation stopped. The results are presented in Table 2. In Figures 5A and 6A, the dependence of n and ΔH_{osc} on [TX-100] is depicted. The nature of dependence of both is found to be exponential. There was a sharp initial decrease at low [surfactant].

TABLE 2: Effect of Triton X-100 Addition at 303 K[a]

[TX-100]/ mol dm^{-3}	n	I_h/J	ΔH_{osc}[b]/ J mol^{-1}
0	11	179	312
10^{-8}	13	198	411
10^{-7}	12	173	325
10^{-6}	10	190	289
10^{-5}	9	190	257
10^{-4}	6	113	209
2 × 10^{-4} [c]	2	120	84
4 × 10^{-4} [c]	–	100	–

[a] [O A] = 0.0625 mol dm^{-3}; [H$_2$SO$_4$] = 1.25 equiv dm^{-3}; [KBrO$_3$] = 0.14 mol dm^{-3}; [MnSO$_4$] = 0.0013 mol dm^{-3}; [acetone] = 1.0 mol dm^{-3}. [b] ΔH_{osc} is expressed per mole of KBrO$_3$. [c] Concentrated ≥ cmc.

TABLE 3: Effects of Tween 20, 40, and 60 Addition at 303 K[a]

[surfactant]/ mol dm^{-3}	n	I_h/J	ΔH_{osc}[b]/J mol^{-1}
	Tween 20		
0	11	179	312
10^{-8}	12	205	379
10^{-7}	10	197	259
10^{-6}	8	184	236
10^{-5}	7	178	201
10^{-4} [c]	6	162	175
2 × 10^{-4} [c]	3	88	93
4 × 10^{-4} [c]	1	70	31
5 × 10^{-4} [c]	–	52	–
	Tween 40		
0	11	179	312
10^{-8}	9	202	244
10^{-7}	8	160	210
10^{-6}	5	158	140
10^{-5}	4	145	118
2 × 10^{-5} [c]	2	131	57
5 × 10^{-5} [c]	–	120	–
	Tween 60		
0	11	179	312
10^{-8}	8	167	226
10^{-7}	7	124	200
10^{-6}	4	125	107
10^{-5} [b]	1	64	30
2 × 10^{-5} [b]	–	43	–

[a] [O A] = 0.0625 mol dm^{-3}; [H$_2$SO$_4$] = 1.25 equiv dm^{-3}; [KBrO$_3$] = 0.14 mol dm^{-3}; [MnSO$_4$] = 0.0013 mol dm^{-3}; [acetone] = 1.0 mol dm^{-3}. [b] ΔH_{osc} is expressed per mole of KBrO$_3$. [c] Concentrated ≥ cmc.

For the surfactants in the Tween series (Tween 20, 40 ,and 60), the n, ΔH_{osc}, and I_h values decrease with increasing [surfactant] in each case. For Tween 20, oscillation ceases at 5 × 10^{-4} mol dm^{-3}. For Tween 40 and Tween 60, significant inhibition starts from a very low concentration of 10^{-8} mol dm^{-3}. The values of n, ΔH_{osc} and I_h are much lower than those without Tweens. Afterward, the decrease is gradual, and finally, the threshold concentrations of Tween 40 and 60, above which $n = 0$, are 2 × 10^{-5} and 10^{-5} mol dm^{-3} respectively. The inhibitory effects of these three Tweens are profiled in Figures 5B and 6B, and the data are given in Table 3. It is seen that Tween 20 has the minimum inhibitory effect on the studied B−Z oscillatory reaction. The order of inhibition is Tween 20 < Tween 40 < Tween 60. The hydrophilic headgroups of the Tweens are the same; they differ with respect to the length of the hydrophobic tail (Figure 1). As the tail lengthens, the inhibition increases. An increase in the number of carbon atoms in the molecule from four to six made a significant difference in the activity.

The inhibitory effects of Brijs (Brij 56, 58, and 76) on n, ΔH_{osc}, and I_h are listed in Table 4. Brij 56 and Brij 58 show

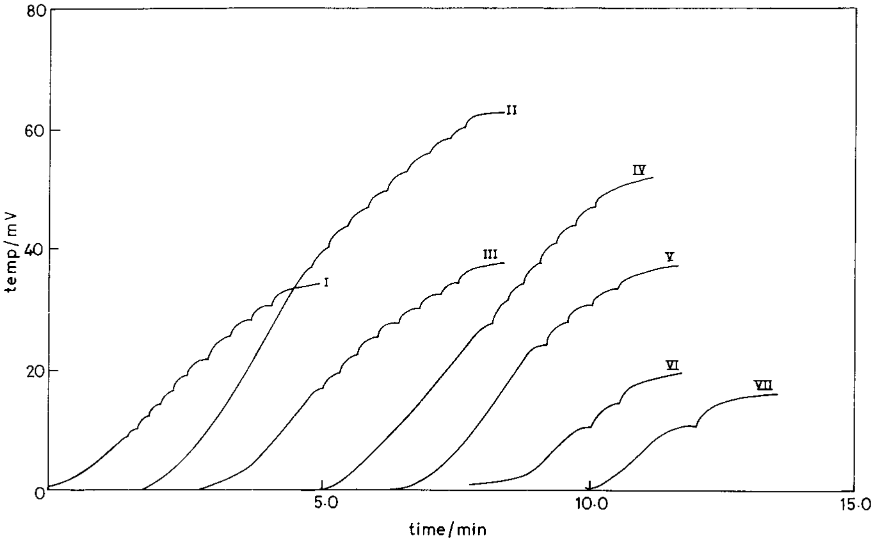

Figure 4. Inhibitory effect of surfactants on the oscillatory process of bromate/oxalic acid/H_2SO_4/$MnSO_4$ at equal concentration of 10 μM at 303 K. [O A] = 0.0625 mol dm^{-3}; [H_2SO_4] = 1.25 equiv dm^{-3}; [$KBrO_3$] = 0.14 mol dm^{-3}; [$MnSO_4$] = 0.0013 mol dm^{-3}; [acetone] = 1.0 mol dm^{-3}. I, Brij 56 (>cmc); II, TX-100; III, Brij 58 (> cmc); IV, Tween 20; V, Tween 40; VI, Brij 76(>cmc); VII, Tween 60.

TABLE 4: Effects of Brij 56, 58, and 76 Addition at 303 K[a]

[surfactant]/ mol dm^{-3}	n	I_h/J	$\Delta H_{osc}{}^b$/J mol^{-1}
		Brij 56	
0	11	179	312
10^{-8}	13	24	362
10^{-7}	12	19	286
10^{-6}	10	18	136
10^{-5c}	10	12	109
10^{-4c}	9	27	94
2×10^{-4c}	6	16	76
4×10^{-4c}	3	15	36
5×10^{-4c}	–	10	–
		Brij 58	
0	11	179	312
10^{-8}	12	15	161
10^{-7}	10	33	141
10^{-6}	9	21	114
10^{-5c}	8	25	94
10^{-4c}	6	18	69
2×10^{-4c}	4	33	51
4×10^{-4c}	2	25	17
5×10^{-4c}	–	28	–
		Brij 76	
0	11	179	312
10^{-8}	8	31	181
10^{-7}	6	29	150
10^{-6}	5	35	121
10^{-5c}	2	15	66
10^{-4c}	–	27	–

[a] [O A] = 0.0625 mol dm^{-3}; [H_2SO_4] = 1.25 equiv dm^{-3}; [$KBrO_3$] = 0.14 mol dm^{-3}; [$MnSO_4$] = 0.0013 mol dm^{-3}; [acetone] = 1.0 mol dm^{-3}. [b] ΔH_{osc} is expressed per mole of $KBrO_3$. [c] Concentrated > cmc.

more or less the same inhibitory behaviors on the studied B−Z oscillatory process. Both n and ΔH_{osc} exhibit gradual decrease with increasing [Brij 56] and [Brij 58] and end up with the same threshold value of 4×10^{-4} mol dm^{-3}. The inhibitory effect of Brij 76 is, on the other hand, significantly different from that of Brij 56 and Brij 58. On addition of 10^{-8} mol dm^{-3} of Brij 76, n decreases markedly, and the oscillation totally stops at 10^{-4} mol dm^{-3} (Figure 5C). The ΔH_{osc} also parallels the trend of n. The I_h value also gets significantly reduced in the presence of the Brijs, but the trend of decline is not regular. The release of I_h has also been observed under the condition of no oscillation. The inhibition by Brijs follow the order Brij 76 > Brij 58 ≈ Brij 56. Structurally, Brij 56 and Brij 58 differ in the number of polyoxyethylene groups on their heads, and their tails contain equal number of carbon atoms. The difference in their headgroups does not have a say on their inhibitory behaviors. In Brij 76, the carbon chain is longer by 2 units, and this produces inhibition on the B−Z oscillatory reaction to a much greater extent.

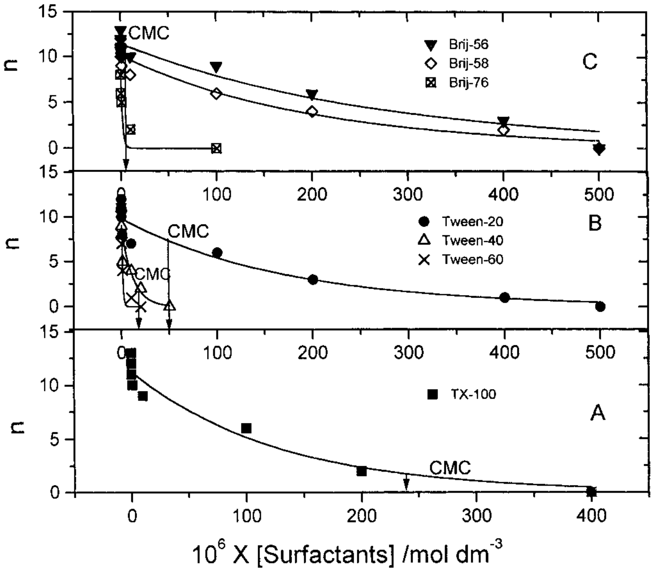

Figure 5. Number of oscillations (n) as a function of [surfactant] at 303 K. [O A] = 0.0625 mol dm^{-3}; [H_2SO_4] = 1.25 equiv dm^{-3}; [$KBrO_3$] = 0.14 mol dm^{-3}; [$MnSO_4$] = 0.0013 mol dm^{-3}; [acetone] = 1.0 mol dm^{-3}. A, TX-100; B, Tweens; C, Brijs.

The correlation between ΔH_{osc} and n for the nonionic surfactants used in the present study is exemplified in Figure 7. There are linear variations in all the cases, and the slopes are also close expecting Brij 56 and Brij 58. The straight lines of the plots pass through the origin, which is expected. The slopes signify that enthalpy changes per oscillation are 29.5 ± 0.94, 28.78 ± 0.57, 23.9 ± 1.11, 25.67 ± 1.73, and 12.29 ± 0.30 J mol^{-1} osc^{-1} for TX-100, Tween (20, 40, and 60), Brij 76, n-heptanol, and Brij 56 and 58, respectively. In this comparison, the results of n-heptanol is included for reasons to be subse-

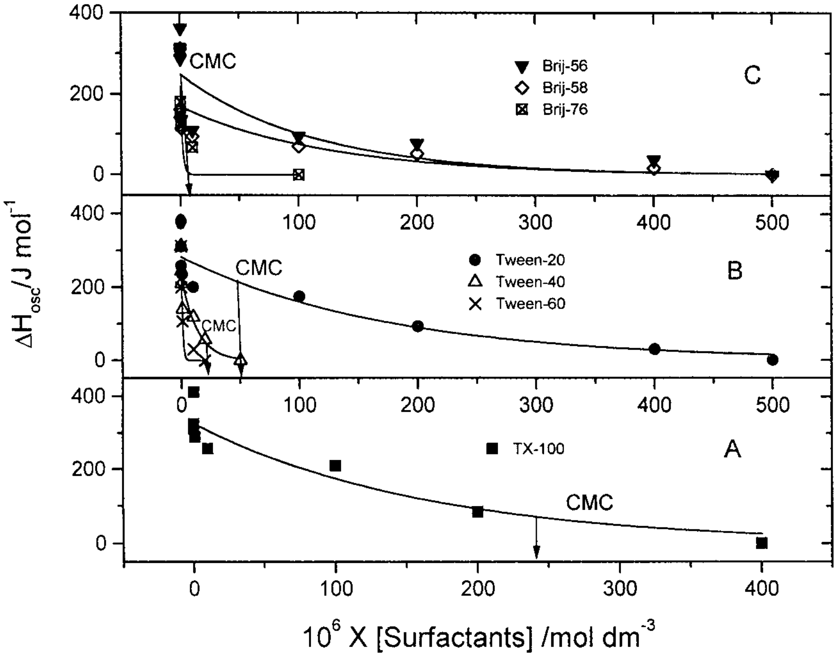

Figure 6. Enthalpy of oscillations (ΔH_{osc}/J mol^{-1}) as a function of [surfactant] at 303 K. [O A] = 0.0625 mol dm^{-3}; [H_2SO_4] = 1.25 equiv dm^{-3}; [$KBrO_3$] = 0.14 mol dm^{-3}; [$MnSO_4$] = 0.0013 mol dm^{-3}; [acetone] = 1.0 mol dm^{-3}. A, TX-100; B, Tweens; C, Brijs.

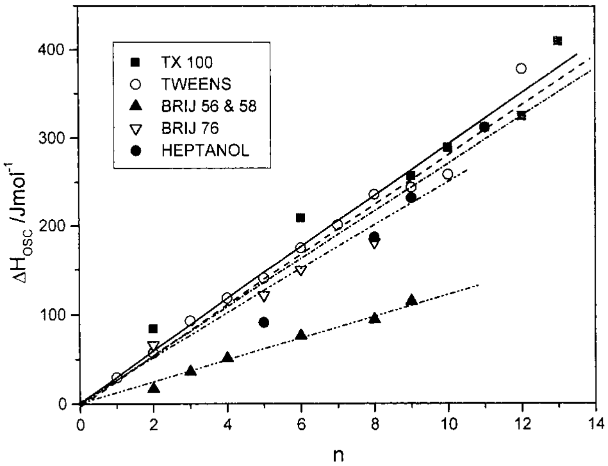

Figure 7. Correlation between ΔH_{osc} and n of the bromate/oxalic acid/H_2SO_4/$MnSO_4$ B−Z reaction in the presence of nonionic surfactants and n-heptanol at 303 K. [O A] = 0.0625 mol dm^{-3}; [H_2SO_4] = 1.25 equiv dm^{-3}; [$KBrO_3$] = 0.14 mol dm^{-3}; [$MnSO_4$] = 0.0013 mol dm^{-3}; [acetone] = 1.0 mol dm^{-3}.

quently discussed. It is observed that Brij 56 and 58 behave differently than the others. A possible explanation for this difference is presently not at hand.

In Figure 8, the dependence of n and ΔH_{osc} on the number of carbon atoms in the hydrophobic tails of the amphiphiles is presented. The dependence has been found to be exponential in nature, with a deviation in the case of n-heptanol. This suggests the functional difference of Brijs and Tweens having large hydrophilic head groups from n-heptanol having a small head group of −OH.

It has been reported earlier that the Brijs and Triton X-100 prevent oscillation of the B−Z system of bromate/malonic acid/$MnSO_4$/H_2SO_4/ferroin.[29] The concentrations of the nonionic surfactants required to inhibit the oscillatory reaction have not been mentioned in the work. We have herein found that low concentrations of the nonionic surfactants can stop the process of oscillation. This is a striking observation. To understand the role of the nonpolar tail on the oscillatory process, we have used n-heptanol, which has a small hydrophilic head; it has also shown a significant inhibitory effect but does not follow the trend of the surfactants. The large hydrophilic headgroups of different types in the studied surfactant classes are found to have different effects, making the dependence nonlinear. The small and entirely different headgroup of n-heptanol makes its effect markedly different. Thus, n-heptanol is not following the trend of the nonionic surfactants used in the present study (Figure 8).

Cavasino et al.[32] have considered nonelectrostatic interaction of cationic and anionic surfactants with the substrates and the intermediates to be the reason for inhibition of the Ce(IV)-catalyzed B−Z reaction with methyl- and ethyl-substituted malonic acids. The nonionic surfactants studied here can also undergo similar nonelectrostatic interaction to inhibit the oscillatory process. A detailed investigation with different nonionic amphiphiles with varied tail and headgroups is thus wanted for further understanding. This is contemplated to be taken up in future. A tentative rationalization of the observations may, however, be forwarded. The B−Z oscillatory system of bromate−oxalic acid−H_2SO_4 is guided by the following overall stoichiometric equation:

$$2H^+ + 2BrO_3^- + 5(COOH)_2 \rightarrow 10CO_2 + Br_2 + 6H_2O$$

It has been shown that CO_2 cannot affect the oscillatory process, but the process is retarded by Br_2, and the oscillations become much more prominent in the presence of a Br_2 scrubber.[33,35] The removal of Br_2 by an inert carrier gas has been also shown to produce oscillations in the system.[33] So Br_2 is the oscillation-controlling species of the system. The role of acetone as the Br_2 scavenger has also been studied in details.[35] We have found that decreasing concentration of acetone produces decreasing oscillations, and in the absence of acetone, the oscillation virtually stops.[39]

The nonionic surfactants used in this study are considered to undergo nonpolar interactions with acetone and thus inhibit its scavenging effect and eventually inhibit the oscillatory process.

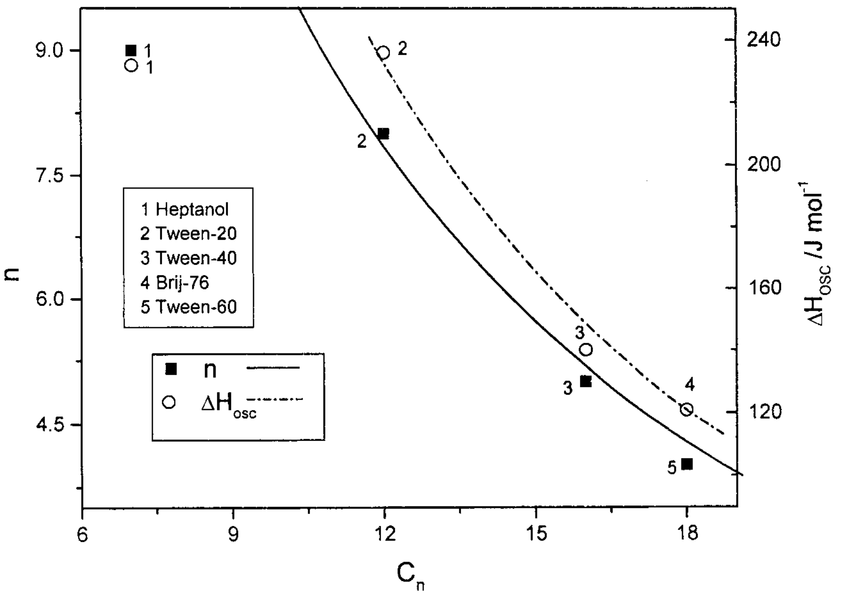

Figure 8. Dependence of *n* and ΔH_{osc} on the carbon number of the nonpolar hydrophobic tails of the studied surfactants of the bromate/oxalic acid/H_2SO_4/$MnSO_4$ B−Z system at 303 K. [O A] = 0.0625 mol dm^{-3}; [H_2SO_4] = 1.25 equiv dm^{-3}; [$KBrO_3$] = 0.14 mol dm^{-3}; [$MnSO_4$] = 0.0013 mol dm^{-3}; [acetone] = 1.0 mol dm^{-3}.

The surfactants can act as inhibitors at concentrations much below their cmc's, but the results in Tables 2−4 and Figures 5 and 6 show that they are much effective at concentrations >cmc. The acetone may get partitioned in the nonpolar interior of the micelles and are thus removed from the sphere of action making scope for the unscavenged Br_2 to efficiently inhibit the oscillatory process.

Effect of Surfactants on the Damping of the Oscillation. The presently studied B−Z reaction is a representative of damped oscillatory systems;[14,15,41] the oscillation of temperature has declines with time and diminishing amplitude. The process is sustained for 15−20 min. It has been reported by us[14,15] and others[41] that stirring has a prominent say on the course of an oscillatory reaction; the number of oscillation gets reduced with an increasing rate of stirring. In our calorimetric experiments, the stirring rate is high, and lower numbers of oscillations are observed. The oscillatory reaction studied by calorimetry has thus shown lower duration time. Lower duration with lower number of oscillation has also been observed by calorimetry compared to potentiometry for the system, BrO_3^-/Ce^{4+}/acetylacetone/H_2SO_4 by Janjic et al.[42] B−Z reactions having lower duration times and damped oscillations studied by potentiometry have been also reported in the literature.[43,44] In this study, we have examined the damped oscillatory process in terms of the damping coefficient according to the relation.[45]

$$\ln \frac{A(t)}{A(t+1)} = \sigma T$$

where $A(t)$ and $A(t+1)$ are the amplitudes of two successive oscillations, T is the time period, and σ is the damping coefficient.

The values of σ calculated from the studied system are presented in Table 6. It is observed that for each surfactant, σ decreases with increasing concentration. At comparable [surfactant], σ follows the order TX-100 > Brijs > Tweens. Like the reduction of oscillation, the damping coefficients are also much reduced at [surfactant] ≥ cmc.

TABLE 5: Effect of *n*-Heptanol Addition at 303 K

[*n*-heptanol]/mol dm^{-3}	*n*	I_h/J	$\Delta H_{osc}{}^a$/Jmol^{-1}
0	11	179	312
10^{-6}	9	193	232
10^{-5}	8	165	187
10^{-4}	5	145	91
2×10^{-4}	2	36	43
4×10^{-4}	−	30	−

[a] ΔH_{osc} is expressed per mole of $KBrO_3$; [O A] = 0.0625 mol dm^{-3}; [H_2SO_4] = 1.25 equiv dm^{-3}; [$KBrO_3$] = 0.14 mol dm^{-3}; [$MnSO_4$] = 0.0013 mol dm^{-3}; [acetone] = 1.0 mol dm^{-3}.

TABLE 6: Effect of Surfactants on the Damping Coefficients of the Oscillatory System at 303 K[a]

[surfactant]/ mol dm^{-3}	$\sigma \times 10^3$/min^{-1}	[surfactant]/ mol dm^{-3}	$\sigma \times 10^3$/ min^{-1}
TX 100		Brij 56	
10^{-7}	122	10^{-8}	91
10^{-6}	107	10^{-6}	107
10^{-5}	102	10^{-4b}	90
10^{-4c}	36	2×10^{-4b}	74
Tween 20		Brij 58	
10^{-7}	136	10^{-7}	130
10^{-6}	80	10^{-6}	96
10^{-5}	76	10^{-5b}	71
10^{-4b}	62	2×10^{-4b}	33
Tween 40		Brij 76	
10^{-8}	100	10^{-8}	155
10^{-7}	51	10^{-7}	126
10^{-6}	40	10^{-6c}	93
10^{-5c}	32		
Tween 60			
10^{-8}	65		
10^{-7}	53		
10^{-6}	37		

[a] Without surfactants, $\sigma \times 10^3$ = 67 min^{-1}. [O A] = 0.0625 mol dm^{-3}; [H_2SO_4] = 1.25 equiv dm^{-3}; [$KBrO_3$] = 0.14 mol dm^{-3}; [$MnSO_4$] = 0.0013 mol dm^{-3}; [acetone] = 1.0 mol dm^{-3}. [b] Concentration > cmc. [c] Concentration ≈ cmc.

Conclusions

The nonionic surfactants TX-100, Tween 20, 40, and 60, and Brij 56, 58, and 76 can have large inhibitory effects on the B−Z oscillatory reaction. Complete inhibition is observed at very low [surfactant]. The inhibitory process is directly dependent on the length of the hydrophobic tail of the surfactant. The role of the hydrophilic head in this regard is not straightforward. The nonionic surfactants inhibit the process by undergoing nonpolar interaction with acetone. The amphiphile *n*-heptanol with a small hydrophilic headgroup has also shown significant inhibitory effect. The damping effects of the surfactants on the oscillatory process follows the order TX-100 > Brijs > Tweens.

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