

The Effect of Anionic, Cationic and Nonionic Surfactants on the Uncatalyzed Bromate Oscillator

Ol'ga Grančičová, Anna Olexová, and Tomáš Zacher

Department of Physical and Theoretical Chemistry, Comenius University, Faculty of Natural Science, Mlynská dolina, 842 15 Bratislava, Slovakia

Reprint requests to O. G.; E-mail: grancicova@fns.uniba.sk

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The response of an uncatalyzed bromate oscillator with phenol as substrate to the increasing concentrations of cationic (CTAN), anionic (SDS) and nonionic surfactants (Brij-30 and Triton X-100) was monitored at $(25 \pm 0.1)^\circ\text{C}$ under stirred batch conditions. Addition of the surfactants influenced the oscillatory parameters: a slight increase of the induction period of the first series of oscillations, a significant increase of the induction period of the second series of oscillations and a gradual decrease of the oscillation numbers of both series until complete disappearance at a certain surfactant concentration. The changes in the oscillatory parameters have been ascribed to solubilization of phenol and of bromination products in the micelles, to inhibition of bromination of the aromatic substrate due to bromine solubilization, and to the catalytic effect of the charged micelle surface.

Key words: Bromate Oscillator; Micelles; Sequential Oscillations.

1. Introduction

Previous work [1,2] has shown that systems containing phenol and bromate in strongly acidic solutions behave as typical uncatalyzed bromate oscillators (UBOs). In a limited range of initial concentrations of reactants and the acid, only one series of a low number of oscillations has been observed in closed batch reactors. The overall reaction is composed of parallel running oxidation and bromination of the organic substrate resulting in a variety of products. The analysis [3,4] of the reaction mixture before, during and after the first oscillation identified the intermediates and products. Some intermediates e. g. mono- and dibromophenols, were found [3] to oscillate under the same experimental conditions as phenol. Orbán et al. [2] have suggested a skeleton mechanism for the description of the oscillation in an UBO. The important steps for the production of HBrO_2 , HOBr , Br_2 and the radical BrO_2^\bullet are identical with the processes in catalyzed bromate oscillators. According to [3], during a pre-oscillatory period, bromide ions are formed during the bromination of phenol, but the major source of bromide is the oxidation of phenols and bromophenols to quinones. With the accumulation of quinone, the concentration of bromide increases to a critical value and the system begins to oscillate. When the forma-

tion of quinones finishes, the oscillations fade. The possible intermediate of the oxidation is a relatively stable semiquinone radical (unbrominated or brominated), which may disproportionate to quinone and dihydroxybenzene and may play the role of a catalyst.

Later, a rather unexpected observation has been made, as reported in [5]. The system bromate-phenol-sulfuric acid exhibits an astonishingly rich dynamic behaviour: After a short induction period, the system switches to a series of five oscillations, next a nonoscillatory period follows, and then the second series of numerous oscillations appears. The oscillations are very sensitive to stirring. Their number has been found to decrease with increasing stirring rate. For the explanation of the second series of oscillations the existence of two subsystems, (phenol + B) and (an oxidation/bromination intermediate or product + B), coupled through the common reactant B (bromate) has been assumed [5]. The product of the first oscillatory subsystem may serve as substrate for the second one. The simple model describes quite accurately [6] the dynamic behaviour of the system, but the origin of the redox potential oscillations is still to be explained.

The dynamics of the oscillation reaction can be controlled by performing the reaction in self-organized surfactant systems, such as micelles. Recent studies [7–10] of Belousov-Zhabotinsky (BZ) reactions

proved the micellar effects on the induction period, oscillation time period and amplitudes or even on initiating oscillations.

In an effort to elucidate the complex oscillatory behaviour of the system, we decided to investigate the effect of cationic, anionic and nonionic surfactants on the uncatalyzed bromate-phenol oscillator. Amphiphilic surfactant molecules spontaneously assemble [11] into micelles at the critical micellization concentration (CMC). In fact, according to the detailed study [12] of amphiphilic aggregation three concentrations are to be distinguished in the process: c_1 , at which some metastable aggregates appear; c_2 , at which a significant amount of metastable aggregates forms, and c_3 , at which the aggregates become stable. The concentration c_3 corresponds to the CMC. The number of surfactant molecules forming the micelle is defined as aggregation number. The micelles of surfactants used in this work have well-defined aggregation numbers that may increase to a lesser extent with increasing concentration of surfactant and of added electrolytes, but considerably with the amount of the solubilize. The micelles can significantly affect the reaction, because firstly the ionic reactants and intermediates can interact with oppositely charged micelle surfaces, secondly, depending on the size, shape and polarity of the molecules, the reactants may be solubilized in different regions of the aggregate structure: in the hydrophobic core of the micelle, between hydrophobic chains (so-called palisade layer), or at the hydrophilic shell of polar heads. The distribution of reactants between the aqueous phase and the micellar pseudophase can result in micellar retarding or accelerating effects [13].

2. Experimental

Sodium bromate, sulfuric acid and phenol were of commercial quality (Merck) and were used without further purification. Sodium dodecyl sulfate (SDS) (Fluka) was recrystallized from ethanol, cetyl trimethyl ammonium nitrate (CTAN) was prepared from the corresponding bromide (Aldrich) as described in [14]. Polyethylene glycol *p*-(1,1,3,3-tetramethylbutyl)-phenyl ether (Triton X-100) (Fluka) and polyethylene glycol dodecyl ether (Brij-30) (Aldrich) were used without purification. The surfactants differ not only in charge but also in the length of hydrophobic chains (Fig. 1). Redistilled water was used to prepare all solutions. The stock solution of sulfuric acid was standardized by acid-base titration.

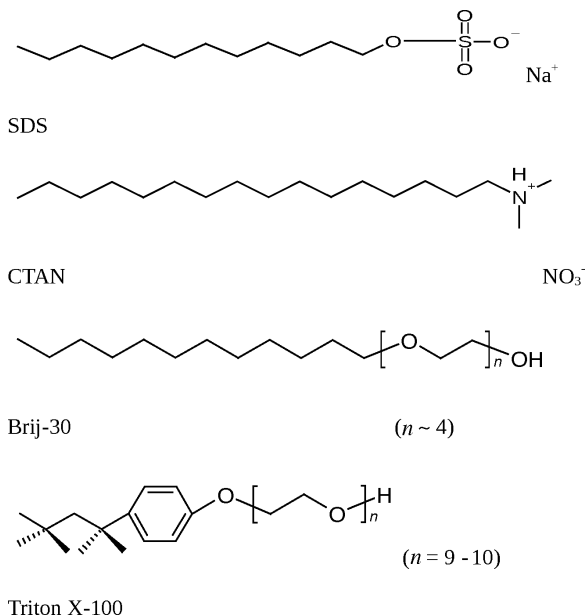


Fig. 1. Chemical structures of surfactants used in this work.

The measurements were carried out in a thermostated cylindrical glass reaction vessel (diameter 3.5 cm, height 7.5 cm) closed with a rubber stopper, through which the commercial platinum electrode and the reference $\text{Hg}/\text{Hg}_2\text{SO}_4$ electrode were inserted into the solution. The volume of the reaction mixture was always 20 cm^3 . The appropriate aliquots of stock solutions of reactants for oscillating mixtures were pipetted into water in the vessel in the following order: sulfuric acid, surfactant, phenol and then, after short stirring and after attainment of the desired temperature $[(25 \pm 0.1)^\circ\text{C}]$, the bromate was injected. The initial reactant concentrations were in all experiments as follows: $[\text{phenol}] = 4 \cdot 10^{-3} \text{ mol dm}^{-3}$, $[\text{BrO}_3^-] = 2.5 \cdot 10^{-2} \text{ mol dm}^{-3}$, $[\text{H}_2\text{SO}_4] = 1.5 \text{ mol dm}^{-3}$. The solution was stirred magnetically with a Teflon-coated stirrer (length 2.0 cm, diameter 0.8 cm). The potentiometric measurements have been carried out under constantly stirred (50 rpm) batch conditions using a digital multimeter METEX M-4650 CR connected to a PC.

As the CMC of ionic surfactants is strongly affected by the presence of added electrolytes, the experimental CMC of CTAN and SDS has been determined by surface tension measurements based on the maximum bubble pressure method. The CMC values of SDS and CTAN in the presence of $1.5 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$ and $4 \cdot 10^{-3} \text{ mol dm}^{-3}$ phenol are $3.1 \cdot 10^{-4} \text{ mol dm}^{-3}$ and $1.8 \cdot 10^{-5} \text{ mol dm}^{-3}$, respectively. The CMC of Brij-

30 and Triton X-100, not affected by the presence of $1.5 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$ and $4 \cdot 10^{-3} \text{ mol dm}^{-3}$ phenol, are $2.3 \cdot 10^{-5} \text{ mol dm}^{-3}$ and $3 \cdot 10^{-4} \text{ mol dm}^{-3}$, respectively. The CMC obtained in aqueous solution agreed with the literature [14, 15].

UV-VIS spectra of Brij-30 and Triton X-100 in the solutions of $1.5 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$ and $2.5 \cdot 10^{-2} \text{ mol dm}^{-3} \text{ NaBrO}_3$ over the whole concentration interval of Brij-30 as well as Triton X-100 used in our experiments and over an hour interval were recorded on a Perkin Elmer spectrometer.

3. Results and Discussion

Having been conscious of the possibility of reacting acidic bromate with polyethylene glycol chains of non-ionic surfactants [16], we tested the stability of Brij-30 and Triton X-100 in solutions of $1.5 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$ and $2.5 \cdot 10^{-2} \text{ mol dm}^{-3} \text{ NaBrO}_3$ over the whole concentration interval of Brij-30 as well as Triton X-100 used in our experiments, i. e. at the lowest concentration where no micelles existed, at the concentrations where the formation of micelles begun, as well as at concentrations higher than the CMC. There were no changes in the UV-VIS spectra during one hour. No peaks corresponding to the bromide ions, bromine or tribromide appeared in the spectra. These results are consistent with the data on direct oxidation of ethers with sodium bromate [17]. For the oxidative cleavage of ethers by sodium bromate at room temperature two reagents are needed: a reducing one (e. g. HBr) in catalytic amount that can initiate the reaction with the bromate to form bromine, and an oxidizing one such as a Ce(IV) salt also only in catalytic amount. Bromine is the main active oxidant, while bromate plays a role in reoxidizing the reduced form of this catalyst and as bromine supplier. A dramatic decrease in oxidation was observed when some bromine scavenger was present.

Contrary to the works on catalyzed BZ reactions, we studied the effect of surfactants on the uncatalyzed bromate oscillator; so in our reacting system one of the two important reagents was missing. Moreover phenol could take over the role of the bromine scavenger.

Figure 2A illustrates the effect of increasing the surfactant concentration (as an example cationic CTAN was chosen) on the plots of potential of a Pt electrode vs. time for the system BrO_3^- -phenol- H_2SO_4 at a stirring rate of 50 rpm. Figure 2B shows the details of the first series of oscillations for various concentrations of

Table 1. Dependence of the oscillatory parameters on the surfactant concentration: NO1 and NO2, number of the first and second oscillations; IP1 and IP2, induction periods in min; DO1 and DO2, duration of the first and second oscillations in min.

C, mol dm ⁻³	NO1	IP1	DO1	NO2	IP2	DO2
0	4	3.3	4.8	27	123	99
CTAN:						
(1–8)·10 ⁻⁵	4→1	3.3→5.5	4.7→1.2	26→14	~124	97→63
(9–200)·10 ⁻⁵	0			14→4	126→142	70→13
300·10 ⁻⁵	0			0		
SDS:						
(1–8)·10 ⁻⁴	4→1	3.1→4.8	4.8→1.3	~26	123→128	~100
(9–110)·10 ⁻⁴	0			~26	127→172	100→85
200·10 ⁻⁴	0			0		
Brij-30:						
(1–9.5)·10 ⁻⁵	4→1	3.2→4.8	4.8→1.2	28→22	119→135	98→65
(10–14)·10 ⁻⁵	0			22→17	141→153	52→40
20·10 ⁻⁵	0			0		
Triton X-100:						
(1–8)·10 ⁻⁵	4→1	3.1→5.0	4.7→1.1	33→21	119→149	115→61
9·10 ⁻⁵	0			20	161	52
10·10 ⁻⁵	0			0		

CTAN. The values of oscillatory parameters are listed in Table 1. The arrow indicates the continuous change in the number of oscillations, induction periods as well as duration of oscillations with increasing surfactant concentration. The data for each surfactant are separated into three groups: The first one corresponds to the concentrations where the first oscillations slowly vanish, the second one to the concentrations where the micelle formation was complete as resulting from the surface tension-concentration plots; at the last surfactant concentration the oscillation disappeared. Figure 3 shows the effect of increasing surfactant concentration (as an example nonionic Triton X-100 was chosen) on the number of first and second oscillations, induction periods and duration of first and second oscillations.

As can be seen in Table 1, the first induction period (IP1) only slightly increases on increasing the surfactant concentration (about 108 s): Initially there is practically no change in the IP1, but with the initializing of micelle formation it begins slowly to increase. A greater increase could not be observed, because as soon as the micelle formation was complete, the first series of oscillations had extinguished. At lower surfactant concentration, the oscillation number of the first series is constant; it comes to diminishing the number of oscillations at the moment when the micelles begin to form in the solution. The increase in the IP1 and the decrease in the oscillation number may be related to progressing solubilization of phenol in the mi-

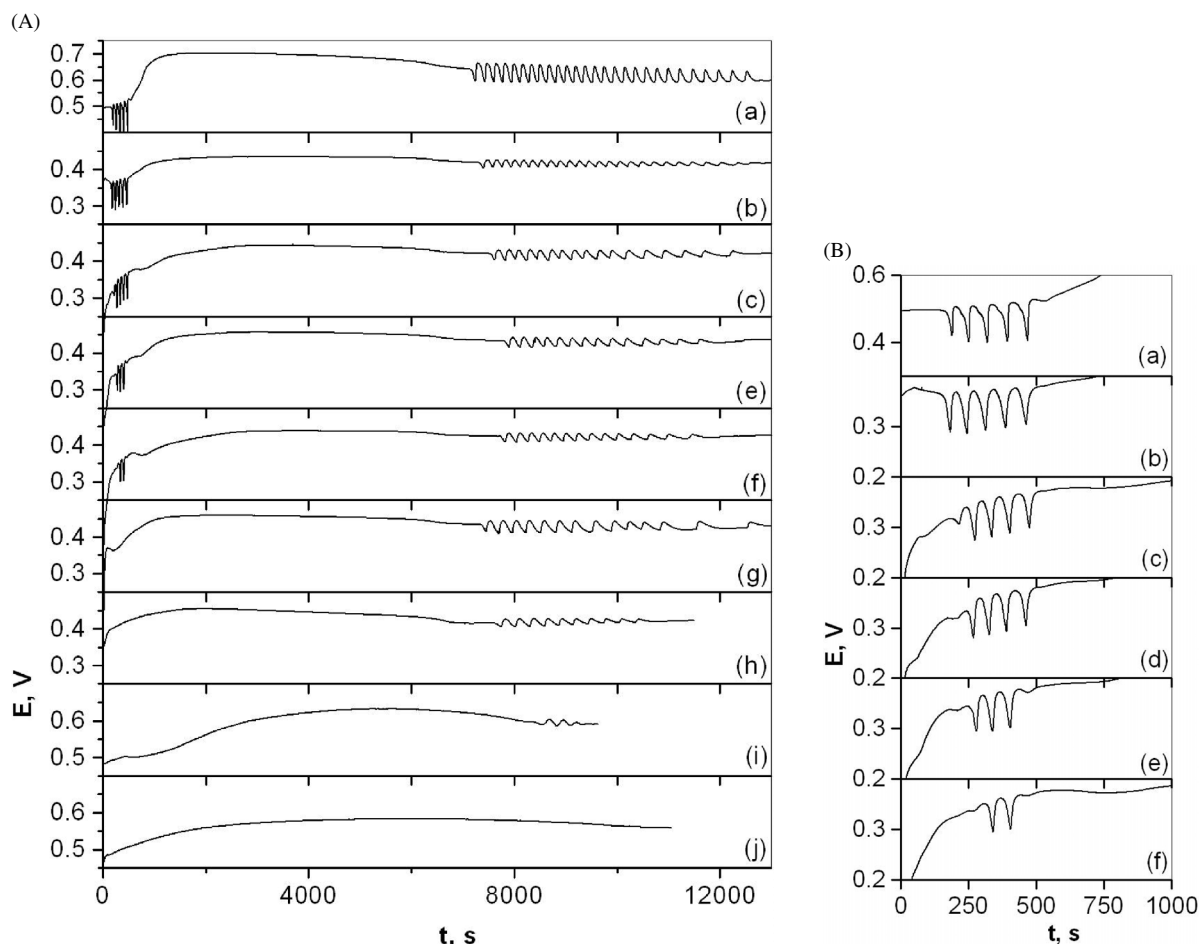


Fig. 2. (A) Time dependence of the redox potential for various concentrations of CTAN: (a) 0; (b) 0.00001; (c) 0.00005; (e) 0.00007; (f) 0.00008; (g) 0.00009; (h) 0.0005; (i) 0.002; (j) 0.004 mol dm⁻³. System: [phenol] = 0.004 mol dm⁻³; [BrO₃⁻] = 0.025 mol dm⁻³; [H₂SO₄] = 1.5 mol dm⁻³; *T* = 298.15 K; 50 rpm. (B) Detail of the first series of oscillations for various concentrations of CTAN: (a) 0; (b) 0.00001; (c) 0.00005; (d) 0.00006; (e) 0.00007; (f) 0.00008 mol dm⁻³.

celles. At first phenol remains to be partitioned between the micellar and aqueous phases. Bromination of phenol can further proceed in micelles, but with some steric restrictions as found for the chlorination of phenol solubilized in cationic and anionic micelles [18]. Consequently the phenol concentration in the aqueous phase decreases under a critical amount at which the system still oscillates. Another reason of increasing the IP1 may be the solubilization of bromine, the most nonpolar species in the system, that prefers the hydrophobic core of the micelle. The bromine solubilization must result in a decrease of the concentration of bromide ions (i. e. the key inhibiting species in the oscillatory system) in the aqueous phase through the

reactions



The oscillation number of the second series gradually decreases on increasing the cationic and nonionic surfactant concentration, until the oscillations completely vanish at a certain concentration. In the case of anionic SDS the number of sequential oscillations is practically untouched with the increasing surfactant concentration, but on reaching a critical value the oscillations suddenly disappear as well. The concentration,

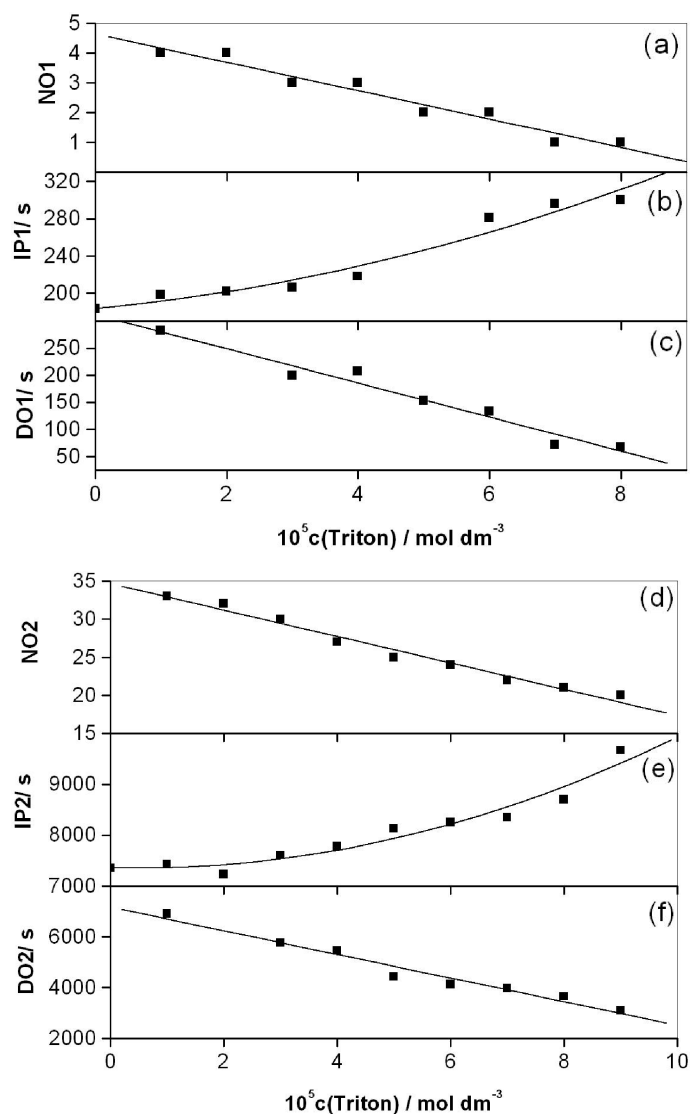


Fig. 3. Dependence of the oscillatory parameters on the surfactant concentrations: (a) number of oscillations NO1; (b) induction period IP1; (c) duration of the first series of oscillations DO1; (d) number of oscillations NO2; (e) induction period IP2; (f) duration of the second series of oscillations DO2.

at which it comes to complete extinction of the sequential oscillations, is related to the solubilization capacity that can be reached for the surfactant. The capacity of micellar systems, expressed as moles of solutes solubilized per mole of surfactant, generally follows the order: nonionics > cationics > anionics for the amphiphiles with the same hydrophobic moiety. The solubilization capacity is larger for a surfactant with a longer alkyl chain. The products of phenol bromination – mono-, di- and tribromophenols – are solubilized inside ionic and nonionic surfactant micelles. The octanol-water partition coefficient used as a reference

to classify the hydrophobic character of chlorophenols showed [19] that an increase in the number of chlorine atoms in the benzene ring increased the hydrophobicity of molecules. The water-micelle distribution coefficients for chlorophenols rank in the same order. Products of oxidation – 1,2- and 1,4-benzoquinone as well as 1,2- and 1,4-dihydroxybenzene – do not solubilize inside the micelles due to their hydrophilic nature as proved [20] by the partition coefficients of 1,4-benzoquinone and 1,4-dihydroxybenzene. The bromination of this oxidation product leads to an increase of hydrophobicity of molecules and hence to progressing

solubilization of bromoderivates. In fact the concentration needed for the extinction of the sequential oscillations was for:

a) nonionic Triton X-100 almost equal to the CMC. It may be related to the aggregation number [21], which is high for this surfactant (at 298 K, $N_{\text{agg}} = 86$). With respect to the structure of Triton X-100, there exists a high probability of the phenol molecule to penetrate the benzene ring in the hydrophobic part of the amphiphilic molecule of Triton X-100 and its interaction can contribute to the extraordinary stability of this kind of micelle;

b) nonionic Brij-30 equal to tenfold of the CMC; the aggregation number is only about half of that of Triton X-100;

c) cationic CTAN almost equal to the phenol concentration;

d) anionic SDS a concentration about six times higher than that of phenol.

This agrees with the determination [22] of the micelle-water distribution coefficients for phenol, that are higher in CTAB than in SDS. It has been found that the surfactant concentration equal to tenfold of the CMC suffices for almost 100% solubilization of phenol from aqueous micellar solutions of CTAB and SDS when the phenol concentration is in the range $(1.1 - 7.4) \cdot 10^{-4} \text{ mol dm}^{-3}$.

As it was not possible to determine the nonoscillatory period, i.e. the time between the last oscillation of the first series and the first oscillation of the second series, we could evaluate the time of the first oscillation of the second series from the very beginning of the reaction. This induction period IP2 has changed much more significantly than the IP1 on increasing the surfactant concentration. Again this can be explained by the inhibition micellar effect on the bromation of oxidation products, and therefore on the formation of some of bromoderivates at the concentration necessary for the initiation of sequential oscillations. The decrease in the concentration of bromide ions as a result of bromine solubilization in micelles must affect the increase in the IP2. The reaction involves ions and neutral molecules, so it can be expected that anionic, cationic and nonionic surfactants will induce different effects on the reaction. Surprisingly, the only difference in the response to the increasing concentration of various surfactants is greater increase in the IP2 in a solution of negatively charged micelles of SDS than of positively charged micelles of CTAN. It is still difficult

to explain this observation; however, one of many reasons could be the catalytic effect of positively charged CTAN micelles on the reaction involving bromide and bromate ions that cannot be supposed for the case of negatively charged SDS micelles.

The second series of oscillations is extremely sensitive to the rate and smoothness of stirring. The stirring effect cannot be caused by the atmospheric oxygen, as follows from [5]. The measurements in the presence and absence of oxygen at two different stirring rates demonstrated no effect on the oscillations. With the micelle formation the viscosity of the solution increases [10] rapidly, and simultaneously the transport of reactants is affected [23] due to the changes in the diffusion of the reactants and in the density of the solution. At the same time marked changes in homogeneity occur in the system as the products of bromination differ distinctively in their solubilities, and due to different hydrophobicity they distinguish also in the hydration shell. Besides, if the semiquinone radical may be considered to act as a traditional one-electron-transfer catalyst, which may disproportionate to quinone and hydroquinone, to the rise of inhomogeneities in the system must contribute hydroquinone which, compared [20] to quinone, is more soluble and can form stronger hydrogen bonds with water. Every subtle rearrangement of the water molecules around the solute on periodic transition from quinone to hydroquinone and back may play a role in the fluid motion. Moreover, many identified products of the reaction, e.g. 1,2- and 1,4-dihydroxybenzene and trihydroxybenzenes, are efficient hydrotropes [24] which can gradually arrange themselves in dimers, trimers and so on by the plane-to-plane stacking of the hydrophobic part of the molecule. The hydrotropes are surface-active, although the decrease in surface tension is not so dramatic as for surfactants; actually it occurs over a large concentration range. Cooperative interactions between hydrotrope molecules, resulting in stepwise association, may begin below the minimal hydrotropic concentration, i.e. below a particular concentration necessary for the formation of larger aggregates. The results of surface tension and heats of dilution measurements support [25] the view of a continuous self-association of hydrotrope molecules. Although there are still some doubts about the mechanism of hydrotropic action, possible formation of highly dynamic loose structures in the solution could explain the extreme sensitivity of the sequential oscillations to the rate of stirring.

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