

## ORIGINAL ARTICLE

# The effect of perturbants on oscillatory behaviour of the hematoxylin- bromate-acid system

Oľga Grančičová\*, Anna Olexová

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

E-mail: grancicova@fns.uniba.sk

Received: 18<sup>th</sup> September, 2013 ; Accepted: 27<sup>th</sup> October, 2013

**Abstract** : The effect of surfactants - anionic sodium dodecyl sulphate (SDS), cationic cetyl trimethyl ammonium nitrate (CTAN), nonionic Triton X-100 as well as tetrabutylammonium ion ( $\text{Bu}_4\text{N}^+$ ) and tert-butanol (t-BuOH) on the catalyzed bromate oscillator with hematoxylin as substrate was investigated at  $30 \pm 0.1^\circ\text{C}$  in stirred and nonstirred batch conditions. The changes in the oscillatory parameters have been ascribed to catalytic effect of charged surface of micelles, to the solubilization of hematoxylin and of bromination products in

the micelles and to the inhibition of bromination of aromatic substrate due to the bromine solubilization. The effect of tert-butanol has been discussed in terms of its ability to act as a radical scavenger. The effect of  $\text{Bu}_4\text{N}^+$  has been ascribed mainly to their ability to act as ion-pairing reagent.

**Keywords** : Belousov-Zhabotinsky system; Micelles; Bromate oscillator; Tert-butanol; Quaternary ammonium ion.

## INTRODUCTION

The systems without metal catalyst, where the organic substrate alone takes its function, are important chemical variant of classical Belousov-Zhabotinsky (B-Z) reaction. The uncatalyzed bromate systems (UBO) consist of bromate, aromatic substrate and acid. For UBO systems a skeleton OKN mechanism<sup>[1]</sup> and later the reduced mechanisms were proposed<sup>[2]</sup>. Although there are still no general rules crucial for the aromatic substrate to give chemical oscillations in the system, on the basis of a number of observations of oscillating UBO

systems Orbán and Körös summarized the assumptions for substrates not to show oscillatory behaviour in the uncatalyzed bromate systems<sup>[3,4]</sup>. Up till now the attention was paid preferably to the structural simpler aromatic molecules as substrates (e. g. mono-, di- and trihydroxybenzenes, ...) in uncatalyzed systems. Hematoxylin - a polyhydroxy aromatic compound (7,11b-dihydroindeno[2,1-c]chromene-3,4,6a,9,10(6H)-pental) - according to those rules could provide the oscillations. The partial oxidation of hematoxylin leads to the formation of hematein<sup>[5]</sup> in many possible conformations including isomeric structures. Hematein-alu-

# ORIGINAL ARTICLE

minium complexes are still used as important stains for histology and cytology. Recently a highly efficient biosensor for the determination of noradrenalin and acetaminophen was constructed on the basis of hematoxylin<sup>[6]</sup>. Oscillatory behaviour of catalyzed and uncatalyzed hematoxylin- $\text{H}_2\text{SO}_4$ - $\text{BrO}_3^-$  system has been reported in<sup>[7]</sup>. Unfortunately the authors used for the monitoring the reaction two Pt electrodes. Therefore they did not record the redox potential but in the case of uncatalyzed reaction very irregular noisy change of potential related to the development of concentration fluctuations and to the motion of solution near the electrodes. More regular oscillations were observed in the catalyzed system, but only in very short time interval 0.4 – 1.5 min.

In this paper we report the detailed study on the effects of temperature, acid and substrate concentrations, stirring as well as of various surfactants on the oscillatory behaviour, as we found that the catalyzed hematoxylin- $\text{H}_2\text{SO}_4$ - $\text{BrO}_3^-$  system in a batch reactor was giving not only this series of very short-lived oscillations but even another series of longer lasting oscillations.

The effect of surfactants forming the micelles in aqueous media was previously studied only in the classical malonic B-Z reaction<sup>[8-11]</sup>, but no attention was paid to their effect in the uncatalyzed bromate oscillators (UBO) with aromatic substrates like phenols, anilines ...although the marked changes in oscillatory behaviour could be expected due to different location of reactants. Depending on the size, shape and polarity of molecules the reactants may be solubilized in different region of the aggregate structure: in the hydrophobic core of micelle, between hydrophobic chains (so called palisade layer) or at the hydrophilic shell of polar heads. Indeed, the solubilization of phenol in the micelles leads gradually to the extinction of oscillations in the phenol-bromate-acid system<sup>[12,13]</sup>. Similar effects of cationic, anionic and nonionic surfactants were observed in uncatalyzed bromate oscillators with 1,4-cyclohexandione, pyrocatechol as well as pyrogallol as substrates (our not published results).

## EXPERIMENTAL

### Chemicals

Sodium bromate, sulfuric acid, hematoxylin and

ferroin ( $\text{Fe}(\text{o-phen})_3\text{SO}_4$ ) (Lachema) were of commercial analytical quality and were used without further purification. Tert-butanol (t-BuOH) (Merck) was distilled before use. Sodium dodecyl sulfate (SDS) (Fluka) was recrystallized from ethanol, cetyl trimethyl ammonium nitrate was prepared from the corresponding bromide (Aldrich) as described in<sup>[14]</sup>. TRITON X – 100 (Fluka) was used without any purification. Tetrabutylammonium perchlorate ( $\text{Bu}_4\text{NClO}_4$ ) was obtained from the reaction of corresponding bromide (Aldrich) and sodium perchlorate. This quaternary ammonium salt was stable against the acid bromate. Redistilled water was used to prepare all solution. Stock solution of sulfuric acid was standardized by acid-base titration.

### Methods and measurements

The measurements were carried out in a thermostatted cylindrical glass reaction vessel (diameter 3.5 cm, height 7.5 cm) closed with a rubber stopper through which the commercial indication platinum electrode and the reference  $\text{Hg}/\text{Hg}_2\text{SO}_4$  electrode were inserted into the solution. The total volume of reaction mixture was always 20 cm<sup>3</sup>. The appropriate aliquots of stock solutions of reactants for oscillating mixtures were added into water in the vessel in the following order: hematoxylin, sulfuric acid, surfactant or other perturbant, ferroin and then after thorough stirring and after attainment of the desired temperature ( $30 \pm 0.1^\circ\text{C}$ ) the bromate was injected. The initial reactant concentrations were in the most of experiments as follows: [hematoxylin] = 0.0064 mol/l, [ $\text{BrO}_3^-$ ] = 0.016 mol/l, [ $\text{H}_2\text{SO}_4$ ] = 1.44 mol/l, [ferroin] = 0.0002 mol/l. 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 constant stirred (50 rpm) batch condition using digital multimeter METEX M-4650 CR connected to a PC.

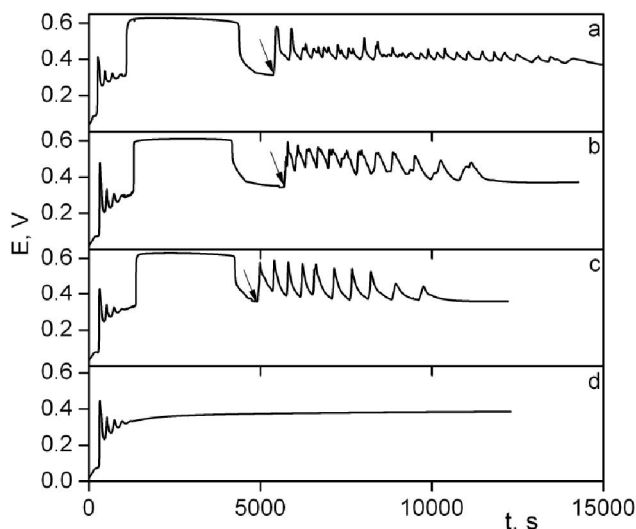
In some experiments the reaction was monitored with a computer-controlled PERKIN-ELMER model Lambda 25 spectrometer in the range 200 – 600 nm in 0.1 cm cuvette at  $30 \pm 0.1^\circ\text{C}$ . The initial reactant concentrations were: [hematoxylin] = 0.001 mol/l, [ $\text{BrO}_3^-$ ] = 0.004 mol/l, [ $\text{H}_2\text{SO}_4$ ] = 1.44 mol/l and [ferroin] = 0.0002 mol/l.

## RESULTS AND DISCUSSION

## Effects of stirring, temperature and acid concentration on oscillatory behavior

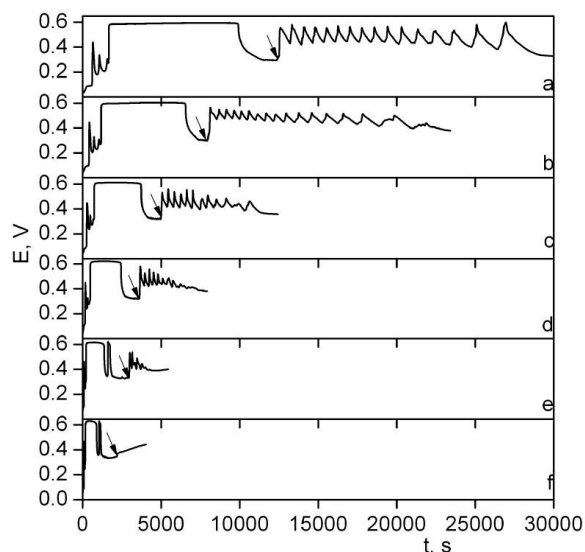
In contrast to results in<sup>[7]</sup> with chaotic noise instead of regular oscillations for both catalyzed and uncatalyzed hematoxylin- $\text{BrO}_3^-$ - $\text{H}_2\text{SO}_4$  system, we could observe for ferriin – catalyzed system 2 series of oscillations: the number of oscillations of the first series is unaffected by stirring, but the second series that appeared only when the stirring had been stopped, was very sensitive to the rate of stirring (Figure 1). As there was still some probability of the rise of second series of oscillations even in stirred system, we stopped the stirring always after sufficiently long period of about 20 – 30 minutes. When the stirring was stopped immediately after the injection of bromate, the number and the shape of oscillations were considerably disturbed (e.g. Figure 5). The stirring effect used to be related to oxygen effects but effect of oxygen on the phenol-sulfuric acid-bromate system has already been studied by our colleagues<sup>[15]</sup> and the measurements in the presence and in the absence of oxygen at two different stirring rates demonstrated no effect on the oscillations. Similarly as in the phenol-sulfuric acid-bromate the change in homogeneity might play important role in extreme sensitivity of system to the stirring. The role of heterogeneities and stirring effects in classical B-Z reaction have already been demonstrated by Menzinger<sup>[16]</sup>. In uncatalyzed bromate oscillators according to the skeleton OKN mechanism<sup>[1]</sup> the semiquinone radical may disproportionate to quinone and hydroquinone. The hydroquinone is more soluble and can form stronger hydrogen bonds with water compared to quinone. Every subtle rearrangement of the water molecules around the solutes on periodic mutual transition from hydroquinone to quinone and back must contribute to the rise of inhomogeneities (or nucleation centers) in the system. Intensive stirring homogenizes the system and transition from one nonequilibrium state to another cannot be initiated<sup>[17]</sup>. Moreover, in the systems with polyphenolic substrates, that can be considered for efficient hydrotropes, they can gradually arrange themselves in dimers, trimers ... by the plane-to-plane stacking of the hydrophobic part of molecules. This possible

formation of highly dynamic loose structure in the aqueous solutions may also contribute to the extreme sensitivity of the oscillations to the stirring.



**Figure 1 :** The effect of stirring on the oscillation behaviour of the system: [hematoxylin] = 0.0064 mol/l,  $[\text{BrO}_3^-]$  = 0.016 mol/l,  $[\text{H}_2\text{SO}_4]$  = 1.44 mol/l, [ferriin] = 0.0002 mol/l,  $T$  = 303.15 K. a – 50, b – 100, c – 150, d – 200 rpm. The arrows indicate the end of stirring.

In noncatalyzed system only the first series of oscillations has been observed but when the ferriin is injected at the time when in a catalyzed system the oscillations just finished ( $\sim 9300$  s), the second series of oscillations could be initiated after an induction period.



**Figure 2 :** The effect of temperature on the oscillation behaviour of the system: [hematoxylin] = 0.0064 mol/l,  $[\text{BrO}_3^-]$  = 0.016 mol/l,  $[\text{H}_2\text{SO}_4]$  = 1.44 mol/l, [ferriin] = 0.0002 mol/l, a - 293.15, b – 297.65, c – 303.15, d – 308.15, e – 313.15, f – 318.15 K, 50 rpm. The arrows indicate the end of stirring.

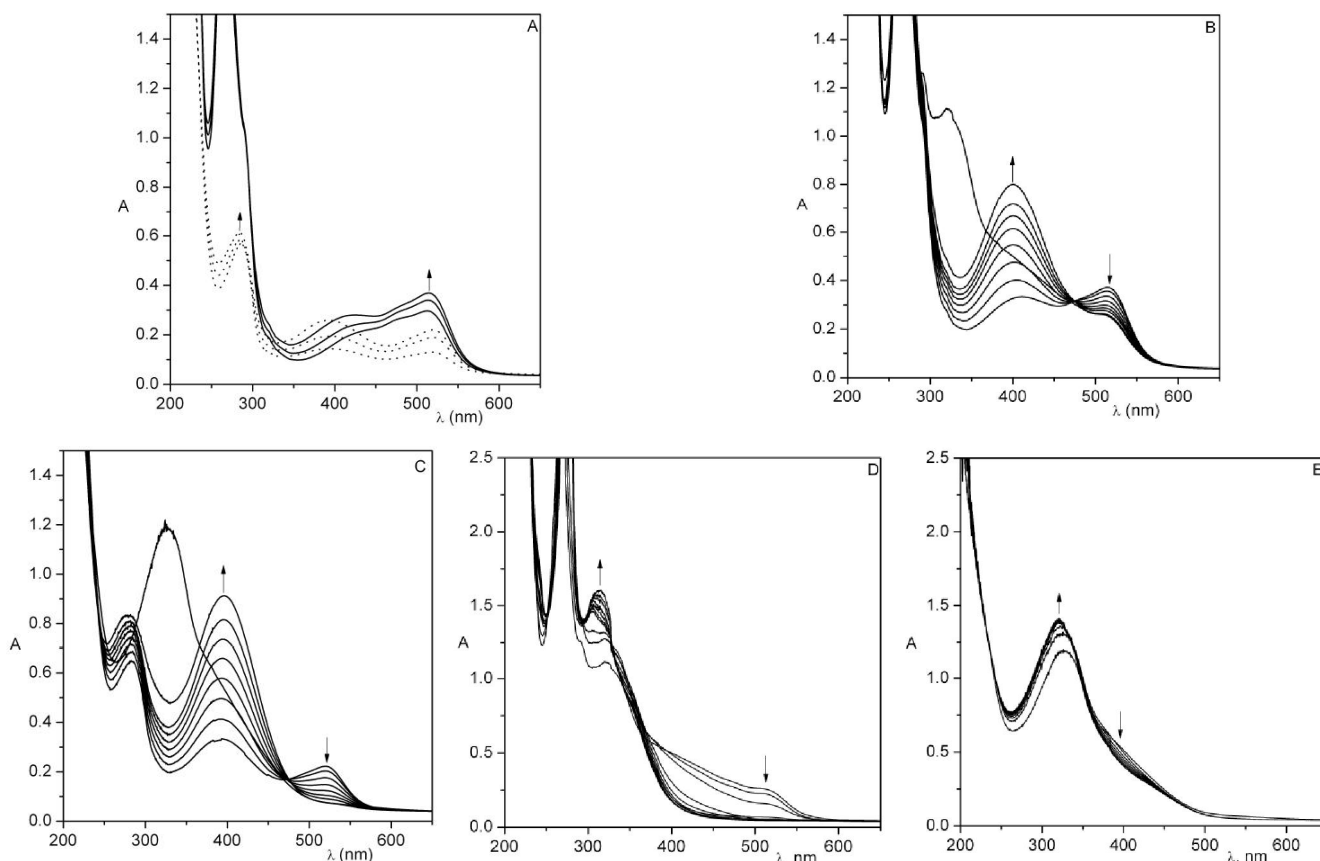
# ORIGINAL ARTICLE

The increasing temperature (Figure 2) affected both series of oscillations: the induction period and the duration of the first series of oscillations decreased distinctly and simultaneously the number and duration of the second series of oscillations gradually decreased and finally fully disappeared at 318.15 K.

The detailed study of the effect of acid concentration on the nonstirred system has shown that the periodic oscillations appeared at the concentration higher than 0.95 mol/l. With increasing acid concentration the induction period and the duration of the first series of

oscillations decreased.

The reaction could be monitored spectrophotometrically on decreasing the hematoxylin concentration to 0.001 mol/l, but the system exhibited the oscillations only at  $[\text{BrO}_3^-]/[\text{hematoxylin}]$  ratio higher than 2.5. At  $[\text{BrO}_3^-]/[\text{hematoxylin}]$  ratio higher than 5-fold or at lower hematoxylin concentration the oscillations did not appeared. When compared the course of both catalyzed and uncatalyzed reaction, it is interesting that there is no significant difference in the first three minutes (Figure 3A) or even in further 4-12 min (Figure 3B, C).



**Figure 3 :** Spectra of of the nonstirred system:  $[\text{hematoxylin}] = 0.001 \text{ mol/l}$ ,  $[\text{BrO}_3^-] = 0.004 \text{ mol/l}$ ,  $[\text{H}_2\text{SO}_4] = 1.44 \text{ mol/l}$ ,  $T = 303.15 \text{ K}$ . A – the first three minutes of the reaction: line - in the presence of  $[\text{ferriin}] = 0.0002 \text{ mol/l}$ , dots – in the absence of ferriin; B, C – 4 – 12 min in the presence and in the absence of ferriin; D – 12,16, 20, 41 – 206 min in the presence of ferriin; E – 12, 32 – 212 min in the absence of ferriin.

The differences (Figure 3D, E) that emerged later, are the reason why the second series of oscillations appeared only in the presence of catalyst. Figure 4 illustrates quite clearly the fact that the maximum in absorbance at 550 nm (ferriin) is corresponding to the minimum in absorbance at 590 nm (ferrin) and similarly the maximum and minimum at 260 and 240 nm are corresponding to the oxidized and reduced forms of uni-

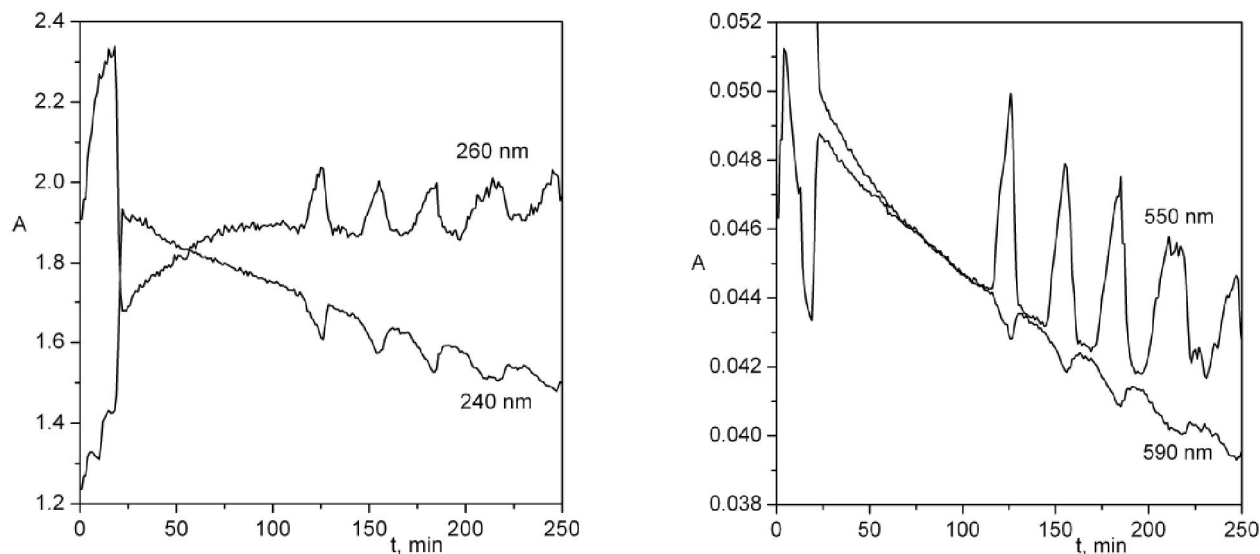
identified substrate crucial for the oscillations.

## Effects of surfactants on oscillatory behavior

As known<sup>[8-11]</sup>, the dynamics of the B-Z reaction can be affected by various surfactants, especially by those spontaneously assembled into micelles. The reactants can associate to micelles in many ways, reflecting the type of interactions between surfactant and sub-

strate molecule. Location of the solubilized substrate in micellar systems depends on the hydrophobicity and structure of the solute. They may be solubilized in different regions of the aggregate structure: in the hydrophobic core of micelle, between hydrophobic chains (so called palisade layer) or at the hydrophilic shell of polar heads. The surfactants used in the study were cationic, anionic and nonionic as the different charged surface of the micelles could significantly affect some of the steps in the complex reaction by means of micellar catalysis. The octanol-water partition coefficient  $\log K_{ow}$  of 0.71 for hematoxylin is higher than the octanol-water partition coefficient  $\log K_{ow}$  of  $-0.070$  for hematein<sup>[18]</sup>, i.e. both substrates must differ in their positions in micelles. The molecule of hematoxylin contains four hydroxyl groups, regarding these polar moieties and the dimension of the molecule, it is possible that the hematoxylin is largely located at the micellar interface near the water. It is unusual, that the keto group in the hematein changes the hydrophobicity in so far as follows from octanol-water partition coefficient values. As a result, the hematein can not penetrate deeper

between the surfactant chains and its further transformation may occur in aqueous phase. Ferroin with its large hydrophobic phenanthroline ligands and positive charge at the central atom is due to electrostatic interactions with negatively charged SDS located at the hydrophilic shell of polar heads. Similarly ferroin is located in micelles of nonionic Triton X-100 due to the interactions with slight negative charge developed on polyoxyethylene chains of surfactant. The spectra of ferroin with varying surfactant concentration have shown that at low concentrations below the CMC, the bands shifted very slightly to the higher wavelengths and the absorbance increased by forming the adducts. Only at  $[SDS] = 0.001$  mol/l, but not at higher surfactant concentrations, a fine precipitate of ferroin-SDS adduct was formed. In the reaction several nonpolar species are formed:  $Br_2$  and radical  $BrO_2\cdot$  as the most nonpolar species in the system prefer the hydrophobic core of the micelle. The solubilization of bromine 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.



**Figure 4 :** Time dependence of absorbance at various wavelengths in nonstirred reaction system with initial concentration of reactants:  $[hematoxylin] = 0.001$  mol/l,  $[BrO_3^-] = 0.004$  mol/l,  $[H_2SO_4] = 1.44$  mol/l,  $[ferroin] = 0.0002$  mol/l,  $T = 303.15$  K in 0.1 cm cuvette

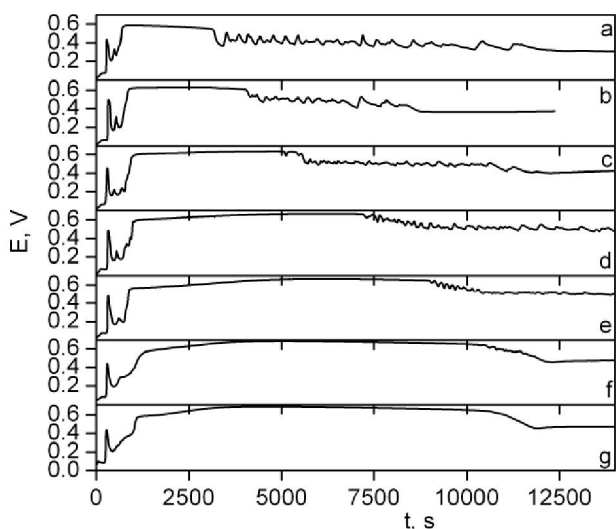
This time, unlike the other oscillating systems<sup>[12,13]</sup>, the effect of surfactants on oscillatory behaviour varies widely depending on whether the surfactant is cationic, anionic or nonionic.

The cationic CTAN shows (Figure 5, 6) the most significant effect on the oscillatory behavior: The first

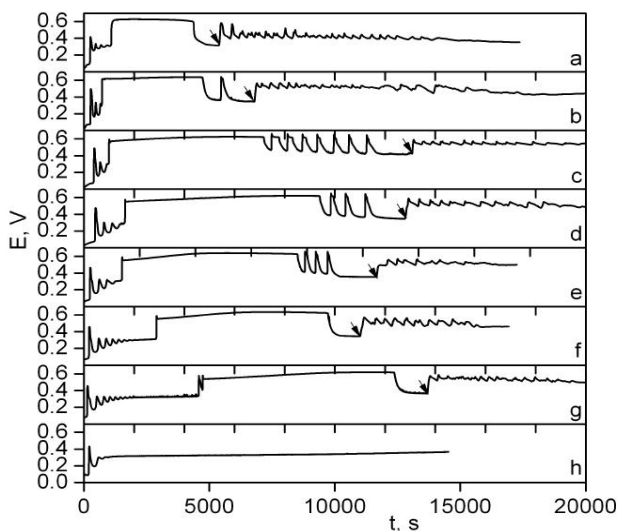
induction period of both stirred and nonstirred system initially increases with increasing concentration of surfactant, but at concentrations greater than 0.005 mol/l again slowly decreases until finally at  $[CTAN] = 0.03$  mol/l to be less than in the absence of surfactant. In stirred system the time needed for the production of intermedi-

# ORIGINAL ARTICLE

ate essential for second series of oscillations increased from 720 s to 4573 s and simultaneously the number of oscillations of the first series increased. Moreover, even when stirring, the new undamped oscillations appeared. At  $[\text{CTAN}] > 0.02 \text{ mol/l}$  these oscillations vanished but again after their extinction the break of stirring lead to the sequential oscillations. Simultaneously the duration of the oscillations of the first series extremely increased.

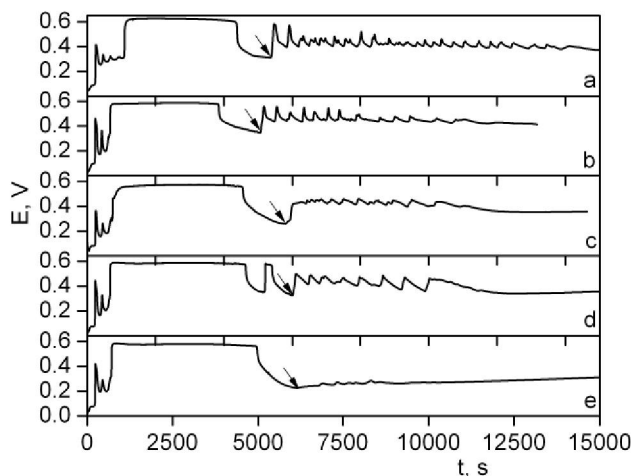


**Figure 5 :** The effect of CTAN concentration on the oscillation behaviour of the nonstirred system:  $[\text{hematoxylin}] = 0.0064 \text{ mol/l}$ ,  $[\text{BrO}_3^-] = 0.016 \text{ mol/l}$ ,  $[\text{H}_2\text{SO}_4] = 1.44 \text{ mol/l}$ ,  $[\text{ferroin}] = 0.0002 \text{ mol/l}$ ,  $T = 303.15 \text{ K}$ . a – 0, b – 0.001, c – 0.002, d – 0.005, e – 0.01, f – 0.02, g – 0.03 mol/l.



**Figure 6 :** The effect of CTAN concentration on the oscillation behaviour of the stirred system:  $[\text{hematoxylin}] = 0.0064 \text{ mol/l}$ ,  $[\text{BrO}_3^-] = 0.016 \text{ mol/l}$ ,  $[\text{H}_2\text{SO}_4] = 1.44 \text{ mol/l}$ ,  $[\text{ferroin}] = 0.0002 \text{ mol/l}$ ,  $T = 303.15 \text{ K}$ . a – 0, b – 0.001, c – 0.005, d – 0.01, e – 0.02, f – 0.021, g – 0.025, h – 0.03 mol/l. The arrows indicate the end of stirring.

The effect of SDS concentration on the oscillation behaviour of stirred and nonstirred system is very similar. The first induction period only slightly increases on increasing surfactant concentration: from 237 s to 389 s for  $[\text{SDS}] = 0 - 0.1 \text{ mol/l}$  for nonstirred system and from 261 s to 524 s for  $[\text{SDS}] = 0 - 0.2 \text{ mol/l}$  for stirred system. Concurrently the time needed for the production of intermediate essential for second series of oscillations increased from 1091 s to 1571 s in stirred system. In stirred system the number of oscillations of the first series is unaffected by  $[\text{SDS}]$ , but the number of oscillations of second series, that appeared only when the stirring had been stopped, gradually decreased on increasing surfactant concentration until the oscillations completely vanished at 0.2 mol/l.

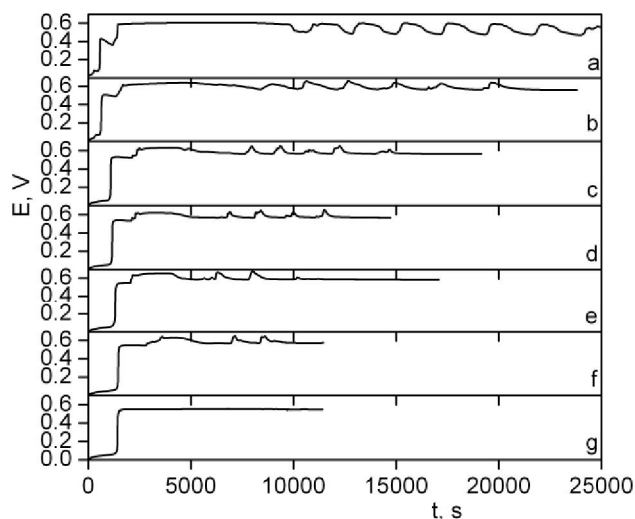


**Figure 7 :** The effect of Triton concentration on the oscillation behaviour of the stirred system:  $[\text{hematoxylin}] = 0.0064 \text{ mol/l}$ ,  $[\text{BrO}_3^-] = 0.016 \text{ mol/l}$ ,  $[\text{H}_2\text{SO}_4] = 1.44 \text{ mol/l}$ ,  $[\text{ferroin}] = 0.0002 \text{ mol/l}$ ,  $T = 303.15 \text{ K}$ , 50 rpm. a – 0, b – 0.0001, c – 0.0005, d – 0.0007, e – 0.001 mol/l. The arrows indicate the end of stirring.

The effect of Triton X-100 concentration on the oscillation behaviour (Figure 7) of stirred and nonstirred system does not differ much. The first induction period (IP1) was changed slightly with surfactant concentration, but the number of oscillations of the first series in stirred system was affected immediately at the minimal  $[\text{Triton}]$ . Simultaneously, the time needed for the production of intermediate essential for second series of oscillations decreased from 1091 s to 666 s in stirred system. The number of oscillations of second series, that appeared only when the stirring had been stopped, gradually decreased on increasing surfactant concen-

tration until the oscillations completely vanished at  $[\text{Triton}] > 0.001 \text{ mol/l}$ . In the nonstirred system the oscillations of the second series disappeared at  $[\text{Triton}] = 0.003 \text{ mol/l}$ .

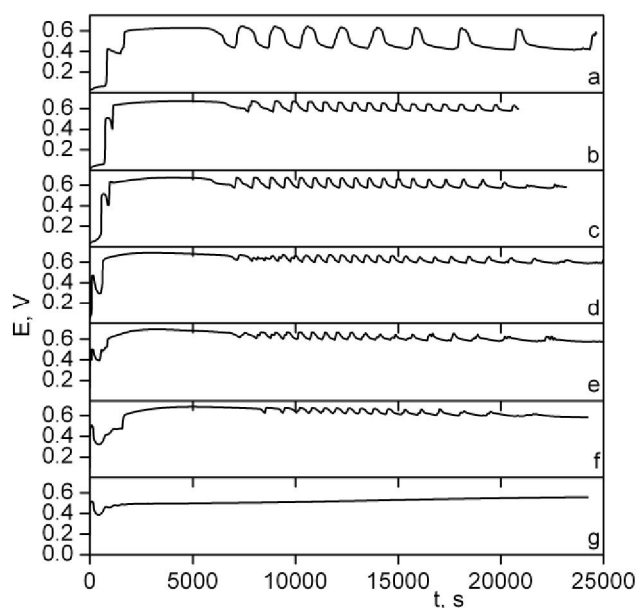
Different effect of surfactants on the oscillations is manifested (Figure 8, 9, 10) even more in nonstirred system with lower hematoxylin concentration but with four-fold bromate/hematoxylin ratio. This time no oscillations of the first series appeared and the oscillations of the second series had been transformed to regular ones due to the change in  $[\text{hematoxylin}]$ .



**Figure 8 :** The effect of SDS concentration on the oscillation behaviour of the nonstirred system:  $[\text{hematoxylin}] = 0.001 \text{ mol/l}$ ,  $[\text{BrO}_3^-] = 0.004 \text{ mol/l}$ ,  $[\text{H}_2\text{SO}_4] = 1.44 \text{ mol/l}$ ,  $[\text{ferroin}] = 0.0002 \text{ mol/l}$ ,  $T = 303.15 \text{ K}$ , a – 0, b – 0.001, c – 0.005, d – 0.01, e – 0.06, f – 0.08, g – 0.1 mol/l.

By comparing the oscillatory behaviour of the studied stirred and nonstirred systems in micellar solutions one can see: The first series with two or three oscillations initiated by the oxidation of hematoxylin to hematein was negligibly affected by various surfactants. The nonoscillatory period was influenced by surfactants: was shortened by the anionic SDS, considerably prolonged by the cationic CTAN and almost without any effect by the nonionic Triton. The number of oscillations in second series gradually decreased on increasing surfactant concentration regardless of the kind of surfactant. The only exception in the oscillatory behaviour could be observed in CTAN micellar solutions (0.001-0.02 M) where the second series of oscillations appeared also in stirred system (Figure 6). The temperature had similar effect on oscillatory behaviour

of stirred system: the sequential oscillations appeared only when the stirring was stopped. On increasing the temperature the number of oscillations decreased and before their fully extinction the only peak appeared even in stirred system (Figure 2). The increase in  $[\text{CTAN}]$  and in temperature shortened the induction period for the first series of oscillations due to their effect on the transformation of hematoxylin into hematein. However, CTAN gradually extended the first oscillation phase probably due to its catalytic effect on the subsequent transformation of hematein to the intermediate crucial for the rise of undamped oscillations.

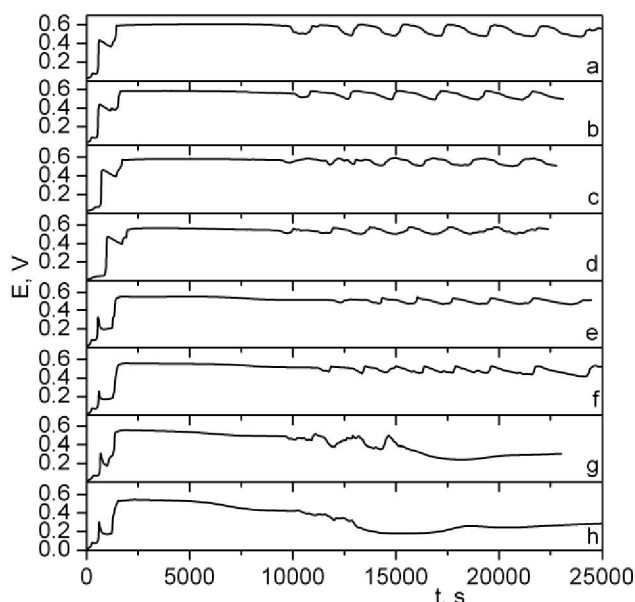


**Figure 9 :** The effect of CTAN concentration on the oscillation behaviour of the nonstirred system:  $[\text{hematoxylin}] = 0.001 \text{ mol/l}$ ,  $[\text{BrO}_3^-] = 0.004 \text{ mol/l}$ ,  $[\text{H}_2\text{SO}_4] = 1.44 \text{ mol/l}$ ,  $[\text{ferroin}] = 0.0002 \text{ mol/l}$ ,  $T = 303.15 \text{ K}$ , a – 0, b – 0.002, c – 0.004, d – 0.008, e – 0.012, f – 0.016, g – 0.018 mol/l.

If the assumption, that the oscillation parameters are largely controlled by the rate of reaction between bromide and bromate ions with the formation of  $\text{HBrO}$  and  $\text{HBrO}_2$ , is correct, distinguished effect of surfactants on the oscillation parameters could be explained by their catalytic micellar effect on this reaction. The inhibition effect of negatively charged micellar surface of SDS on the reaction between  $\text{BrO}_3^-$  and  $\text{Br}^-$  as well as the penetration of bromine into the micelles due to its nonpolar character is reflected in extending of time required for the increase of the potential. However, at the same time the induction period for the development of subsequent oscillations was shortened with the increas-

# ORIGINAL ARTICLE

ing [SDS] and the number of the oscillations gradually decreased. The effect of cationic CTAN resulted in gradually shortening the time necessary for formation of the peak corresponding to the transformation of hematoxylin into hematein due to electrostatic interactions of bromide and bromate ions and positively charged micelles. The induction period for the development of subsequent oscillations increased. Nonionic Triton X-100 affects the beginning of the reaction associated with the conversion of hematein to the intermediate important for the development of subsequent oscillations. At 0.0005 mol/l Triton the induction period and number of oscillations begun to decrease.



**Figure 10 :** The effect of Triton concentration on the oscillation behaviour of the nonstirred system: [hematoxylin] = 0.001 mol/l,  $[\text{BrO}_3^-]$  = 0.004 mol/l,  $[\text{H}_2\text{SO}_4]$  = 1.44 mol/l, [ferroin] = 0.0002 mol/l, T = 303.15 K, a – 0, b – 0.00002, c – 0.00005, d – 0.0001, e – 0.0005, f – 0.0006, g – 0.0007, h – 0.001 mol/l.

Only significantly higher surfactant concentration compared with their CMC<sup>[12]</sup> led to the disappearance of subsequent oscillations: at 0.1 mol/l SDS, 0.018 mol/l CTAN and 0.001 mol/l Triton. The concentration, at which the complete extinction of the subsequent oscillations occurred, is related to the solubilization capacity characteristic for the surfactant. 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<sup>[20]</sup>. In addition to catalytic effect of charged surface of micelles the changes in the oscil-

latory parameters probably reflect the solubilization of reactants and products of bromination as well as of catalyst in micelles and the inhibition of aromatic substrate bromination due to bromine solubilization.

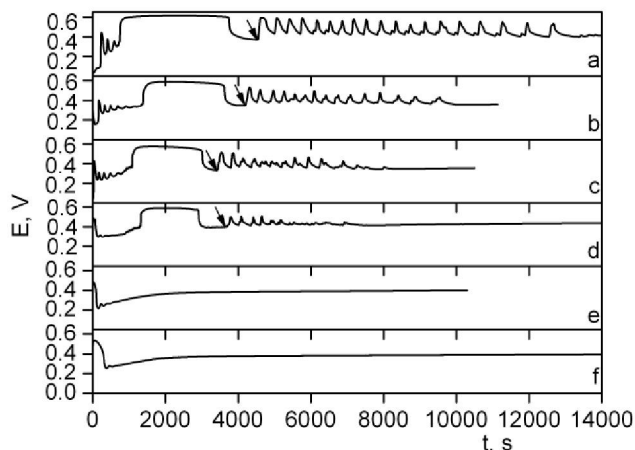
The surfactants can even at lower concentrations effectively change the surface tension of solution. With the micelle formation the viscosity of the solution increases<sup>[9]</sup> and the transport of reactants to the micellar interface is affected due to the changes in the diffusion of the reactants and in the density of the solution<sup>[19]</sup>. This may also contribute to the extreme sensitivity of oscillatory behaviour to stirring.

The aqueous solution of tetraalkylammonium halides offers another possibility of affecting the oscillation reaction. They also are surface active: initially on increasing concentration the surface tension decreases slightly, the steep decrease begins at a higher concentration (0.01 mol/l). The tetraalkylammonium halides do not conform<sup>[21]</sup> to “normal” electrolyte behaviour. They can increase<sup>[22]</sup> the solubility of organic solutes (non-polar and polar) in water, *i.e.* they show the salting-in effect. The salting effects can play a key role in changes in reaction rates. In the case of tetrabutylammonium halides there are assumed the changes in the structure of liquid water due to the interaction of  $\text{Bu}_4\text{N}^+$  with the water (hydrophobic hydration). Besides tetrabutylammonium ions can associate in aqueous solutions due to hydrophobic interactions and form aggregates that can influence the solubility and properties of the other solutes. The increase in solubility of tris(1,10-phenanthroline)iron (II) perchlorate in water by the addition of hydrophobic tetrabutylammonium ion was interpreted in terms of its stabilization by the hydrophobic interaction with added hydrophobic ion<sup>[23]</sup>.

Finally the tetrabutylammonium ions associate with the small inorganic anions ( $\text{Br}^-$ ,  $\text{BrO}_3^-$ ) or radicals (e.g.  $\text{BrO}_2^\cdot$ ) forming hydrophobic ion-associates, and thus decreasing the mobility of anions that are important in controlling the oscillations. The evaluation<sup>[24]</sup> of ion association constants between n-tetrabutylammonium ion and bromide ( $\log K_{\text{ass}} = 0.44$ ) as well as bromate ( $\log K_{\text{ass}} = 0.27$ ) ions favours this opinion. Figure 11 illustrates the effect of increasing  $\text{Bu}_4\text{NClO}_4$  concentration on the stirred systems. In both stirred and nonstirred cases it markedly reduced the induction



period for oscillations of the first series, extended the time required for the potential increase and increased the number of oscillations of the second series. Moreover, it shortened the induction period for the formation of second oscillations, which at the same time gradually disappeared. Unfortunately it is not possible to decide unambiguously, which of the options mentioned above has the greatest influence on changes in the oscillation behavior.

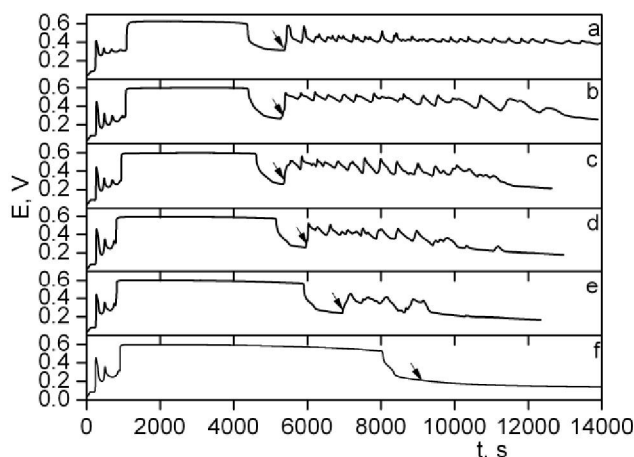


**Figure 11 :** The effect of  $\text{TBAClO}_4$  concentration on the oscillation behaviour of the stirred system: [hematoxylin] = 0.0064 mol/l,  $[\text{BrO}_3^-]$  = 0.016 mol/l,  $[\text{H}_2\text{SO}_4]$  = 1.44 mol/l, [ferroin] = 0.0002 mol/l,  $T = 303.15 \text{ K}$ , a – 0, b – 0.003, c – 0.005, d – 0.0055, e – 0.006, f – 0.015 mol/l. The arrows indicate the end of stirring.

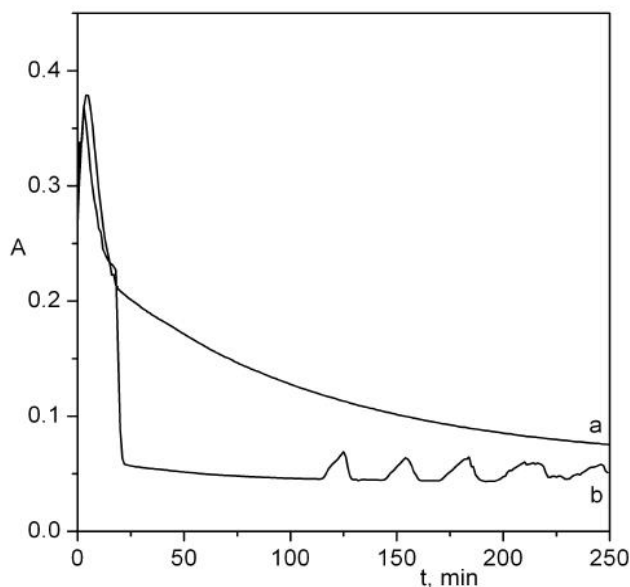
As we found<sup>[25]</sup> that tert-butanol significantly speeds up the reaction  $\text{BrO}_3^- + 5\text{Br}^- + 6\text{H}^+ \rightarrow 3\text{Br}_2 + 3\text{H}_2\text{O}$ , we decided to investigate the effect of tert-butanol on the oscillatory behaviour. This alcohol not only causes the change in relative permittivity of media, but can act as the scavenger of OH and Br radicals. Moreover, it can influence the hydrogen-bonded water structure. Figure 12 illustrates the effect of tert-butanol on the redox potential of studied system. Surprisingly, t-BuOH has almost no effect on the position of the first peak both stirred and nonstirred systems, but extremely prolonged the time required for the formation of intermediate crucial for the development of second series of oscillations. At the same time the number of oscillations of the second series gradually decreased until finally disappeared in the stirred system at 5 vol% and in the nonstirred system at 8 vol%. In nonstirred system with lower hematoxylin concentration but with four-fold bromate/hematoxylin ratio the oscillations completely van-

ished even at 0.5 vol% t-BuOH.

When monitoring the reaction spectrophotometrically it has been showed that the reaction at 0.5 vol% t-BuOH differed significantly from that without t-BuOH. The oscillations did not appear because, as shown in Figure 13, ferroin was not engaged in the reaction. As shown previously, the presence of ferroin is essential for the second series of oscillations. We have investigated the aqutation of ferroin in water and aqueous mix-



**Figure 12 :** The effect of t-BuOH concentration on the oscillation behaviour of the stirred system: [hematoxylin] = 0.0064 mol/l,  $[\text{BrO}_3^-]$  = 0.016 mol/l,  $[\text{H}_2\text{SO}_4]$  = 1.44 mol/l, [ferroin] = 0.0002 mol/l,  $T = 303.15 \text{ K}$ , 50 rpm. a – 0, b – 0.5, c – 1.5, d – 2, e – 3.5, f – 5 vol.%. The arrows indicate the end of stirring.



**Figure 13 :** Time dependence of absorbance at 510 nm in nonstirred reaction system with initial concentration of reactants: [hematoxylin] = 0.001 mol/l,  $[\text{BrO}_3^-]$  = 0.004 mol/l,  $[\text{H}_2\text{SO}_4]$  = 1.44 mol/l, [ferroin] = 0.0002 mol/l,  $T = 303.15 \text{ K}$  in 0.1 cm cuvette, a – 0.5 vol.% t-BuOH, b – no t-BuOH.

# ORIGINAL ARTICLE

tures of t-BuOH as well as the reaction of ferroin with bromate under the same conditions as in the oscillation system but surprisingly there were no marked changes in the reaction rates with solvent composition.

Such a marked effect of very low concentration of t-BuOH on the oscillations cannot be ascribed to the change in relative permittivity or in surface tension not even to its effect on the water structure. The only possible explanation seems to be its role as radical scavenger in the complex reaction mechanism. In the mechanism suggested for the  $\text{BrO}_3^-$ -1,4-cyclohexanedione-ferroin<sup>[26]</sup> the reaction between ferroin and radical  $\text{BrO}_2\cdot$  plays an important role in the oscillatory behaviour of the system, but if t-BuOH has affected just this reaction in the studied system remains still unclear.

## CONCLUSIONS

The hematoxylin proved to be the substrate with very rich oscillation behavior, easily and effectively affected by various perturbants. Our study of hematoxylin- $\text{BrO}_3^-$ - $\text{H}_2\text{SO}_4$  system with the ferroin as a catalyst showed three series of oscillations that could be influenced very significantly by various perturbants. Anionic, cationic as well as nonionic surfactants affected the oscillation behaviour through the catalytic effect of charged surface of micelles, the solubilization of reactants and of products in the micelles and the inhibition of bromination of aromatic substrate due to the bromine solubilization. Surface active tetrabutylammonium ion and tert-butanol changed dramatically the oscillation parameters – the first one due to the formation of ion-pairs and the effect of the second one has been attributed to its plausible role as a scavenger of  $\text{BrO}_2\cdot$  radicals.

## ACKNOWLEDGEMENTS

This work was supported by Grant No. 1/0039/09 from the Scientific Grant Agency VEGA of MESR.

## REFERENCES

[1] M.Orbán, E.Körös, R.M.Noyes; *J.Phys.Chem.*, **83**, 3056 (1979).  
 [2] J.Liu, S.K.Scott; *J.Phys.Chem.*, **96**, 9870 (1992).

[3] M.Orbán, E.J.Körös; *Phys.Chem.*, **82**, 1672 (1978).  
 [4] M.Orbán, E.Körös; *React.Kinet.Catal.Lett.*, **8**, 273 (1978).  
 [5] K.Shirai, M.Matsioka; *Dyes and Pigments*, **32**, 159 (1996).  
 [6] N.Nasirizadeh, H.R.Zare; *Talanta*, **80**, 656 (2009).  
 [7] A.Mittal, P.K.R.Nair, K.Srinivasulu; *React.Kinet.Catal.Lett.*, **13**, 259 (1980).  
 [8] A.Paul; *J.Phys.Chem.B*, **109**, 9639 (2005).  
 [9] L.Sciascia, R.Lombardo, M.L.Turco Liveri; *J.Phys.Chem.B*, **111**, 1354 (2007).  
 [10] F.P.Cavasino, R.Cervellati, R.Lombardo, M.L.Turco Liveri; *J.Phys.Chem.B*, **103**, 4285 (1999).  
 [11] M.Rustici, R.Lombardo, M.Mangone, C.Sbriziolo, V.Zambrano, M.L.Turco Liveri; *Faraday Discuss*, **120**, 39 (2001).  
 [12] O.Grančičová, A.Olexová, T.Zacher; *Z.Naturforsch.*, **63a**, 475 (2008).  
 [13] O.Grančičová, A.Olexová; *Z.Phys.Chem.*, **223**, 1451 (2009).  
 [14] C.A.Bunton, G.Cerichelli; *Int.J.Chem.Kinet.*, **12**, 519 (1980).  
 [15] Ľ.Adamčíková, Z.Farbulová, P.Ševčík; *New J.Chem.*, **25**, 487 (2001).  
 [16] (a) M.Menzinger, P.Jankowski; *J.Phys.Chem.*, **90**, 1217 (1986); (b) **94**, 4123 (1990).  
 [17] J.C.Roux, P.DeKepper, J.Boissonade; *Phys.Lett.A*, **97**, 168 (1983).  
 [18] <http://toxnet.nlm.nih.gov>  
 [19] X.Yang, M.A.Matthews; *J.Colloid.Interface.Sci.*, **229**, 53 (2000).  
 [20] H.Adamczak, K.Materna, R.Urbański, J.Szymanowski; *J.Colloid.Interface.Sci.*, **218**, 359 (1999).  
 [21] F.Franks; *The Hydrophobic Interaction*, Chapter 1, in F.Franks, (Ed); *Water-A Comprehensive Treatise*, Plenum Press, New York, **4**, (1973).  
 [22] R.C.da Silva, M.Spitzer, L.H.M.da Silva, W.Loh; *Thermochimica Acta*, **328**, 161 (1999).  
 [23] K.Miyoshi, C.Shimada, H.Yoneda; *Bull.Chem.Soc.Jpn.*, **48**, 3403 (1975).  
 [24] J.Mbuna, T.Takayanagi, M.Oshima, S.Motomizu; *J.Chromatogr.A*, **1022**, 191 (2004).  
 [25] Results not published  
 [26] I.Szálai, K.Kurin-Csörgei, M.Orbán; *Phys.Chem.Chem.Phys.*, **4**, 1271 (2002).