Effects of non-ionic micelles on transient chaos in an unstirred Belousov–Zhabotinsky reaction

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The behaviour of the Ce(IV)-catalyzed Belousov–Zhabotinsky (BZ) system has been monitored at 20.0 °C in unstirred batch conditions in the absence and presence of different amounts of the non-ionic micelle-forming surfactants hexaethylene glycol monodecyl ether ($C_{10}E_6$) and hexaethylene glycol monotetradecyl ether ($C_{14}E_6$). The influence of the non-ionic surfactants on both the kinetics of the oxidation of malonic acid (MA) by Ce(IV) species and the behaviour of the BZ reaction in stirred batch conditions has also been studied over a wide surfactant concentration range. The experimental results have shown that, in unstirred batch conditions, at surfactant concentrations below the critical micelle concentration (c.m.c.) no significant change in the dynamics of the Belousov–Zhabotinsky system occurs. Beyond this critical concentration the presence of micelles forces the BZ system to undergo a chaos → quasi-periodicity → period-1 transition. Thus, the surfactant concentration has been considered as a bifurcation parameter for a Ruelle–Takens–Newhouse (RTN) scenario. Addition of increasing amounts of non-ionic surfactants has no significant effect on the kinetics of the reaction between MA and Ce(IV), but it influences the oscillatory parameters of the stirred BZ system. At surfactant concentrations below the c.m.c. all the oscillatory parameters are practically unaffected by the presence of surfactant, while beyond this critical value the induction period is the same as in aqueous solution but both the oscillation period and the duration of the rising portion of the oscillatory cycle decrease. In all cases, the experimental trends have been ascribed to the enhancement in the medium viscosity due to the presence of micelles.

Introduction

The numerous theoretical and experimental studies on oscillating reactions indicate a continuing interest in these systems. Multistability, periodicity, multiperiodicity or chaotic oscillations are observed[1–4] in perfectly open stirred systems. Thermodynamic considerations dictate that closed chemical systems cannot undergo sustained oscillations because as the reactants are used up the systems settle into thermodynamic equilibrium.[5] However, in a closed reactor, the initial reactants are often present in large excess making the intermediates behave like an open subsystem for a substantial period of time. This phenomenon can be sustained for significant periods of time before the system reaches chemical equilibrium. It is well established that closed chemical systems

can exhibit various dynamic regimes. Nevertheless, these are strictly transient because closed systems naturally move through the parametric space.

Transient behavior may be sustained for a significant period of time and the chemical mixture can be considered to evolve in consecutive different pseudo-steady states by spontaneous transitions. Not only simple oscillations but also chaotic behavior can occur in closed Belousov–Zhabotinsky (BZ) systems.[6–10] Transient scenarios in the BZ system have also been the object of investigation.[11–13] For example Wang *et al.*[14] showed experimental evidence of successive transient chaos in a closed well mixed BZ system. Our attention has been turned to the closed unstirred BZ system. It is well known that an autocatalytic reaction performed in an unstirred batch reactor can support a constant velocity wavefront resulting from the coupling between diffusion and kinetics.[15] As a front propagates both concentration and thermal gradients are formed that alter the density of the solution, often causing convection.[16,17] The chemical wave may have features that differ significantly from the familiar reaction–diffusion wave when convective mass transport plays a relevant role. The effects of convection on chemical wave propagation have been observed experimentally in several oscillating systems.[16,18–20] In these systems convection enhances the chemical wave speed and affects the curvature of the front. Natural convection disturbs a travelling wave, and the disturbed wave affects the convection pattern.[21] This hydrodynamic effect, which sometimes perturbs the initial spatial patterns caausing them to bifurcate into more complex structures, can be either practically eliminated by stirring the solution or diminished by increasing the viscosity of the medium.[22] The addition of micelle-forming surfactants, polymers and other macromolecules, to an aqueous solution allows one to achieve increased viscosity and the extent of the increase depends[23] on the nature of the additive used. In fact, the contribution to the solution viscosity is greater for non-ionic additives than for anionic ones. Among the non-ionic surfactants the alkyl polyoxyethylene glycol monoethers are the most extensively used and studied. There is evidence[24] that, for these systems, the effect of the monomers on the medium viscosity is negligible due to their very low c.m.c. while beyond this critical value a sharp increase in the viscosity can be detected with increasing surfactant concentration. Moreover, the viscosity of non-ionic surfactants that have different alkyl chain lengths[24] is almost the same, whereas for systems having different head groups, *i.e.*, different polyoxyethylene chain length, the viscosity is enhanced when the number of ethylene oxides is increased.

The present work followed from a previous[25] study on dynamic behaviour of the BZ reaction where we found that the system, before reaching equilibrium in an unstirred batch reactor, spontaneously[7,26] gives the following sequence: period-1 → quasiperiodicity → chaos → quasiperiodicity → period-1. Two transition scenarios *i.e.* at the onset of chaos and at its end, are observed. One appears as the mirror image of the other. This transition is known[27] as the Ruelle–Takens–Newhouse (RTN) scenario. The onset of chaos starts spontaneously as soon as convection motion couples to diffusion and local kinetics. We have also shown[25] that when different amounts of the non-ionic polymer polyethyleneglycol with high molecular weight is added to the BZ system the chaotic dynamics interval disappears by a RTN scenario. The polyethyleneglycol concentration, and as a consequence the medium viscosity, has been set as a bifurcation parameter for the chaos–periodicity transition in an unstirred batch reactor. Nevertheless, it has not been excluded that the polymer also acts on the kinetics of the reactions.

In this paper we report the results of a kinetic study of the behaviour of the Ce(IV)-catalyzed Belousov–Zhabotinsky system at 20.0 °C in unstirred batch conditions in the absence and the presence of different amounts of the non-ionic micelle-forming surfactants hexaethylene glycol monodecyl ether ($C_{10}E_6$) and hexaethylene glycol monotetradecyl ether ($C_{14}E_6$). These two surfactants allow us to vary[24] the medium viscosity and the extent of the increase is not dependent on the alkyl chain length. In addition, they do not react with the components of the BZ systems. This has been verified by monitoring the UV–VIS spectra of the Ce(IV) species in sulfuric acid solution as a function of both the surfactant concentration and the time. It has been found that, in all cases examined, the spectra do not show any significant change with respect to that obtained in aqueous acidic solution.

In order to obtain further useful information we have studied the kinetics of oxidation of malonic acid by cerium(IV) species in the absence and presence of the two non-ionic surfactants over a wide concentration range. This latter process, as is well known, is an important component

of the oscillatory BZ reaction. Moreover, the effects of the addition of increasing amount of surfactant on the behaviour of the stirred BZ system have also been monitored.

Experimental methods

Potassium bromate, $Ce(SO_4)_2 \cdot 4H_2O$, malonic acid, hexaethylene glycol monodecyl ether, hexaethylene glycol monotetradecyl ether and sulfuric acid were of commercial analytical quality (Fluka) and used without further purification. Deionized water from reverse osmosis (Elga, model Option 3), having a resistivity higher than 1 MΩ cm, was used to prepare all solutions. Stock solutions of sulfuric acid were standardized by acid–base titration.

All the oscillating mixtures for the kinetic runs and the Ce(IV)–MA subsystems were obtained from freshly prepared stock solutions in 1.00 mol dm^{-3} sulfuric acid. The unstirred experiments were performed in a batch reactor and the dynamics of the system were monitored by following the Ce(IV) absorbance changes at 320 nm using quartz UV grade spectrophotometer cuvettes (1 × 1 × 4 cm^3). A double beam spectrophotometer (Varian, series 634) was used. The cross-sectional area of the spectrophotometer light beam was 30 mm^2. The volume spanned by the beam was 300 mm^3 (7.5% of the total volume) and was located 2 cm away from the liquid/air interface, 1 cm away from the bottom of the cuvette and about 0.4 cm away from the sides. The spectrophotometer was connected to an IBM compatible PC for data acquisition by an analog to digital board converter with a 12 bit resolution. The absorbance was recorded with a sampling time (τ_s) of 1 s. Time series points were recorded and stored in the computer for data analysis.

The spectra analysis was performed by fast Fourier transform (FFT) on sequential 1024 point portions of a time series. In order to increase the spectral resolution, we applied the zero filling technique. The short time fragments (1024 points) were transformed into longer time series sequences (2048 points) by adding a constant value equal to the minimum of the signal amplitude at the end of the fragments. In this way the spectral resolution $\Delta f = 1/N \tau_s$, where N is the number of points of the considered time fragment and τ_s is the sampling time, was doubled. Discontinuities at the window edges have been reduced by multiplying the considered data by a Hanning window function. This operation suppressed side lobes, which would otherwise be produced in the power spectrum of the signal.

The following concentrations of reactants stock solutions were used: Ce(IV) 0.004 mol dm^{-3}, malonic acid 0.30 mol dm^{-3}, KBrO$_3$ 0.09 mol dm^{-3}.

The surfactant concentration was varied in the range 1 × 10^{-4}–4.3 × 10^{-4} mol dm^{-3}.

The oscillator was started by mixing equal volumes of reactant solutions in a flask. This solution was stirred for 10 min without surfactant with a Teflon-coated magnetic stirrer of 1 cm length, at a constant high stirring rate; then the surfactant solution at the desired concentration was added and the final solution was stirred for about 2 min. The solution was then poured into the cuvette until the sample reached the top, and measurement of the signal began.

The kinetics of the oxidation of the malonic acid by cerium(IV) were studied in the absence and presence of the two non-ionic surfactants. In all cases studied, a large excess of organic substrate over the Ce(IV) species was used. The observed pseudo-first-order rate constants, k_{obs}, were obtained from the linear least-squares fit of the plot of $\ln(A_t - A_\infty)$ vs. time (A = absorbance) and were reproducible to within ±3%. The k_{obs} values were found to be independent of the initial Ce(IV) concentration and, consequently, the oxidation rates are first order with respect to the oxidizing species. The kinetic runs in stirred batch conditions were carried out spectrophotometrically by recording the changes in the Ce(IV) absorbance at 320 nm with a computer-controlled Beckman model DU-640 spectrophotometer, equipped with thermostatted compartments for 1.00 cm cuvettes and an appropriate magnetic stirring apparatus. The following concentrations of the stock solutions were used: Ce(IV) 1.60 × 10^{-3} mol dm^{-3}, malonic acid 0.400 mol dm^{-3}, KBrO$_3$ 0.12 mol dm^{-3}. The surfactant concentration was varied in the range 1 × 10^{-4}–4 × 10^{-2} mol dm^{-3}.

For these kinetic measurements a wider surfactant concentration range has been used in order to better establish the role played by the surfactant on the behaviour of the BZ system.

The temperature of all the experiments was regulated to 20.0 ± 0.1 °C with a thermostat Heto model DT HetoTerm.

Critical micelle concentrations of the two non-ionic surfactants used were determined, in the presence of the components of the BZ mixture without the catalyst, by surface tension measurements with a KSV–Sigma 70 automatic tensiometer.

Results and discussions

1.   Critical micelle concentrations

The critical micelle concentrations of $C_{10}E_6$ and $C_{14}E_6$ were obtained from the typical plots of the surface tension *vs.* the logarithm of the surfactant concentration. The c.m.c. data obtained are 1.6×10^{-4} and 1.3×10^{-6} mol dm^{-3} for $C_{10}E_6$ and $C_{14}E_6$, respectively. Under the experimental conditions of this work the c.m.c. values are slightly lower than those obtained[23c,28] in aqueous solution. The lower c.m.c. values can be attributed both to the presence of organic compounds and the very high value of the ionic strength.

2.   Ce(IV)-catalyzed BZ system behaviour in unstirred batch conditions

Fig. 1(a) shows a typical spectrophotometric time series recording of the BZ system in the absence of both stirring and surfactant. Perusal of this figure suggests that two transitions occurs. At the first transition the system passes from a periodic to an aperiodic behaviour and, then, at the second one the periodic behaviour appears once again. This behaviour can be referred to as a periodicity → chaos → periodicity transition, since it has been previously[6] shown that the aperiodic behaviour can be considered as an example of chaotic transient. This is confirmed by a FFT, shown in Fig. 1(c), of the spectrophotometric recording evidenced in Fig. 1(b). A broadband spectrum typical of chaotic systems is obtained. The broadband spectrum does not discriminate between chaos and random motion. Nevertheless, this system[6] shows the dependence on the initial conditions which is the major distinctive signature of chaos. Actually the chaotic regime observed in Fig. 1(b) is bounded by two quasiperiodic zones. The existence of a torus can be detected at the onset of chaos and at its end. Moreover, a Ruelle–Takens–Newhouse scenario[7] occurs. The chaotic behaviour has been attributed[7] to the interplay between chemical kinetics and diffusion-convective processes.

As for the oscillatory behaviour of the BZ system in the presence of $C_{10}E_6$, it has been found that the spectrum is not distinguishable from that obtained in the absence of surfactant until the surfactant concentration reaches a given concentration value. It is interesting to note that this value coincides with the critical micelle concentration obtained by surface tension measurement. It has been found, also in this case, that the Fourier transform of the signal shows a typical broadband spectrum like that depicted in Fig. 1(c). Since either chaos or random motion give broadband spectra it is not possible to distinguish between them from the Fourier transform alone; even if there is no reason to believe that the presence of surfactant induces a transition from chaos to random motion. Thus, it can be deduced that the behaviour of the BZ system in the presence of $C_{10}E_6$ at a concentration below the c.m.c. is a manifestation of chaos. Beyond the critical micelle concentration a new feature in the behaviour of the BZ system appears. In fact, as can be seen in Fig. 2(a)–(c) in the presence of 3.2×10^{-4} mol dm^{-3} of $C_{10}E_6$ the BZ system shows periodic behaviour instead of the aperiodic pattern. Fig. 2(c) is a typical pattern of a periodic signal and it is also possible to observe the fundamental frequencies and a few harmonics. In order to investigate the transition scenario as a function of surfactant concentration, series of measurements have been performed over the concentration range $1.8 \times 10^{-4} < [C_{10}E_6]/\text{mol dm}^{-3} < 2.8 \times 10^{-4}$. The temporal series monitored in this concentration range is shown in Fig. 3(a). The Fourier transform depicted in Fig. 3(c) clearly shows the existence of two frequencies, not rationally related, and their combinations. This pattern is characteristic of quasi-periodic motion.

The effects on the behaviour of the Belousov–Zhabotinsky system due to the addition of different amounts of surfactant can be explained taking into account that the solution viscosity[24] increases with increasing surfactant concentration. At very low surfactant concentration the contribution of the monomers to the viscosity is negligible (see Introduction) and the BZ system shows the same behaviour as in aqueous solution. When the solution viscosity increases the BZ system shows different patterns.
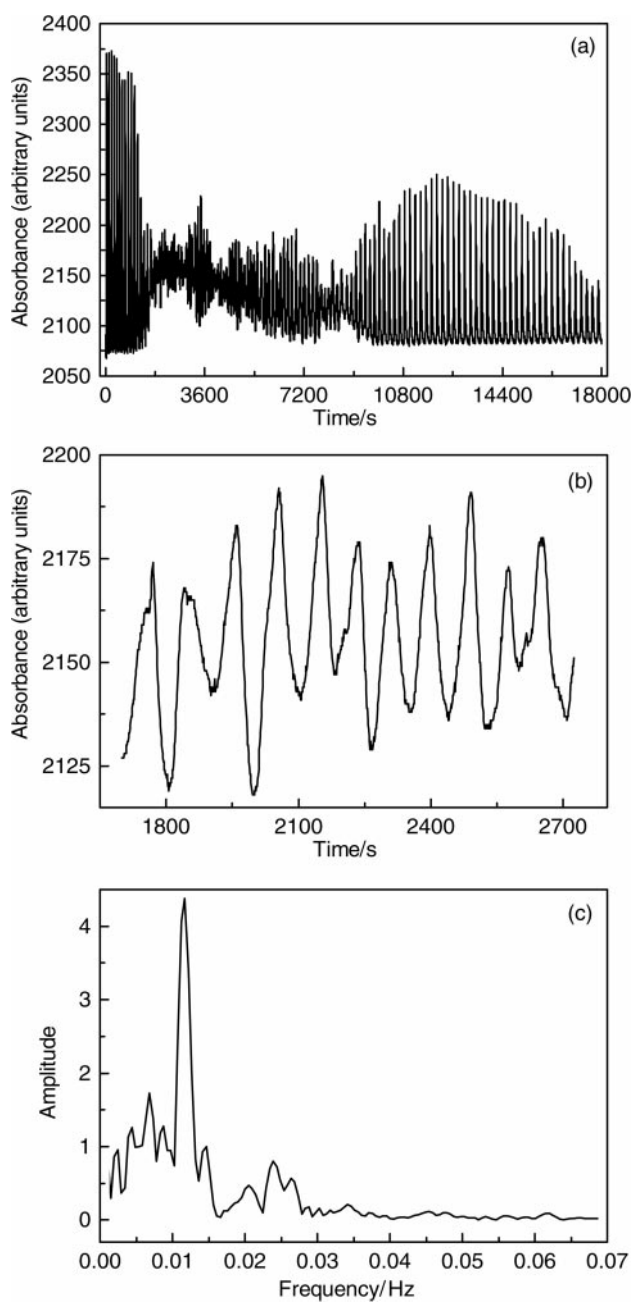
Fig. 1 (a) Typical spectrophotometric recording of the Ce(IV) absorbance in the absence of stirring and without $C_{10}E_6$. (b) Detail of (a) in the range 1800–2700 s. (c) Fourier transform of (b) evidencing a broadband spectrum typical of chaotic signal. $\lambda = 320$ nm, $\tau_s = 1$ s, $T = 20\,^\circ$C.

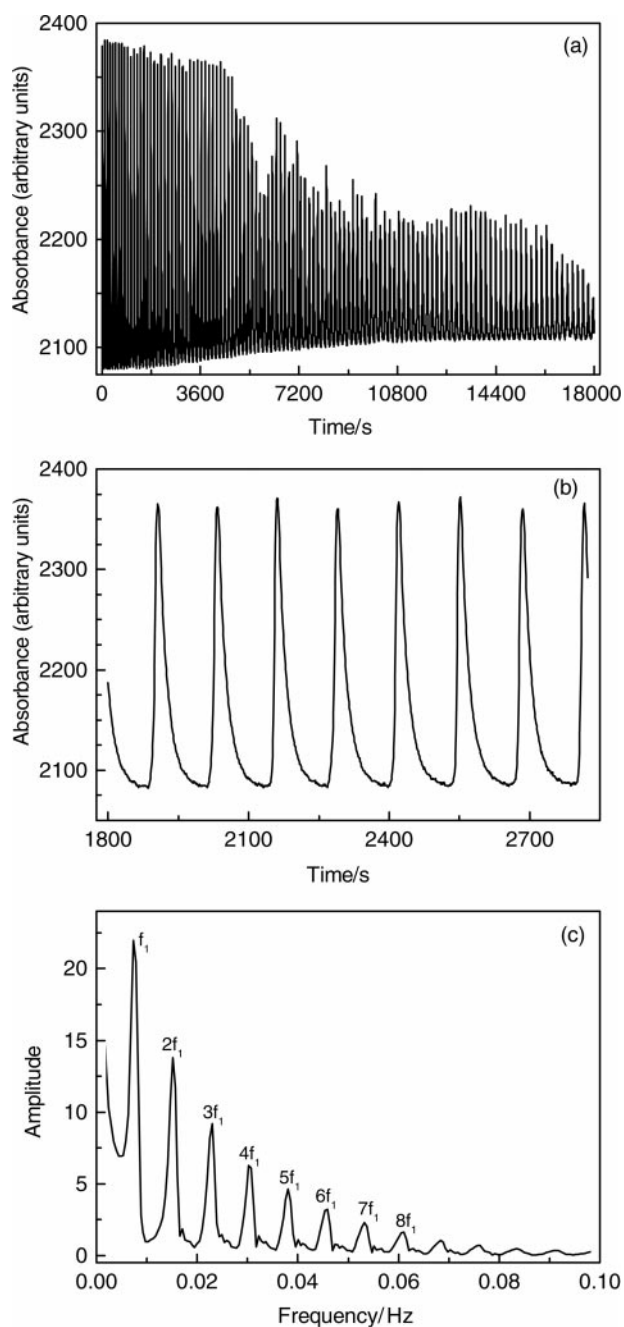**Fig. 2** (a) Typical spectrophotometric recording of the Ce(IV) absorbance in the absence of stirring with 3.2×10^{-4} mol dm^{-3} of C$_{10}$E$_6$. (b) Detail of (a) in the range 1800–2700 s. (c) Fourier transform of (b) showing the fundamental frequencies and a few harmonics. This is a typical pattern of a periodic signal. Experimental conditions are the same as in Fig. 1.
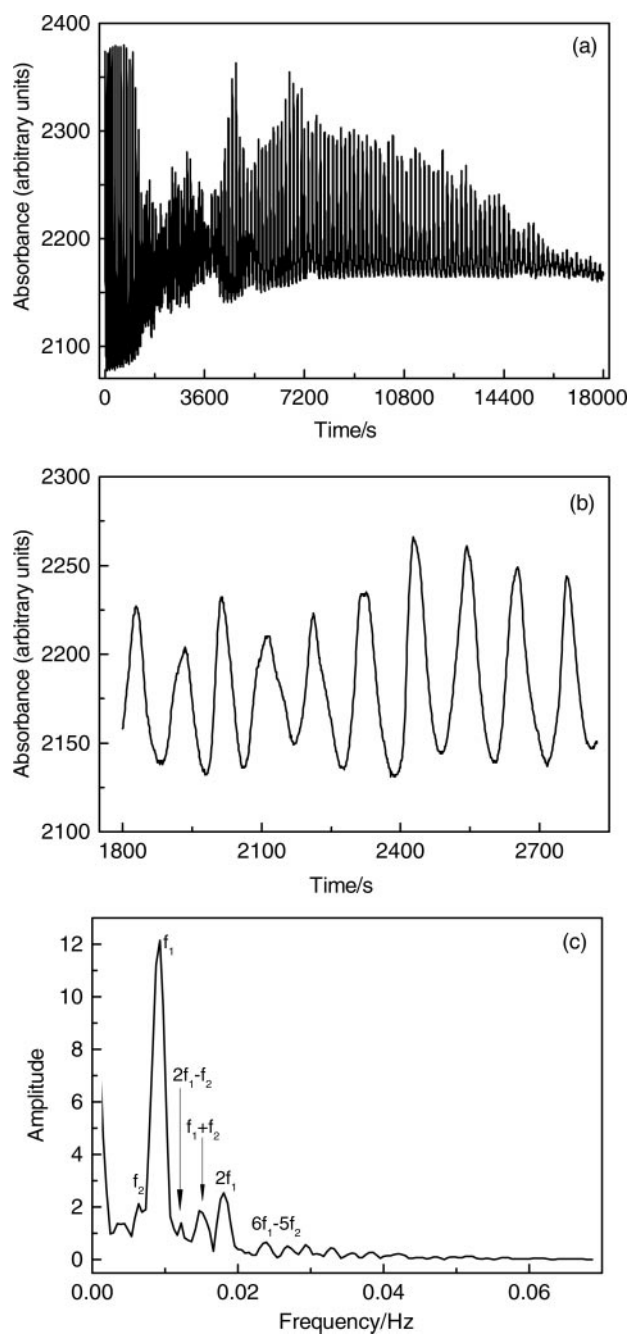
Fig. 3 (a) Typical spectrophotometric recording of the Ce(IV) absorbance in the absence of stirring with 3.1×10^{-4} mol dm^{-3} of $C_{10}E_6$. (b) Detail of (a) in the range 1800–2700 s. (c) Fourier transform of (b) showing two frequencies not rationally related and their combinations; typical of a quasi-periodic dynamics. Experimental conditions are the same as in Fig. 1.

We can conclude that the increase in medium viscosity induces the disappearance of the chaotic behaviour and this sets the viscosity as an important control parameter for the chaos of the system.

The experimental results can be summarized in the following scheme

<div align="center">

chaotic oscillation

$$1 \times 10^{-4} \leqslant [C_{10}E_6]/\text{mol dm}^{-3} \leqslant 2.9 \times 10^{-4}$$

↓

quasi-periodic oscillation

$$3.0 \times 10^{-4} \leqslant [C_{10}E_6]/\text{mol dm}^{-3} \leqslant 3.1 \times 10^{-4}$$

↓

periodic oscillation

$$3.2 \times 10^{-4} \leqslant [C_{10}E_6]/\text{mol dm}^{-3} \leqslant 4.3 \times 10^{-4}$$

</div>

The observed sequence sets the surfactant concentration as a bifurcation parameter of the unstirred BZ system and, as the parameter is changed, a chaotic attractor appears or disappears depending on whether the surfactant concentration decreases or increases. This scenario in the phase plane corresponds to the strange attractor → torus → cycle transition. This type of behaviour could be interpreted using a RTN scenario where the system undergoes three Hopf bifurcations.

Analogous effects on the behaviour of the unstirred BZ system have been monitored in the presence of different amounts of the non-ionic surfactant $C_{14}E_6$ (the figures are not shown for the sake of simplicity).

3. Kinetics of the Ce(IV)–malonic acid subsystem

In order to better ascertain the role played by the surfactant in inducing the behaviour discussed in the above section we have studied the kinetics of the cerium(IV) oxidation of malonic acid in the presence of the surfactants $C_{10}E_6$ and $C_{14}E_6$ over a wide surfactant concentration range. As is well known[29–32] organized surfactant assemblies can affect the rates and the mechanism of a chemical reaction by selectively sequestering the reagent substrates by means of electrostatic and/or hydrophobic interactions. The study of the kinetics of reactions offers the twofold advantage of affording insight into the reactivity and the reaction mechanism in these reaction media[30–32] and of obtaining useful information on the solubilization[30–32] of the reagents and, in some cases, the location of the solubilizate in the micellar structure.
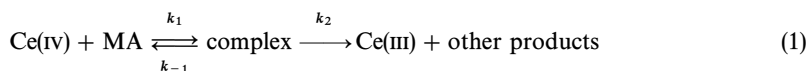
First, we have studied the kinetics of the redox process in the absence of surfactant at various substrate concentrations. Table 1 collects the observed pseudo-first-order rate constants obtained for this reaction. It can be noted that the k_{obs} values depend on the MA concentration. The plot of

Table 1 Observed pseudo-first-order rate constants $k_{obs}/10^{-2}$ s^{-1} for the Ce(IV) oxidation of MA at varying substrate concentrations. $t = 20.0\,°C$

$[MA]/10^{-2}$ mol dm^{-3}	$k_{obs}{}^a/10^{-2}$ s^{-1}
0.5	0.461
1.00	0.807
2.00	1.48
5.00	3.3
10.0	6.7

^{a} $k_2 = 0.101 \pm 0.001$ s^{-1}; $K_m = 0.107 \pm 0.003$ mol dm^{-3}.

k_{obs} *vs.* [MA] is curved, whereas a linear trend with positive intercept is obtained when $1/k_{obs}$ is plotted as a function of 1/[MA]. This indicates that the reaction order with respect to substrate lies between zero and unity and that the oxidation process can be interpreted by the sequential Michaelis–Menten-like mechanism given in eqn. (1). This mechanism involves[33–38] initial complex formation between the organic substrate and the reactive cerium(IV) species. Subsequently, the intermediate complex decomposes in the rate-determining electron-transfer step yielding a free carbon radical and the cerium(III) species. The final reaction products are obtained by the subsequent fast oxidation of the organic radical.

This type of mechanism has been proposed previously[33–38] for the oxidation of a variety of organic substrates by cerium(IV) in sulfuric acidic media (*i.e.*, malonic acid and its alkyl derivatives, tartronic, tartaric, citric, glycolic, benzilic, lactic, substituted mandelic acids, *etc.*).

$$\text{Ce(IV)} + \text{MA} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \text{complex} \xrightarrow{k_2} \text{Ce(III)} + \text{other products} \qquad (1)$$

According to the reaction mechanism (1) the rate constant k_{obs} is equal to $k_2[\text{MA}]/(K_m + [\text{MA}])$, where $K_m = (k_{-1} + k_2)/k_1$, and, consequently, the $1/k_{obs}$ *vs.* 1/[MA] plot yields $1/k_2 (=\text{intercept})$ and $K_m/k_2 (=\text{slope})$. The k_2 and K_m values obtained from this plot are also reported in Table 1. It should be noted that, if the rate constant k_2 is much smaller than k_{-1}, the parameter K_m reduces to k_{-1}/k_1 and represents the reciprocal of the equilibrium constant for the intermediate complex formation.

For the Ce(IV)–MA reaction previously[34a] studied at 30 °C in 1.5 mol dm^{-3} sulfuric acid medium, Kasperek *et al.* obtained k_2 and K_m values of 0.53 s^{-1} and 0.53 mol dm^{-3}, respectively. The k_2 and K_m values obtained in the present work are lower than those obtained by Kasperek *et al.* The difference can be attributed to the different experimental conditions used, *i.e.*, lower temperature and sulfuric acid concentration. As to the effects of added surfactants on the redox reaction under examination, it has been found that addition of increasing amounts up to a concentration value of 0.04 mol dm^{-3} of either $C_{10}E_6$ or $C_{14}E_6$ has no significant influence on the rate of the redox process (the data are not shown for sake of simplicity).

The observed surfactant effects on the redox reactions can be qualitatively interpreted by the pseudophase model[29,30] bearing in mind that the reactive Ce(IV) species, as has been previously suggested,[37,39] in sulfuric (or sulfate) acidic media with $[\text{HSO}_4^-]$ (or $[\text{SO}_4^{2-}]) \gg [\text{Ce(IV)}]$), may exist in a number of sulfate and protonated sulfate complex forms, which may be neutral species [*e.g.*, $\text{Ce(SO}_4)_2$] or bear either positive [*e.g.*, $\text{Ce(HSO}_4)_3^+$] or negative [*e.g.*, $\text{Ce(SO}_4)_3^{2-}$, $\text{H}_2\text{Ce(SO}_4)_4^{2-}$] charges. From a kinetic point of view, the existence of various cerium(IV) complexes implies serious difficulties[37] for the identification of the actual reacting complex involved in the oxidation process. However, all these complexes do not seem to take part significantly in the overall redox rate[35,37] and only limited complex species, usually the anionic ones, have been assumed by different investigators as the reactive cerium(IV) species. This hypothesis has been corroborated[40] by Cavasino *et al.* They have substantiated the view that negatively charged cerium(IV) species are involved in the redox process by examining the effects of either cationic or anionic micelle-forming surfactant micelles on the reaction rate of Ce(IV) with benzyl malonic acid. These two types of differently charged micelles influence the rate of the redox process in an opposite way. Therefore, on the basis of the pK_a values[41] for the first and second dissociations of the malonic acid and the experimental conditions used it is reasonable to consider the undissociated acid to be the predominant species present in solution. Since it has been previously[42] suggested that the Ce(IV) species do not interact with non-ionic micelles only the partition of the neutral substrate between the aqueous pseudophase and the micellar pseudophase has to be considered. This implies that two reaction pathways involving the hydrophilic Ce(IV) species in the aqueous phase and the MA solubilized in both the aqueous region and the micellar pseudo-phase contribute to the progress of the redox reaction. According to this reaction scheme it has to be expected that the distribution of MA will cause a small reduction in the substrate concentration in water and, as a consequence, determine a small inhibitory surfactant effect on the reaction rate. Moreover, this reduction would increase as the surfactant concentration increases. Since this effect has not been detected we have to draw the conclusion that the redox reaction takes place only in the aqueous pseudophase and no partition of the malonic acid occurs.
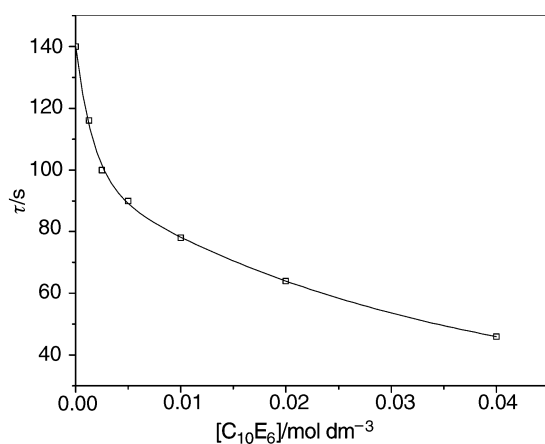
Fig. 4 Plot of τ against $[C_{10}E_6]$ for the stirred BZ system. $\lambda = 320$ nm, $T = 20\,°C$.
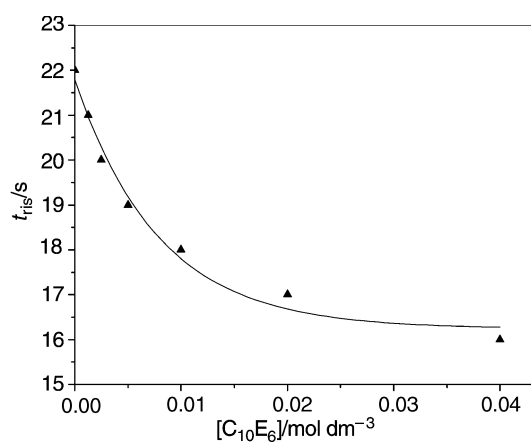

Fig. 5 Plot of t_{ris} against $[C_{10}E_6]$ for the stirred BZ system. Experimental conditions are the same as in Fig. 4.
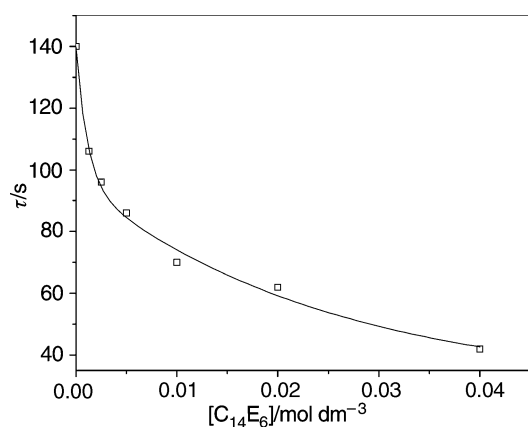

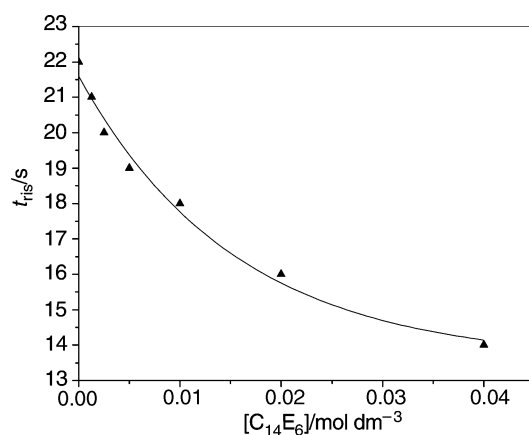**Fig. 6** Plot of τ against $[C_{14}E_6]$ for the stirred BZ system. Experimental conditions are the same as in Fig. 4.

Fig. 7 Plot of t_{ris} against $[C_{14}E_6]$ for the stirred BZ system. Experimental conditions are the same as in Fig. 4.

This result is reasonable and in accordance with previous[40] suggestions. In fact, it has been observed that binding of monosubstituted malonic acid to different types of micelles depends significantly on the hydrophobicity of the group present in the malonic acid. Thus, MA, having the more hydrophilic character, is the less solubilized substrate in the micellar pseudophase as compared to the other monosubstituted malonic acid.

4. Ce(IV)-catalyzed BZ system behaviour in stirred batch conditions

In order to provide additional information on the effect of non-ionic micelles, hence the medium viscosity, we have monitored the behaviour of the BZ system in the absence and presence of different amounts of non-ionic surfactants in stirred batch conditions. In the absence of surfactants, oscillations in the BZ system have been found to begin after an induction period (I. P.) of 16 min with an oscillation period (τ) and the duration of the rising portion (t_{ris}) of an oscillatory cycle of 140 and 22 s, respectively. We wish to point out that the oscillatory parameters values reported in this work are the mean of five different experiments and both the τ and t_{ris} values represent[43] the means of the first five oscillatory cycles.

The presence of surfactant does not influence the oscillatory behaviour of the stirred BZ system until the surfactant concentration reaches a given concentration value. In fact, the oscillatory parameters keep the same values as those obtained in the absence of surfactants. As for the BZ system in unstirred batch conditions, the concentration at which the change in the behaviour occurs coincides with the critical micelle concentration. Once the c.m.c. is reached the oscillatory behaviour of the BZ system changes. The presence of micelles in the reaction medium has no dramatic effects on the I. P. while either $C_{10}E_6$ or $C_{14}E_6$ markedly influence, to the same extent, τ and t_{ris}.

Fig. 4–7 show that both τ and t_{ris} decrease and tend to reach a plateau value at high surfactant concentrations.

The findings can be explained by considering that many substances react simultaneously during the induction period but, due to their hydrophilic nature, the reactions take place, as we have found for the MA oxidation by Ce(IV), only in the aqueous pseudophase.

As to the decrease in both τ and t_{ris} as a function of surfactant concentration, it has to be take into account that, as shown by Noszticzius *et al.*,[44] the reaction of the malonyl radicals, which are formed during the reaction of Ce(IV) with malonic acid, with the $BrO_2 \cdot$ radicals (which are formed during the autocatalytic reaction step) occurs at a nearly diffusion-controlled rate. As a consequence, an increase in the medium viscosity hampers this process and, at the same time, promotes the oxidation of Ce(III) by $BrO_2 \cdot$ radicals.

This aforementioned result together with those found above leads to the concluding suggestion that significant changes in the oscillatory behaviour of the Belousov–Zhabotinsky system occur when the medium viscosity is increased.

Acknowledgement

References

1 A. M. Zhabotinsky, *Chaos*, 1991, **1**, 379.
2 S. K. Scott, *Chemical Chaos*, Oxford University Press, Oxford, 1991.
3 I. R. Epstein, *Nature*, 1995, **374**, 321.
4 I. R. Epstein and J. A. Pojman, *An Introduction to Nonlinear Chemical Dynamics*, Oxford University Press, Oxford, 1998.
5 G. Nicolis and J. Portonow, *Chem. Rev.*, 1973, **73**, 365.
6 M. Rustici, M. Branca, C. Caravati and N. Marchettini, *Chem Phys. Lett.*, 1996, **263**, 429.
7 M. Rustici, C Caravati, E. Petretto, M. Branca and N. Marchettini, *J. Phys. Chem. A*, 1999, **103**, 6564.
8 S. K. Scott, B. Peng, A. S. Tomlin and K. Showalter, *J. Chem. Phys.*, 1991, **94**, 1134.
9 B. R. Johnson, S. K. Scott and B. W. Thompson, *Chaos*, 1997, **7**, 350.
10 P. V. Coveney and A. N. Chaudry, *J. Chem. Phys.*, 1992, **97**, 7448.
11 P. Ruoff and R. M. Noyes, *J. Phys. Chem.*, 1985, **89**, 1339.
12 J. Kawahito and Fujieda, *Thermochim. Acta*, 1992, **210**, 1.
13 P. E. Strzhak and A. L. Kawczynski, *J. Phys. Chem.*, 1995, **99**, 10830.
14 J. Wang, P. G. Sorensen and F. Hynne, *J. Phys. Chem.*, 1994, **98**, 725.
15 J. A. Pojman and I. Epstein, *J. Phys. Chem.*, 1990, **94**, 1966.
16 J. A. Pojman, I. R. Epstein and I. P. Nagy, *J. Phys. Chem.*, 1991, **95**, 1306.
17 J. A. Pojman, A. Komlosi and I. P. Nagy, *J. Phys. Chem.*, 1996, **100**, 16209.
18 G. Bazsa and I. R. Epstein, *J. Phys. Chem.*, 1985, **89**, 3050.
19 I. Nagypal, G. Bazsa and I. R. Epstein, *J. Am. Chem. Soc.*, 1986, **108**, 3635.
20 H. Miike, S. C. Muller and B. Hess, *Chem. Phys. Lett.*, 1988, **144**, 515.
21 B. Legawiec and A. L. Kawczynski, *J. Phys. Chem. A*, 1997, **101**, 8063.
22 T. Yamaguchi, L. Kuhnert, Zs. Nagy-Ungvarai, S. C. Muller and B. Hess, *J. Phys. Chem.*, 1991, **95**, 5831.
23 (*a*) P. Mukerjee, *J. Colloid Sci.*, 1964, **19**, 722; (*b*) D. C. Robins and L. Thomas, *J. Colloid Interface Sci.*, 1968, **26**, 415; (*c*) P. Becher, in *Nonionic Surfactants*, ed. M. J. Schick, Marcel Dekker, New York, 1966.
24 M. Abe and K. Ogino, *Mixed Surfactant Systems*, Marcel Dekker, New York, 1993, p. 1.
25 N. Marchettini and M. Rustici, *Chem. Phys. Lett.*, 2000, **317**, 647.
26 M. Rustici, M. Branca, A. Brunetti, C. Caravati and N. Marchettini, *Chem. Phys. Lett.*, 1988, **293**, 145.
27 J. P. Eckmann and D. Ruelle, *Rev. Mod. Phys.*, 1985, **57**, 617.
28 V. Degiorgio, in *Physics of Amphiphiles: Micelles Vesicles and Microemulsioni*, ed. V. Degiorgio and M. Conti, North-Holland, Amsterdam, 1985.
29 (*a*) I. V. Berezin, K. Martinek and A. K. Yatsimirsckii, *Russ. Chem. Rev.*, 1973, **42**, 787; (*b*) J. H. Fendler and E. J. Fendler, *Catalysis in Micellar and Macromolecular Systems*, Academic Press, New York, 1975; (*c*) L. S. Romsted, in *Micellization, Solubilization and Microemulsions*, ed. K. L. Mittal, Plenum Press, New York, 1977, vol. 2, p. 509; (*d*) C. A. Bunton, in *Solution Chemistry of Surfactants*, ed. K. L. Mittal, Plenum Press, New York, 1979, vol. 2, p. 519; (*e*) J. H. Fendler, *Membrane Mimetic Chemistry. Characterization and Application of Micelles, Microemulsions, Monolayers, Bilayers, Vesicles, Host–Guest Systems and Poly-ions*, Wiley, New York, 1982; (*f*) L. S. Romsted, in *Surfactants in Solution*, ed. K. L. Mittal and B. Lindman, Plenum Press, New York, 1983, vol. 2, p. 1015; (*g*) C. A. Bunton and G. Savelli, *Adv. Phys. Org. Chem.*, 1986, **22**, 213; (*h*) J. Burgess and E. Pelizzetti, *Gazz. Chim. Ital.*, 1988, **12**, 803.
30 (*a*) G. Calvaruso, F. P. Cavasino, C. Sbriziolo and M. L. Turco Liveri, *J. Chem. Soc., Faraday Trans.*, 1995, **91**, 1075 and references therein; (*b*) G. Calvaruso, F. P. Cavasino and C. Sbriziolo, *J. Chem. Soc., Faraday Trans.*, 1996, **92**, 2263 and references therein.
31 F. P. Cavasino, S. Di Stefano and C. Sbriziolo, *J. Chem. Soc., Faraday Trans.*, 1997, **93**, 1585.
32 F. P. Cavasino, C. Sbriziolo and M. L. Turco Liveri, *J. Phys. Chem. B*, 1998, **102**, 5050 and references therein.
33 Y. F. Chen, H. P. Lin, S. S. Sun and J. J. Jwo, *Int. J. Chem. Kinet.*, 1996, **28**, 345.
34 (*a*) G. J. Kasperek and and T. C. Bruice, *Inorg. Chem.*, 1971, **10**, 382; (*b*) J. J. Jwo and R. M. Noyes, *J. Am. Chem. Soc.*, 1975, **97**, 5422; (*c*) S. Barkin, M. Bixon, R. M. Noyes and K. Bar-Eli, *Int. J. Chem. Kinet.*, 1978, **10**, 619.
35 P. Ruoff and G. Nevdal, *J. Phys. Chem.*, 1989, **93**, 7802.
36 P. O. Kvernberg, E. W. Hansen, B. Pedersen, A. Rasmussen and P. Ruoff, *J. Phys. Chem. A*, 1997, **101**, 2327 and references therein.
37 (*a*) G. Arcoleo, G. Calvaruso, F. P. Cavasino and C. Sbriziolo, *Inorg. Chim. Acta*, 1977, **23**, 227 and references therein; (*b*) G. Calvaruso, F. P. Cavasino, C. Sbriziolo and R. Triolo, *Int. J. Chem. Kinet.*, 1983, **15**, 417 and references therein; (*c*) G. Calvaruso, F. P. Cavasino and C. Sbriziolo, *Int. J. Chem. Kinet.*, 1984, **16**, 1201.
38 S. B. Hanna and S. A. Sarac, *J. Org. Chem.*, 1977, **42**, 2063 and references therein.

39 (*a*) T. J. Hardwick and Robertson, *Can. J. Chem.*, 1951, **29**, 828; (*b*) L. T. Bugaenko and H. Kuan-Lin, *Russ. J. Inorg. Chem.*, 1963, **8**, 1299.
40 F. P. Cavasino, R. Cervellati, R. Lombardo and M. L. Turco Liveri, *J. Phys. Chem. B*, 1999, **103**, 4285.
41 (*a*) G. Arcoleo, F. P. Cavasino and E. Di Dio, *Gazz. Chim. Ital.*, 1978, **108**, 597; (*b*) G. Calvaruso, A. I. Carbone and F. P. Cavasino, *J. Chem. Soc., Dalton Trans.*, 1985, 1683 and references therein.
42 G. Calvaruso, F. P. Cavasino and C. Sbriziolo, *J. Chem. Soc., Faraday Trans.*, 1991, **87**, 3033.
43 A. M. Zhabotinsky, F. Buchholtz, A. B. Kiyatkin and I. R. Epstein, *J. Phys. Chem.*, 1993, **97**, 7578.
44 H. D. Försterling and Z. Noszticzius, *J. Phys. Chem.*, 1989, **93**, 2740.