

New substrates in the oscillatory uncatylsed bromate system employing mixed media

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Abstract. The oscillatory characteristics of seven new substrates in the uncatylsed bromate system are presented. Mixed media consisting of aqueous-organic mixtures have been employed for the first time in the study of chemical oscillators. This is an important breakthrough in the study of chemical oscillators in a pioneering attempt at bringing new types of compounds within the purview of the investigation.

Keywords. Oscillatory reaction; uncatylsed bromate system; new substrates; mixed media.

1. Introduction

The oscillatory system with acidified bromate in the absence of a metal ion employed diazonium salt as the substrate (Kuhnert and Linde 1977). The scope of the system was considerably extended by employing different substrates including phenols and anilines (Koros and Orban 1978; Farage and Janjic 1982; Gupta and Srinivasulu 1982). Mechanistic aspects of the uncatylsed system have been presented (Orban *et al* 1979; Herbine and Field 1980).

The potentiometric follow up of the oscillatory system of the Belousov–Zhabotinsky (B–Z) type with and without the metal ion has brought to light several new facts of considerable significance (Ramaswamy 1982; Ramaswamy and Ramanathan 1983; Ramaswamy and Krishnaratnam 1986).

Stationary potential measurements relating to the uncatylsed bromate system have not only furnished deeper insight into the mechanistics of the reaction but also provided a simple technique for the quantitative determination of the concentration (nearly 10^{-4} M) of various organic and inorganic substances (Ramaswamy and Lalitha 1990).

A serious limitation in all oscillatory systems reported hitherto has been the limited solubility of the substrate. The unfortunate consequence of such limited solubility in water is two-fold.

- (i) A large number of interesting compounds cannot be employed as substrates.
- (ii) The limited concentration range of the substrate employed has often provided incomplete information about the system studied.

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The use of aqueous-organic mixed media in the Briggs-Rauscher and Belousov-Zhabotinsky reactions enabled the study of the oscillatory behaviour of a large number of new substrates (water-insoluble) (Lalitha and Ramaswamy 1992a; Lalitha *et al* 1992). The use of mixed media has enabled the quantitative estimation ($\sim 10^{-4}$ M) of several water insoluble substances (Lalitha and Ramaswamy 1992d).

The use of mixed media leading to an increase in the solubility of the substrate has considerably widened the scope of the investigation as described in the present communication.

2. Materials and methods

All the chemicals used were of AnalaR grade and used without further purification. Triply distilled water was used for preparing all the solutions. The potential oscillations were recorded using a Siemens Kompensograph to which a platinum indicator electrode/bromide selective electrode and a saturated calomel electrode were connected through a potassium nitrate salt bridge. The temperature was maintained constant ($32 \pm 0.1^\circ\text{C}$). The reaction was started by adding potassium bromate solution to all other constituents kept well stirred in a polythene beaker. The total volume of the reaction mixture was kept constant (25 ml).

3. Results and discussion

The fact that oscillatory systems have hitherto been studied exclusively in aqueous media would necessitate comparison of the oscillatory behaviour of a certain substrate in pure aqueous medium with that in other mixed media. Gallic acid, a substrate well studied in the aqueous medium (Orban and Koros 1978; Ramaswamy and Krishnaratnam 1986), was chosen for the study. The mixed medium contained 80% of water and 20% (v/v) of organic solvent. The mixtures were homogeneous with the exception of benzene.

Table 1. Oscillatory behaviour of gallic acid in aqueous as well as aqueous-organic (20% v/v of organic solvent) media, conditions as in figure 1.

Solvent	T_{ind} (min)	T_{total} (min)	No. of oscillations	Time/ oscillation (min)	Amplitude (mV)	Potential range V (vs SCE)
Water	1.2	7.5	8	0.79	470	0.43-0.90
AN-water	0.1	5.0	8	0.61	360	0.58-0.94
THF-water	1.0	2.0	1	1.0	60	0.56-0.62
DMF-water	1.1	8.5	9 (4 large + 5 small)	0.82	370	0.43-0.80 (damped oscillations)
Benzene-water	0.3	3.5	10 (6 large + 4 small)	0.32	380	0.45-0.83 (damped oscillations)
1,4-Dioxan-water	3.5	10.5	11 (4 large + 7 small)	0.64	270	0.47-0.74 (damped oscillations)
DMSO-water		No oscillation; precipitation occurs				
Methanol-water		No oscillation; interaction occurs				

The solvents used were acetonitrile (AN), tetrahydrofuran (THF), dimethyl formamide (DMF), benzene, 1,4-dioxan, dimethylsulphoxide (DMSO) and methanol. The results obtained with gallic acid as the substrate in pure aqueous as well as in different aqueous-organic mixed media are presented in table 1.

In acetonitrile (20% v/v), the induction time and the time per oscillation are smaller than that in pure aqueous medium, the number of oscillations being the same (figure 1). The base and peak potentials are higher compared to those in pure aqueous medium. The smaller amplitude of 360 mV in acetonitrile (20% v/v) is a consequence of a higher base potential of 0.58 V (vs SCE) resulting from a faster rate of bromine formation. The increase in frequency of oscillations in acetonitrile (20% v/v) is due to an increase in the rate of consumption of bromine by the substrate as well as its rate of formation.

The results obtained with benzene (20% v/v) lend further support to these conclusions. The amplitude, induction time and time per oscillation are smaller than

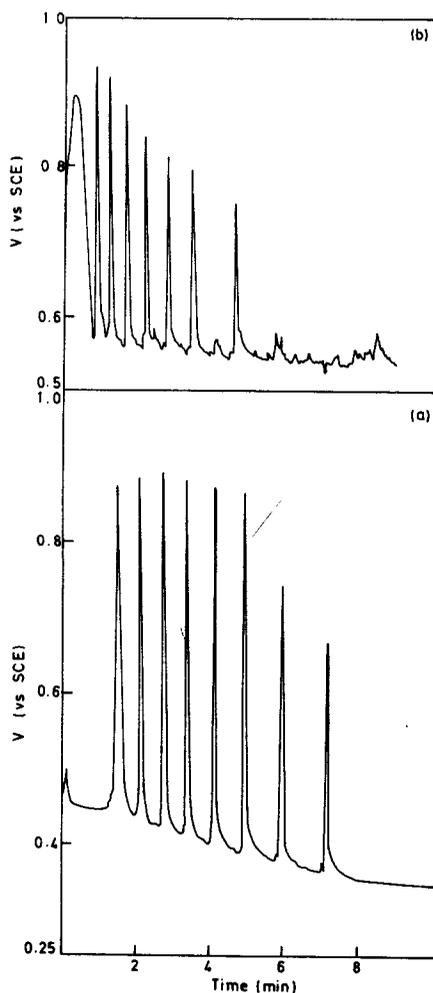


Figure 1. Oscillatory behaviour of gallic acid in (a) aqueous medium (b) acetonitrile (20% v/v) using Pt electrode. Concentration conditions: gallic acid - 0.02 M; sulphuric acid - 2 M; potassium bromate - 0.06 M, temperature: 32°C.

in aqueous medium. The peak value of 0.83 V (vs SCE) is probably due to the immiscibility of benzene with water and the higher solubility of bromine in benzene due to partitioning of bromine. In DMF (20% v/v) the induction time, total time and the time per oscillation are almost the same as those in pure aqueous medium. However, the oscillations are damped and have smaller amplitudes.

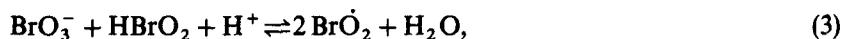
In dioxan (20% v/v), the system is characterised by the highest induction time, total duration and number of oscillations. But the amplitude of oscillations is small. In mixed media involving DMSO (20% v/v) or methanol (20% v/v), there are no oscillations. When DMSO (20% v/v) was used as the medium, there was vigorous reaction and precipitation when all the other constituents except potassium bromate were mixed. In a separate experiment, it was observed that bromine at lower concentrations was decolourised immediately on the addition of methanol. These interferences are responsible for the absence of the oscillatory behaviour in presence of DMSO or methanol (20% v/v). There was a single oscillation when THF (20% v/v) was employed as the medium.

Among the different mixed solvents used, the oscillatory behaviour of gallic acid is found to be satisfactory in mixed media involving 20% v/v of acetonitrile, DMF, benzene or 1,4-dioxan.

The alterations in the oscillatory behaviour of gallic acid in presence of acetonitrile can be understood in terms of the mechanism presented for the uncatalysed bromate oscillator. The sequence of the reaction involves the following steps:



The key role in the occurrence of oscillations is played by the concentration of Br^- . When the $[\text{Br}^-]$ falls below the critical value, i.e., $[\text{Br}^-] < [\text{Br}^-]_{\text{crit}}$, the system switches over to another state where bromine is produced by the following steps:



Reaction (3) is an autocatalytic step for the formation of $\text{Br}\dot{\text{O}}_2$. Then, the regeneration of bromide ions occurs by (6), thus repeating the cycle leading to oscillations.

In solution, complex formation between Br^- and Br_2 occurs according to the reaction,



The value of equilibrium constant (K_c) for the above reaction is ~ 16 in pure aqueous medium whereas its value is $\sim 10^7$ in pure acetonitrile. This shows that the K_c value in acetonitrile (20% v/v) would be much higher than that in pure aqueous medium (~ 250 , obtained by interpolation). Thus in acetonitrile (20% v/v), the concentration of Br^- falls below $[\text{Br}^-]_{\text{crit}}$ compared to that in pure aqueous medium. The concentration of free bromine also decreases as a result of (8).

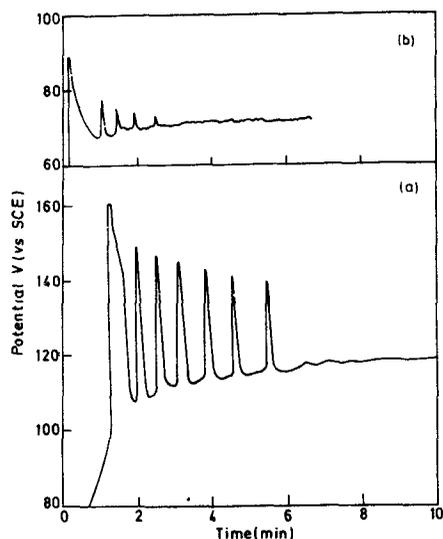


Figure 2. Oscillatory behaviour of gallic acid using bromide selective electrode in (a) aqueous medium (b) acetonitrile (20% v/v). Concentration conditions as in figure 1.

The decrease in $[\text{Br}^-]$ is confirmed by following the experiment using bromide selective electrode. In acetonitrile (20% v/v), the amplitude of oscillations, which is a measure of $[\text{Br}^-]$, is much smaller than that in pure aqueous medium (figure 2).

The decrease in the concentration of free bromine in presence of acetonitrile is confirmed by the optical density measurements. It is found that the optical density values for different concentrations of bromine in acetonitrile (20% v/v) are very much smaller than those in pure aqueous medium (Lalitha and Ramaswamy 1992d). For a system containing 10^{-4} M Br^- , 10^{-1} M H^+ and different concentrations of bromine, the optical density values obtained are given in table 2.

Further, the alterations observed in aqueous-acetonitrile medium can be attributed to the solvation effects. Bromination is an electrophilic reaction where Br^+ is the attacking agent. In pure aqueous medium the extent of solvation is more than in presence of acetonitrile (due to the higher dielectric constant of about 80 for water compared to ~ 37.5 for acetonitrile). Thus, the concentration of free Br^+ would be larger in acetonitrile (20% v/v) than that in pure water. This would lead to an increase in the rate of bromination in presence of acetonitrile, resulting in an increase in the frequency of oscillations.

The mixed medium containing acetonitrile 20% (v/v) is well suited for the study of the uncatalysed bromate system. The oscillatory behaviour of the system is nearer to that of the aqueous system when the percentage of acetonitrile is small. However, for a comparative study involving a large number of substrates, a concentration of 20% (v/v) has been employed.

The use of mixed media has enabled the study of several new substrates hitherto unreported in the uncatalysed bromate system. The results obtained with seven new substrates are presented in table 3. The substrates, being structurally different (figure 3), vary considerably in their reactivity with bromine.

The concentration conditions of different constituents employed for various

Table 2. Spectrophotometric data.[KBr] = 10^{-4} M, [H₂SO₄] = 10^{-1} M, λ = 460 nm

[Br ₂] × 10 ³ (M)	Optical density	
	in pure water	in acetonitrile (20% v/v)
2.5	0.35	0.20
7.5	1.13	1.05

Table 3a. Concentrations of different constituents for different substrates.

Temperature 32°C; acetonitrile: 20% (v/v).

Substrate (S)	[S] (M)	[H ₂ SO ₄] (M)	[KBrO ₃] (M)
Syringic acid	0.03	0.5	0.04
Propyl gallate	0.046	1.6	0.067
Veratric acid	0.03	0.5	0.017
Veratronic acid	0.02	0.5	0.03
<i>p</i> -Vanillin	0.024	0.71	0.10
2,5-Dihydroxy- 1,4-benzoquinone	0.006	1.0	0.08
Asaronic acid	0.02	1.6	0.04

Table 3b. Oscillatory characteristics of different substrates in aqueous-acetonitrile (20% v/v of acetonitrile) medium corresponding to the concentration conditions given in table 3a.

Substrate	<i>T</i> _{ind.} (min)	<i>T</i> _{total} (min)	No. of oscillations	Time/ oscillation (min)	Amplitude (mV)	Potential range V (vs SCE)
Syringic acid	1.3	4.5	3	1.07	290	0.51–0.80
Propyl gallate	0.4	6	6	0.94	370	0.48–0.85
Veratric acid	1	5	4	1.0	370	0.48–0.85
Veratronic acid	6.8	80	21	3.5	250	0.58–0.83
<i>p</i> -Vanillin	0.1	2.5	9	0.27	190	0.67–0.86
2,5-Dihydroxy- 1,4-benzoquinone	0.3	9	3	2.9	290	0.39–0.68
Asaronic acid	1	50	3	16.33	290	(highly damped) 0.58–0.87 (highly damped)

substrates are presented in table 3a. In view of the fact that these substrates have different reactivities towards bromination, uniform concentration conditions cannot be employed. The oscillatory characteristics for different substrates at the given concentration conditions are presented in table 3b.

From the oscillatory characteristics it can be inferred that the reactivity of veratric acid is much higher than that of veratronic acid towards bromination. This is evident

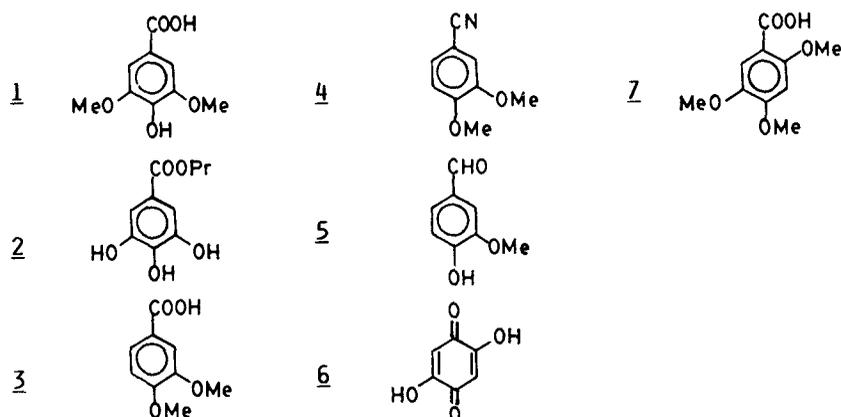


Figure 3. Structures of the substrates used: **1** – syringic acid; **2** – propyl gallate; **3** – veratric acid; **4** – veratronic nitrile; **5** – *p*-vanillin; **6** – 2,5 – dihydroxy-1,4-benzoquinone; **7** – asaronic acid.

from the smaller induction time (1.0 min) and time per oscillation (1.0 min) (the corresponding values for veratronic nitrile are 6.8 min and 3.5 min, respectively). Veratronic nitrile, in spite of its moderate reactivity, is a good substrate for the oscillatory study as the system is characterised by high amplitude oscillations (21) for a long duration of time (80 min) (figure 4).

The high reactivity of *p*-vanillin, towards bromination, is reflected on its oscillatory parameters (induction time 0.1 min. and time per oscillation 0.26 min). *o*-Vanillin, which is an isomer of *p*-vanillin, is not found to oscillate in the uncatalysed system under the conditions employed, which shows the higher reactivity of the latter

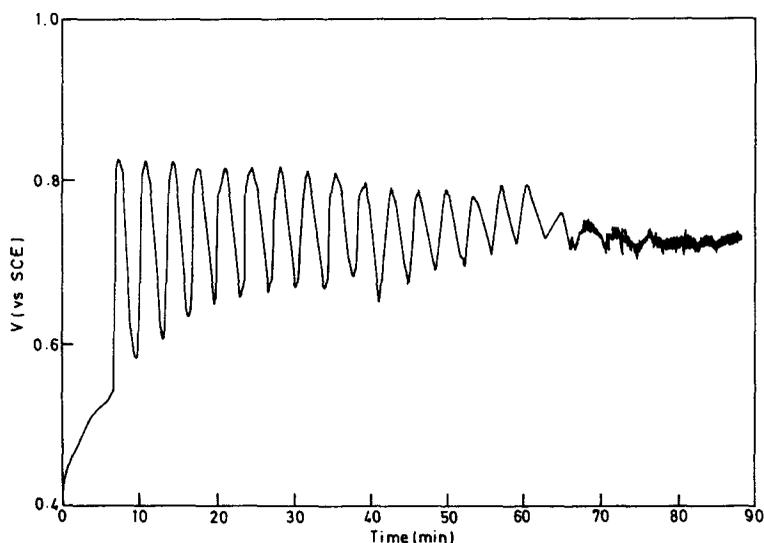


Figure 4. Oscillatory behaviour of veratronic nitrile in aqueous-acetonitrile (20% v/v acetonitrile) medium. Concentration conditions: veratronic nitrile – 0.02 M; sulphuric acid – 0.5 M; potassium bromate – 0.03 M.

compared to the former. However both these substrates show satisfactory oscillatory behaviour in the catalysed bromate systems (Lalitha and Ramaswamy 1992a, b). Syringic acid and propyl gallate are also well suited for the oscillatory study. However, 2,4-dihydroxy-1,4-benzoquinone and asaronic acid, characterised by a small number of damped oscillations, are not found to be suitable substrates in uncatalysed systems.

4. Conclusions

The results obtained in this study establish that oscillatory behaviour can be studied in several mixed media. It enables the study of new classes of water-insoluble substances which would not have been possible otherwise. Structurally related compounds can be investigated, since the poor solubility of the substrate would no longer be a limitation. The generally accepted mechanism for the uncatalysed bromate oscillator in pure aqueous medium is found to be valid even in aqueous-organic mixed media. Thus, the use of mixed media widens the scope of study in the field of oscillatory chemical reactions.

References

- Farage V J and Janjic D 1982 *Chem. Phys. Lett.* **88** 301
Gupta V K and Srinivasulu K 1982 *React. Kinet. Catal. Lett.* **19** 193
Herbine P and Field R J 1980 *J. Phys. Chem.* **84** 1330
Koros E and Orban M 1978 *Nature (London)* **273** 371
Kuhnert L and Linde H 1977 *Z. Chem.* **17** 19
Lalitha P V and Ramaswamy R 1992a *React. Kinet. Catal. Lett.* **47** 133
Lalitha P V and Ramaswamy R 1992b *J. Phys. Chem.* (submitted)
Lalitha P V and Ramaswamy R 1992c *Collect. Czech. Chem. Commun.* (in press)
Lalitha P V and Ramaswamy R 1992d *Indian J. Chem.* (submitted)
Lalitha P V, Ramaswamy R, Ramakrishnan G and Sambasiva Rao P 1992 *J. Phys. Chem.* (in press)
Orban M and Koros E 1978 *J. Phys. Chem.* **82** 1672
Orban M, Koros E and Noyes R M 1979 *J. Phys. Chem.* **83** 3056
Ramaswamy R 1982 *Proc. Symp. on Interactions at Electrode-Electrolyte Interfaces* (Bombay: Dept. Atomic Energy) pp. 30-42
Ramaswamy R and Krishnaratnam M 1986 *Indian J. Technol.* **22** 510
Ramaswamy R and Lalitha P V 1990 *Bull. Electrochem.* **6** 339
Ramaswamy R and Ramanathan S 1983 *Proc. Indian Acad. Sci. (Chem. Sci.)* **92** 221