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Oscillatory Reaction of Bromate-Gallic acid. A Calorimetric and Electrometric Study in Aquo-Organic Solvent Media

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The oscillatory reaction between potassium bromate and gallic acid (in presence of sulfuric acid and ferroin indicator) has been calorimetrically and potentiometrically studied in binary mixtures of water and organic solvents viz. dimethyl formamide, acetonitrile, tetrahydrofuran and 1,4-dioxan. The effects of solvent polarity, stirring condition, indicator concentration, aerial oxygen and chloride ion on the oscillatory process have been examined. The oscillatory behaviour of the reaction probed by the potentiometric method has a general agreement with the calorimetric method. An attempt has been made to determine the order of the $Fe^{2+} \rightarrow Fe^{3+}$ oxidation reaction. The damping coefficients of the oscillatory process in aqueous and mixed solvent media have been estimated.

Introduction

Belousov-Zhabotinsky (B-Z) reaction is basically the oscillations of oxidised and reduced forms in definite time intervals. The mechanism of such a reaction is given by Noyes *et al.* [1]. Mathematical models for the interpretation of the mechanism of B-Z reaction have been recently reported by Zhabotinsky *et al.* [2], Rovinsky and Zhabotinsky [3], and Rovinsky [4]. Most commonly studied B-Z systems are bromate/malonic acid/H_2SO_4/cerium ion, and bromate/gallic acid/H_2SO_4/ferroin. Quite a large number of studies have been

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made on these reactions using different methods viz. spectrophotometry [5, 6], potentiometry [7], and thermometry [7–10]. In the recent past, a number of organic and mixed substrates have been used to obtain more informations regarding the mechanism of such reactions [11–18]. In our earlier communication [19], we have reported the temperature oscillation of bromate/gallic acid/sulfuric acid system as a function of bromate concentration with and without ferroin in a calorimeter with elaborate thermodynamic and mechanistic analysis of the results. The B-Z reaction has been also investigated in microheterogeneous media viz. micelles, reverse micelles, liquid crystals, etc. [20, 21].

In the present contribution, we have extended our study on bromate/gallic acid/H_2SO_4/ferroin system in mixed solvent media of binary aquo-organic solvents employing dimethyl formamide (DMF), acetonitrile (ACN), 1,4-dioxan (DX) and tetrahydrofuran (THF). The B-Z reactions in mixed solvent media are only scantily studied [12, 22–24]. Chemical reactions are known to be greatly affected by the solvent type, and B-Z reactions are also expected to be affected by the solvent environment. Thermometric investigations of the B-Z reaction is also not very common [7–10, 25]; it remains practically unexplored in mixed solvent media. The present study is, therefore, unique in describing the thermo-chemical behaviours of the (bromate/gallic acid/H_2SO_4) oscillatory B-Z reaction in mixed aquo-organic environments. Along with thermometric measurements, potentiometric probing of the process has been also performed for a general understanding of the reacting system. An attempt has been made to quantify the results in the light of thermodynamics and kinetics.

Experimental

Potassium bromate, sulfuric acid and gallic acid used were of E. Merck, Germany. Ferroin indicator was prepared in the usual way. The solvents dimethyl formamide (DMF), acetonitrile (ACN) and dioxan (DX) were A.R. grade products of S.D. Chemical, India. Tetrahydrofuran (THF) was obtained from E. Merck, Germany. The purity of the solvents were checked by determining their specific gravity and refractive index and comparing them with the literature values. Potassium chloride and ammonium nitrate were of A.R. grade from Glaxo, India. Doubly distilled conductivity water was used in all preparations.

Calorimetry

The reaction was studied in a TRONAC 458 (U.S.A.) isoperibol titration calorimeter. The procedure of measurement was described in our earlier communication [19].

Potentiometry

The oscillations of the potential during the reaction were measured by constructing a cell with a platinum wire as one electrode coupled with a reference saturated calomel electrode through a salt-bridge (NH_4NO_3 – Agar -agar) and recording the oscillation of the cell e.m.f on a strip chart Recorder of SEKONIC, SS – 100F, Japan.

Results and discussion

Demonstrations of oscillation

The thermal and electrochemical oscillations of the studied bromate/gallic acid B-Z reaction system in aqueous and aquo-organic solvent media are presented in Fig. 1. In the calorimetric event, an initial prominent oscillation followed by successive smaller oscillations with increasing time intervals (Fig. 1a) were observed. The voltage oscillations also started with a large spike which successively got reduced in height with increasing intervals in between (Fig. 1b). The demonstrated oscillations are comparable with the existing reports in literature [12, 19].

The addition of bromate in gallic acid/H_2SO_4 medium resulted production of a large quantity of exothermic initial heat (I_h), continued for a definite period of time, irrespective of the composition of the mixed media (Table 1 and 2). The oscillation started after the addition of bromate was complete [19], the oscillatory events were systematic. A short-term large exothermic heat evolution followed by oscillations with increasing time-period and finally ending in no oscillation state were observed. Comprehensive results of the studied system in different solvent media are presented in Table 1. The features are discussed in what follows. The results in the Fig. 1a and b reveal lower number of oscillation (n) by thermal method than electrochemical method. The state of agitation, unequal contact with air, etc. (subsequently discussed) are considered to be vital factors guiding the oscillatory process. Rationalization of the results of unequal number of oscillations in the thermal and electrochemical methods needs a separate and intimate study which we have not done at present.

Number of oscillations (n)

The number of oscillation has been found to depend strikingly on the type of the mixed solvent and its v/v percent composition. The results of calorimetric measurements are given in Table 1. Oscillations determined by the potentiometric method are given in the parenthesis. It is found that the n values by calorimetry is much lower than potentiometry. This results from the much higher stirring condition of the reacting solution in the calorimetric cell. The varied rate of stirring has been found to have a declining effect on n.

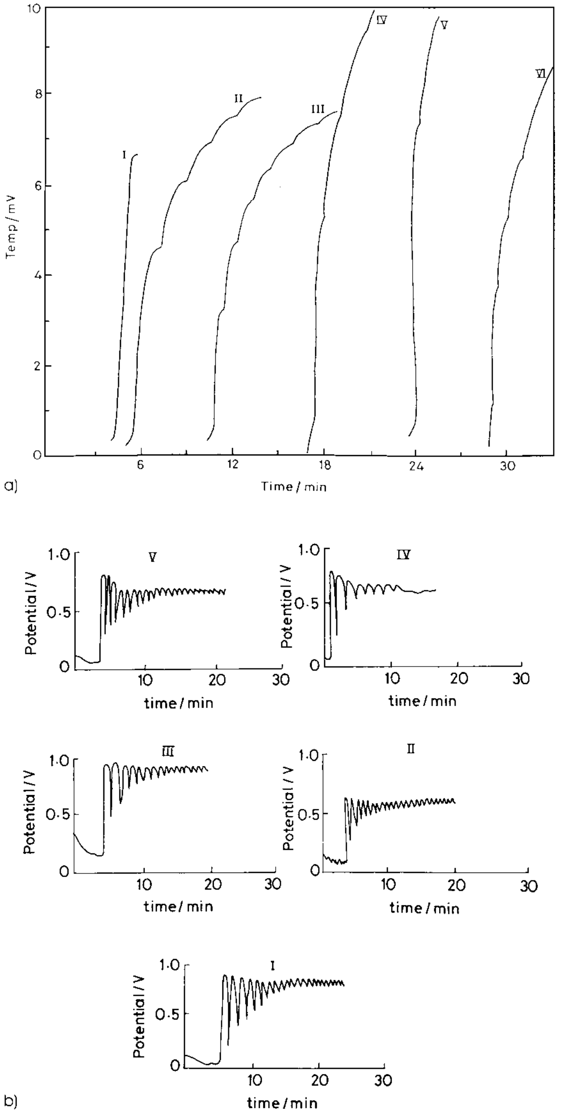

Fig. 1. (a) Oscillatory thermograms of the bromate/gallic acid/sulfuric acid B-Z reaction at 303 K. [GA] = 4.4 mmol dm^{-3}; [BrO_3^-] = 0.02 mol dm^{-3}; [H_2SO_4] = 3.6 equiv dm^{-3}; [In] = 50 μmol dm^{-3}. I. Representative initial heat release due to addition of bromate to gallic acid in H_2SO_4 medium: (pure water); II. Oscillatory representation of the same system; III. Same system in 2%(v/v) DMF; IV. Same system in 5%(v/v) DX; V. Same in 10%(v/v) ACN; VI. Same in 3%(v/v) THF. (b) Voltage oscillation of the bromate/gallic acid/sulfuric acid B-Z reaction at 303 K. [BrO_3^-] = 0.02 mol dm^{-3}; [GA] = 4.4 mmol dm^{-3}; [H_2SO_4] = 3.6 equiv dm^{-3}; [In] = 50 μmol dm^{-3}. I. In aqueous medium; II. In 2%(v/v) DMF; III. In 5%(v/v) DX; IV. In 10%(v/v) ACN; V. In 2%(v/v) THF.

Table 1. Calorimetric results of the solvent effect on the bromate/gallic acid oscillatory reaction[a] at 303 K in different aquo-organic solvent media.

Medium[b]	n	I_h/J	Heat released in respective oscillations/J	$\Delta H_{osc}{}^{c}$/J mol^{-1}
Water	5(22)	22.4	14.1, 4.57, 2.06, 1.28, 0.698	1135
DMF(0.5%)	5	25	10.8, 4.2, 2.26, 1.45, 0.6	965
DMF(1%)	6	18.4	11.2, 4.0, 2.49, 1.35, 0.73, 0.45	1010
DMF(2%)	7(23)	19.3	8.06, 4.12, 1.86, 1.12, 0.67, 0.5, 0.3	830
DX(0.5%)	3	19.0	14.0, 3.57, 1.87	972
DX(1%)	5	19.1	12.1, 4.2, 1.74, 1.0, 0.76	990
DX(2%)	6(22)	18.3	13.9, 3.2, 1.48, 0.75, 0.62, 0.4	1018
DX(3%)	7	23.3	13, 3.7, 2.5, 1.37, 0.9, 0.7, 0.33	1125
DX(4%)	5	18.3	13.3, 2.74, 1.92, 1.2, 0.37	975
DX(5%)	4(16)	16.6	13.5, 3.4, 1.66, 0.37	945
DX(10%)	2	14.7	7.8, 2.7	525
ACN(0.5%)	5	18.6	14.55, 3.95, 2, 0.87, 0.66	1102
ACN(1%)	4	16.6	14, 3.5, 1.66, 0.82	1000
ACN(2%)	4(14)	26.2	13.7, 3.78, 2.12, 0.91	1025
ACN(3%)	4	27.8	14.96, 6.18, 1.47, 0.62	1160
ACN(4%)	4	19.1	15.25, 4.0, 1.58, 1.12	1098
ACN(5%)	3	18.7	14.13, 3.74, 1.08	948
ACN(6%)	3	27.8	16.2, 5.0, 1.88	1154
ACN(10%)	2(7)	22.0	20.0, 3.66	1183
ACN(15%)	2	20.0	15.6, 1.35	848
ACN(20%)	1	24.5	13.3	665
THF(0.5%)	8(25)	25.4	14.1, 3.6, 2.29, 2.29, 0.79, 0.58, 0.554, 0.33	1225
THF(1%)	7	26.6	11.1, 3.49, 1.83, 1.66, 0.83, 0.73, 0.50	1007
THF(2%)	6(22)	25.7	8.3, 3.65, 2.08, 1.49, 1.08, 0.54	857
THF(3%)	4	25.7	5.9, 2.9, 2.0, 1.48	614
THF(4%)	3	27.8	0.47, 0.37, 0.2	52

[a] $[\mathrm{KBrO_3}] = 0.02\ \mathrm{mol\,dm^{-3}}$; $[\mathrm{GA}] = 4.4\ \mathrm{mmol\,dm^{-3}}$; $[\mathrm{In}] = 50\ \mu\mathrm{mol\,dm^{-3}}$; $[\mathrm{H_2SO_4}] = 3.6$ eqiuv dm^{-3}; [b] Solvent %(v/v); [c] ΔH_{osc} is expressed per mole of $\mathrm{KBrO_3}$

It has been observed that in Wa-DMF environment, the number of oscillations has increased from 5 to 7 as the DMF content is increased from 0.5% to 2%. Higher concentration of DMF could not be used due to its interaction with bromate, which gets reduced in basic medium. In Wa-DX medium, the number of oscillations has passed through a maximum at 3% of dioxan. The oscillations have been observed to appear up to 10% of DX in water, thereafter oscillation does not appear. In the Wa-ACN environment, the number of oscillations has been found to decrease with the increasing proportion of ACN upto 20%, where only a single oscillation occurred. In-

Table 2. Calorimetric results of the effect of indicator concentration on the bromate/gallic acid oscillatory reaction[a] at 303 K in water and in different aquo-organic solvent media.

Medium[b]	$[\mathrm{In}] \times 10^5$ mol dm^{-3}	n	I_h/J	$\Delta H_{osc}{}^c$/J mol^{-1}
Water	0	2	25.0	498
Water	2.5	5	17.0	906
Water	5	5	22.4	1135
Water	10	4	22.8	1140
Water	20	3	25.0	1163
DMF(2%)	0	2	15.58	436
DMF(2%)	2.5	6	17.88	830
DMF(2%)	5	7	19.33	830
DMF(2%)	10	11	17.29	915
DMF(2%)	20	11	18.54	1060
DX(3%)	0	3	23.7	625
DX(3%)	2.5	7	21.6	935
DX(3%)	5	7	23.28	1125
DX(3%)	10	7	25.0	1227
DX(3%)	15	6	22.8	1205
DX(3%)	20	3	23.28	1100
ACN(3%)	0	3	14.5	530
ACN(3%)	2.5	4	15.38	1018
ACN(3%)	5	4	27.8	1160
ACN(3%)	10	2	18.7	908
ACN(3%)	15	1	24.1	436
THF(2%)	0	2	16.6	108
THF(2%)	2.5	6	20.7	644
THF(2%)	5	6	25.7	857
THF(2%)	10	3	25.6	330
THF(2%)	15	3	25.3	415

[a] $[\mathrm{KBrO_3}] = 0.02$ mol dm^{-3}; $[\mathrm{GA}] = 4.4$ mmol dm^{-3}; $[\mathrm{H_2SO_4}] = 3.6$ equiv dm^{-3}; [b] Solvent %(v/v); [c] ΔH_{osc} is expressed per mole of $\mathrm{KBrO_3}$

creasing proportion of THF in Wa caused a decrease in n. A volume of more than 2% of THF could not be used because of release of bromine from bromate.

Lalitha and Ramaswamy [12] have studied the same system at a fixed composition (20% v/v) of the organic solvents (DX, THF, ACN, DMF) in water. The medium dependent order of n has been reported to be DMF>THF>ACN>DX. In this study, we have used variable compositions whereby variable n values have been observed. A comparison of the results at a fixed composition (2% v/v) gives the order DMF>THF= DX>ACN. Except DX, the sequence agrees with that reported by Lalitha and Ramaswamy [12]. Such a sequence fails at higher proportions of the organic solvents. But the use of 20% of the nonaqueous solvents DX, THF, ACN and DMF reported by Lalitha and Ramaswamy [12] is contrary to our experience stated above. Even the authors have included the solvent benzene in their tabulation (Table 1) which is an impossibility (may be it is erroneously printed).

Jha *et al.* [24] have observed smooth oscillations in mixed solvents in general and in Wa-DMF and Wa-DX in particular. The frequency of oscillations have been found to increase in presence of the nonaqueous solvents, DMF and DX. It is considered that the bromination of the active methylene compound is an important factor for an oscillatory reaction, and it occurs through electrophilic substitution by bromonium ion (Br^+) formed by the electromeric effect. Such electromeric effect producing Br^+ from Br_2 liberated from $KBrO_3$ in acid medium has been considered to be the route to the substitution reaction of the benzene ring by bromine in presence of Fe^{2+} [25a]. The results of the solvent effect may be rationalized from two points of view, (a) the reaction equilibrium $Br_2 + Br^- = Br_3{}^-$ [25b] and (b) the solvation of the Br^+ ion formed by electromeric effect. If we consider ACN, the equilibrium constant for the process (a) is 10^7 in ACN and only 16 in water [23]. In Wa-ACN medium, with increasing ACN content, $[Br^-]$ may fall below the critical value much faster than in water making the oxidation process (2), $4\,Fe^{2+} + BrO_3{}^- + 5H^+ \rightarrow 4Fe^{3+} + HOBr + 2H_2O$ (discussed later) to predominate to increase the oscillation frequency. But reverse was the observation. This may be the result of poor solvation of the formed Br^+ ion which is free to perform faster bromination thereby decreasing the oscillation frequency. In general, the process (a) and (b) mentioned above, contribute their shares depending on the type of solvent medium the oscillatory system is put into. In some solvents, one of them may be the guiding factor, in some other both may contribute. Perhaps dioxan is such an example where the frequency passes through a maximum at 3% (v/v). Until quantitative data on the equilibrium constant for the process (a) and the solvation efficiency of the process (b) are at hand, speculative discussion is with held.

Enthalpy of oscillation (ΔH_{osc})

In each studied case, there occurs a large initial release of heat (Fig. 1a, curve I) related to the oxidation of the gallic acid which is one of the vital steps of the oscillatory process [19, 26]. On the addition of bromate, in the first step, gallic acid is oxidised to its quinonoid form, Q and the process is exothermic [19].

The enthalpies of oscillation for all the solvent systems are recorded in Table 1; the final column is the sum of all the enthalpy changes observed in different oscillatory steps during the reaction. Features of the individual mixed solvent media are discussed below.

With increasing proportion of DMF in water, ΔH_{osc} has practically remained invariant though the number of oscillations has increased. The enthalpies of the consecutive oscillations of course have decreased at all the levels of the solvent addition. In the Wa-DX medium, like the number of oscillations, ΔH_{osc} also has passed through a maximum (at 3% v/v) with increasing proportion of the solvent DX in water. By the use of ACN in water, the ΔH_{osc} as also the number of oscillations decreased with increasing ACN content in water. By the addition of increasing concentration of THF in water, the ΔH_{osc} has continuously declined like the decrease of *n* under the same condition. A representative bar diagram showing the heat released per minute (H_{R}) vs time associated with the oscillation in several solvent media is presented in Fig. 2.

In general, the total ΔH_{osc} increases with increasing number of oscillation, the process is thermodynamically sustained. A process occurring in multistep should produce/absorb much more heat than when it occurs in a single step. The ΔH_{osc} on the whole bears a linear relation with *n* in all the studied cases. Poor correlations are observed for experiments with DMF and ACN at a constant [ferroin], and DX at varying [ferroin].

Both voltage and temperature oscillations declines with time with declining amplitude. The oscillations get damped; the amplitudes progressively change with time. The process is, of course, specifically dependent on the environmental conditions. The subtle nature of the oscillatory process makes explicit understanding of it difficult although it is important to know how the oxidation

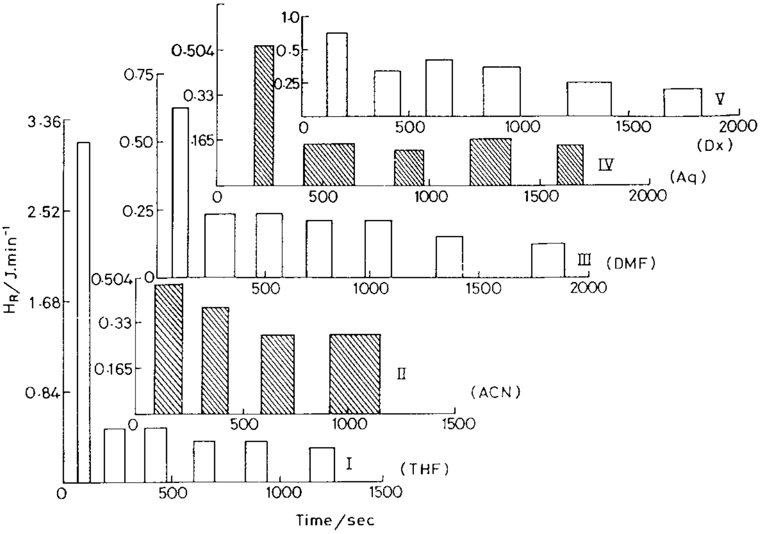

Fig. 2. The heat change at different steps for the thermal oscillation as a function of time. $[\mathrm{BrO_3}^-] = 0.02\,\mathrm{mol\,dm^{-3}}$; $[\mathrm{GA}] = 4.4\,\mathrm{mmol\,dm^{-3}}$; $[\mathrm{In}] = 50\,\mu\mathrm{mol\,dm^{-3}}$; $[\mathrm{H_2SO_4}] = 3.6\,\mathrm{equiv\,dm^{-3}}$. I. In 2%($v/v$) THF; II. In 2%($v/v$) ACN; III. In 2%($v/v$) DMF; IV. In aqueous medium; V. In 2%(v/v) DX.

Table 3. Rate constants of formation kinetics of $Fe^{2+} \rightarrow Fe^{3+}$ for bromate/gallic acid oscillatory system in different aquo-organic solvent media at 303 K.

Medium[a]		Rate constants/$mol^{-1/2}\ dm^{3/2}\ min^{-1}$	
		Calorimetry	Potentiometry
Water		0.13	0.15
% DX	2	0.23	0.25
	5	—	0.36
% ACN	2	0.18	0.16
	10	—	0.44
% THF	0.5	—	0.25
	2	0.18	0.28
% DMF	2	0.17	0.38
	5	—	0.44

[a] Solvent % (v/v)

and reduction processes in the oscillatory reactive system are affected by the added variants. A separate study in this direction is worthwhile.

We herein present the damping coefficient of representative cases (which are exemplified in the oxidation kinetics in Table 3) in different solvent media based on the following relation, with respect to voltage oscillation

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

where $A(t)$ and $A(t+1)$ are the amplitudes of two successive oscillations, T is the time period and σ is the damping coefficient [27].

The σ values obtained from both the oxidation and reduction steps are presented in Table 4. The values closely agree with each other. It is also observed that the σ in aqueous medium is lower than those in presence of the non-aqueous solvents; the results in the mixed solvents are more or less all alike. In a recent work [28], we have reported the damping coefficients of the bromate-gallic acid system in electrolyte solutions where a dependency of σ on the type of added electrolyte and its concentration has been observed. Compared to the added electrolyte environment, the solvent influenced σ values are larger; the non-aqueous solvents damp the oscillatory process more than the electrolytes.

Effect of medium polarity

It is observed that the number of oscillations has no direct bearing on the polarity of the medium. It depends on the nature of the solvent. As the polarity of the

Table 4. Effect of aquo-organic solvents on the damping coefficients of the oscillatory system at 303 K.

Medium[a]		$10^3\ \sigma/\text{min}^{-1}$	
		oxidation	reduction
Water		83	87
% DX	2	132	113
	5	110	100
% ACN	2	97	94
	10	88	77
% THF	0.5	113	91
	2	110	95
% DMF	2	102	90
	5	100	87

[a] Solvent %(v/v)

medium decreases, the number of oscillations decreases in Wa-ACN and Wa-THF media, but it increases with the decreasing polarity in Wa-DMF medium. Dioxan has its own trend in this respect, where the number of oscillations at first has increased, then decreased with decreasing polarity. The dependence of n on the dielectric constant of the medium is illustrated in Fig. 3. In constructing the diagram, the dielectric constant ε_M of the medium has been computed by the formula, $\varepsilon_\mathrm{M} = X_\mathrm{w}\varepsilon_\mathrm{W} + X_\mathrm{o}\varepsilon_\mathrm{o}$, where X_w and X_o are the mole fractions of water and organic solvent respectively, and ε_W and ε_O are the corresponding dielectric constants taken from standard literature.

Effect of stirring

The rate of stirring of the reacting solution has affected the oscillatory process; increased stirring has decreased n. The e.m.f and temperature traces of the reactive systems have evidenced equal inhibitory features. Similar observations have been recently reported by Chen *et al.* [11] who have observed dampening of oscillations for $\mathrm{BrO_3}^-$ reaction with ethyl or n-butyl-malonic acid catalyzed by Ce(III), Mn(II) and $\mathrm{Fe(Phen)_3}^{2+}$ in aqueous $\mathrm{H_2SO_4}$ medium in a stirred bath experiment. In this work for a comparative understanding we have studied the reacting system under constant stirring condition.

Effect of indicator concentration

In aqueous medium, the indicator concentration has positive and negative effects on n in the lower and higher range of [In] respectively. The Wa-ACN,

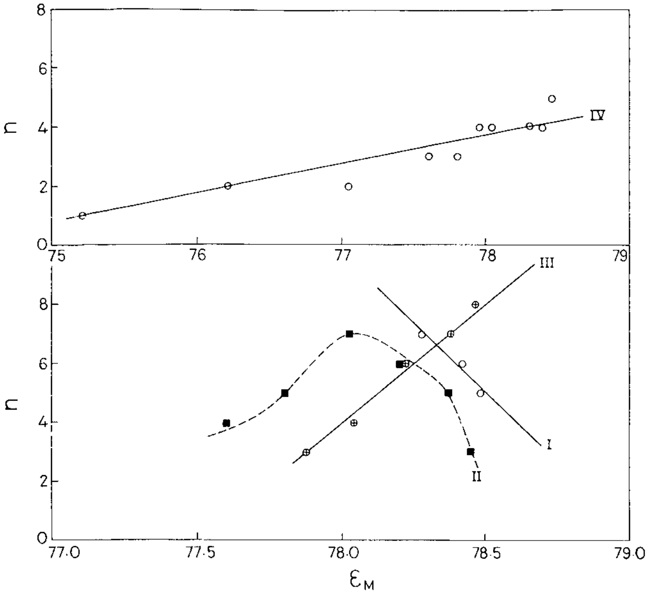

Fig. 3. The effect of dielectric constant on the mixed solvent medium on the number of B-Z oscillations at 303 K. $[BrO_3^-] = 0.02\,mol\,dm^{-3}$; $[GA] = 4.4\,mmol\,dm^{-3}$; $[In] = 50\,\mu mol\,dm^{-3}$; $[H_2SO_4] = 3.6\,equiv\,dm^{-3}$. I. In Wa-DMF; II. In Wa-DX; III. In Wa-THF; IV. In Wa-ACN.

Wa-DX and Wa-THF media have shown similar effects of [In] on *n*; with Wa-DMF, the [In] has shown a hyperbolic saturation curve for the *n*. The results are depicted in Fig. 4.

The *n* values at different [In] in the mixed solvent media are presented in Table 2. It has almost the same trend as that of [In] on ΔH_{osc}. The increasing effect of [In] on *n* of the reaction in the lower range of concentration is in accordance with the positive catalytic effect of the ferroin indicator [29]. The decline in the trend in the higher range of [In] (except for Wa-DMF where *n* has progressively increased and maximized at $[In] > 100\,\mu mol\,dm^{-3}$) remains at present to be unexplained. The maxima in the profiles are at $[In] = 0.05\,mmol\,dm^{-3}$ for aqueous, aquo-ACN and aquo-THF media: it is $0.075\,mmol\,dm^{-3}$ in aquo-DX medium.

The *n* lowering effect of ferroin at higher concentrations may be due to complex formation of ferroin with any of the reacting species at higher concentration, thereby making it unavailable for the main reaction. This aspect of the B-Z reaction is worth exploration. The complexation possibility of ferroin with gallic acid (and BrGA) is supported by similar complex formation with malonic acid reported by Kasperek and Bruice [6] and considered by Chen *et al.* [11].

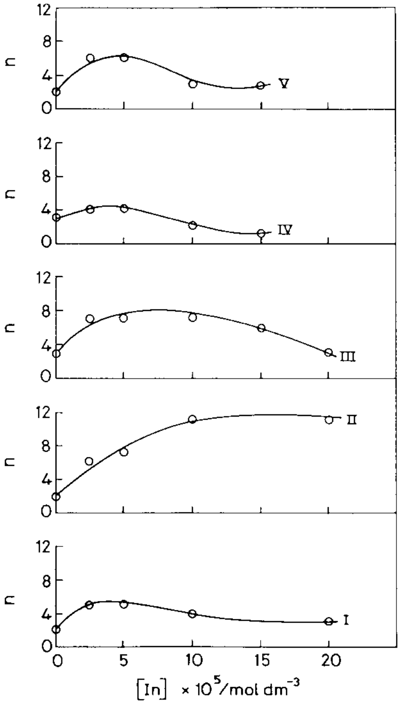

Fig. 4. The effect of indicator concentration on the thermal oscillation of the bromate/gallic acid/sulfuric acid B-Z reaction at 303 K. I. In water; II. In 2%(*v*/*v*) Wa-DMF; III. In 3%(*v*/*v*) Wa-DX; IV. In 3%(*v*/*v*) Wa-ACN; V. In 2%(*v*/*v*) Wa-THF.

Overall oscillatory steps

The B-Z reaction is a complex multistep process. The distinctive steps for the $BrO_3^-/GA/H_2SO_4$/ferroin catalyzed B-Z reaction are given below, which are in accordance with the propositions made by Field *et al.* [7], Liu *et al.* [26] and Ruoff *et al.* [30].

$$BrO_3^- + 5Br^- + 6H^+ \rightarrow 3Br_2 + 3H_2O \tag{1}$$

$$4Fe^{2+} + BrO_3^- + 5H^+ \rightarrow 4Fe^{3+} + HOBr + 2H_2O \tag{2}$$

$$4Fe^{3+} + BrGA + H_2O \rightarrow Br^- + 4Fe^{2+} + \text{ketonic acid} + 5H^+ . \tag{3}$$

For the uncatalyzed reaction (without ferroin) steps (2) and (3) can be represented as

$$BrO_3^- + 2Q + 3H^+ \rightarrow HBrO_2 + 2\dot{Q} + H_2O , \tag{4}$$

$$2\dot{Q} + BrGA + H_2O \rightarrow Br^- + 2Q + \text{ketonic acid} + H^+ , \tag{5}$$

where Q = Quinonoid form of GA and BrGA = Bromogallic acid. The $[Br^-]$ essentially controls the B-Z reaction. In this paper, the characteristic behaviours of the catalyzed reaction have been considered.

The effect of aerial oxygen on the reaction

The effect of aerial O_2 have been studied by several workers in the past [31, 32]. Aerial O_2 may change the potential of the different red-ox systems in the medium, thereby affecting the reaction process. The change in *n* in the presence and absence of aerial O_2 is given in Fig. 5. The reduction process is delayed and the *n* gets reduced in presence of aerial O_2. In the figure, the oxidation and the reduction stages are indicated by circle and square symbols in non-aerated and aerated conditions respectively. The aerated (broken) and non-aerated (full) courses are like waves having phase differences, which during their progress may also show inphase behaviours (identified by arrow heads in the diagram). In the aqueous medium, the number of oscillations monitored for 1000 secs are both ten in non-aerated and aerated conditions. Similar are the observations in the Wa-DMF and Wa-ACN media (in the latter medium, the period of observation has been 1200 secs). In the Wa-DX and Wa-THF media, oscillations are significantly reduced. In the former environment, in the pres-

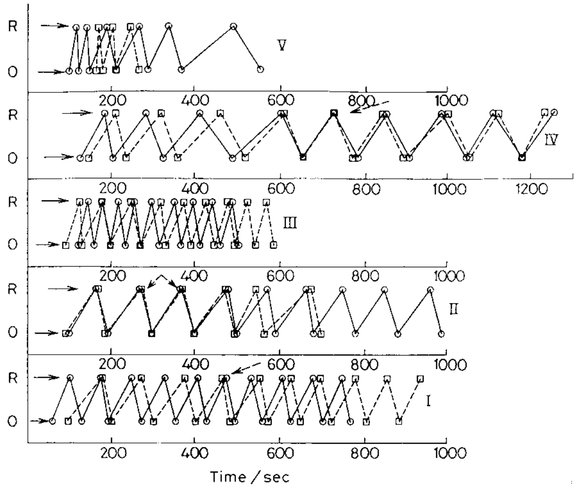

Fig. 5. The voltage oscillations of the bromate/gallic acid/sulfuric acid B-Z reaction in the absence and presence of air at 303 K. $[BrO_3^-] = 0.02\ \mathrm{mol\,dm^{-3}}$; $[GA] = 4.4\ \mathrm{mmol\,dm^{-3}}$; $[In] = 50\ \mu\mathrm{mol\,dm^{-3}}$; $[H_2SO_4] = 3.6\ \mathrm{equiv\,dm^{-3}}$. Circle and square symbols represent non-aerated and aerated conditions. Top and bottom points in each section represent reduction and oxidation respectively. I. In water; II. In 5%(*v*/*v*) DX; III. In 5% (*v*/*v*) DMF; IV. In 5% (*v*/*v*) ACN; V. In 2%(*v*/*v*) THF.

ence of air, the oscillatory phenomenon has not progressed beyond 700 secs, which has sustained up to 270 secs in aerated condition in the Wa-THF environment.

Oxygen inhibition of the reduction process has been explained by Drummond *et al.* [31] and Ruoff and Noyes [32]. In the presence of oxygen, conversion of $Fe^{2+} \rightarrow Fe^{3+}$ in the process (2) can occur without the consumption of BrO_3^-, and HOBr is not formed. The reduction of Fe^{3+} in the process (3) is also hindered.

Formation kinetics of the species $Fe^{2+} \rightarrow Fe^{3+}$ i.e. oxidation kinetics (for red → blue color change)

The oscillatory process is associated with oscillations in potential. This has been electrometrically recorded (Fig. 1b). The voltage increases, reaches a maximum (color changes from red to blue during the process) and then decreases (color changes from blue to red). This event occurs periodically. The peak height of the oscillatory curve decreases with time. Considering that the peak height is proportional to the concentration of the controlling species (Br^-) during the progress of the reaction, the kinetics of the oxidation has been studied from the traces of the voltage-oscillation profiles. The peak height has been plotted against time for different systems, the order of the oxidation reaction has been determined by the differential method from the curve in each case and has been found to be 1.5. The rate equation taking order as 1.5 of the reaction gives a straight line passing through the origin in each case (exemplified in Fig. 6) from which the rate constants have been determined. The temperature oscillation profiles monitored in the calorimeter have been also used for the kinetic analysis similar to voltage oscillation (Fig. 7). Here also oxidation process (large exothermic heat change) at different time intervals are taken into consideration. The results realized on the basis of the two modes of analysis are presented in Table 3. The rate constants by calorimetry and potentiometry fairly agree with each other for aqueous, aquo-DX and aquo-ACN media; in aquo-THF and aquo-DMF media, the values derived from calorimetry are lower than that from electrometry. The comparison has been made at two compositions of the mixed solvents. The equation representing the observed rate of the overall oscillatory reaction is given below.

$$k(t_n - t_1) = 2\left[\frac{1}{\sqrt{a - x_n}} - \frac{1}{\sqrt{a - x_1}}\right],$$

where k is the rate constant, a is the initial concentration of Br^-, and x_1 and x_n are the decrease in $[Br^-]$ for the first and nth oscillations respectively.

The rate constant values have ranged grossly between 0.12–0.44 $\text{mol}^{-1/2}\,\text{dm}^{3/2}\,\text{min}^{-1}$. An analysis of kinetic results in different aquo-organic solvent media would be helpful in further understanding of the basis of the B-Z oscillatory process. This may be taken up in a future study.

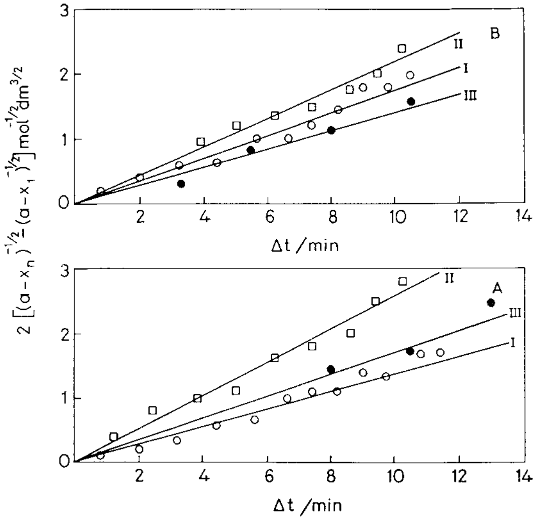

Fig. 6. Kinetic plots for the evaluation of the Fe^{2+}→Fe^{3+} oxidation rate constant of the oscillatory bromate/gallic acid/sulfuric acid B-Z reaction of order 1.5 followed electrometrically at 303 K. $[\mathrm{BrO_3}^-] = 0.02$ mol dm^{-3}; [GA] = 4.4 mmol dm^{-3}; [In] = 50 μmol dm^{-3}; $[\mathrm{H_2SO_4}] = 3.6$ equiv dm^{-3}. A. From the direction of oxidation: I. In water; II. In 2%(v/v) DX; III. In 2%(v/v) ACN. B. From the direction of reduction: I. In water; II. In 2%(v/v) DX; III. In 2%(v/v) ACN.

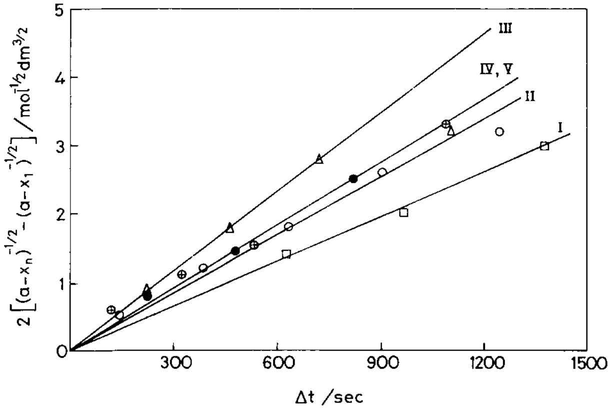

Fig. 7. Kinetic plots for the evaluation of the rate constants of the oscillatory bromate/gallic acid/sulfuric acid B-Z reaction of order 1.5 followed thermochemically from the direction of oxidation at 303 K. $[\mathrm{BrO_3}^-] = 0.02$ mol dm^{-3}; [GA] = 4.4 mmol dm^{-3}; [In] = 50 μmol dm^{-3}; $[\mathrm{H_2SO_4}] = 3.6$ equiv dm^{-3}. I. In water (□); II. In 2%(v/v) DMF(○); III. In 2%(v/v) DX(△); IV. In 2%(v/v) ACN(●); V. In 2%(v/v) THF(⊗).

The kinetics of the early phase of BrO_3^-–GA reaction has been also studied by Jwo and Chang [29] potentiometrically. A second order reaction between BrO_3^- and GA with rate constants varying in the range of 0.264–8.1 $mol^{-1}\,dm^3\,min^{-1}$ at 25 °C at $[H_2SO_4]$ in the range of 0.41–2.0 mol dm^{-3} respectively has been reported by them.

Chen *et al.* [11] have studied the pseudo first order reduction kinetics of Ce^{4+} and ferroin $[Fe(Phen)_3{}^{3+}]$ in excess concentration of methyl-, ethyl- and butyl-malonic acid spectrophotometrically and compared the results on the basis of the types of catalyst and the substitution on the malonic acid. Pal and Banerjee [33], and Dutta and Banerjee [23], have attempted to evaluate the activation parameters for the B-Z reaction (bromate/gallic acid/H_2SO_4 or $HClO_4$/ferroin) from the temperature effect on the process assuming first order kinetics. Koros and Orban [10a] have also reported activation parameters for the same uncatalyzed B-Z reaction.

It should be noted that the order of the oxidation reaction and the rate constant values, reported in the present case of damped oscillatory system are only apparent. Such apparent kinetic parameters have been also reported in previous studies [11]. In those cases the oscillatory process has been assumed to be unimolecular. It is a difficult task to assign a molecular mechanism to rationalize the order of the oscillatory process. Our results fit into an order of one and a half.

Effect of chloride ion

The ionic nature of the B-Z reaction is expected to be influenced by electrolytes. Certain ions, such as Cl^-, have been found to have specific effect on the process [34–36]. It is for this reason, in the construction of the cell to study voltage oscillation, NH_4NO_3 was used in the salt bridge instead of KCl. In this report results of a preliminary study on the effect of KCl on voltage oscillation has been presented. It has been found that the number of oscillations decreases with increasing concentration of KCl from 0.1 $\mu mol\,dm^{-3}$ to 0.5 $mmol\,dm^{-3}$. No oscillation has been observed at and above $[KCl] = 0.5\,mmol\,dm^{-3}$. The change in the number of oscillations with increasing concentration of KCl is illustrated in Fig. 8. It has been found that though the number of oscillations decreases, the peak height increases with increasing [KCl]. So KCl has an inhibitory effect on the oscillatory process. The drastic effect of KCl at appreciably low concentration suggests the specificity of the salt (Cl^- particularly) on the B-Z reaction. The inhibitory role of the Cl^- on the oscillatory process of malonic acid/bromate and gallic acid/bromate systems using the salt KCl has been attempted to rationalize by others [34–36]. The drastic effect of KCl on the presently studied oscillatory system is worthy to explore further using chloride salts of alkali and alkaline earth metals. This will be taken up in a future study of salt effects on the B-Z reactions.

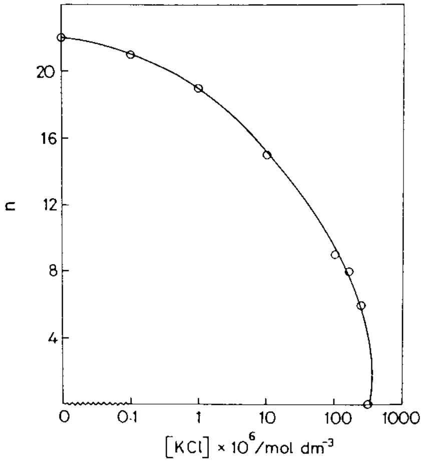

Fig. 8. The effect of chloride ion on the electrometrically monitored bromate/gallic acid/H_2SO_4 B-Z oscillatory reaction at 303 K. $[BrO_3^-] = 0.02$ mol dm^{-3}; [GA] = 4.4 mmol dm^{-3}; [In] = 50 μmol dm^{-3}; $[H_2SO_4] = 3.6$ equiv dm^{-3}.

Conclusions

The bromate/gallic acid/H_2SO_4/ferroin(indicator) B-Z oscillatory reaction has been observed to be essentially retarded by the presence of DMF, ACN, DX and THF. The overall heat released bears in most cases a linear relation with the number of oscillation. The aerial oxygen, increasing indicator concentration and stirring also have retarding effects on the oscillatory process, the mechanism of which is at present unknown. It has been observed that the $Fe^{2+} \rightarrow Fe^{3+}$ oxidation reaction rate follows an overall order of 1.5 in aqueous and as well as in aquo-organic solvent media. It has been found that a very low concentration of Cl^- ion has a significant inhibiting effect on the oscillatory process: the process become totally inhibited at $[Cl^-] = 0.5$ mmol dm^{-3} at 303 K. The coefficient of the damped oscillatory process has been found to increase in presence of non-aqueous solvents, and remain independent of the solvent type.

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