

## SHORT COMMUNICATIONS

MOSSBAUER EFFECT STUDIES  
ON ZINC BORATE GLASSES  
CONTAINING IRONR. V. ANAVEKAR, N. DEVARAJ and  
J. RAMAKRISHNA\**Department of Physics, Bangalore University,  
Bangalore 560001, India.**\*Department of Physics, Indian Institute of Science,  
Bangalore 560012, India.*

MOSSBAUER effect studies on borate glasses containing iron have been made on alkali borate, alkaline earth borate and lead borate glasses<sup>1-3</sup>. This technique has been successfully used to study the role of iron in these glasses and their structure. In this paper we report Mossbauer effect studies on zinc borate glasses containing iron.

Glasses were prepared in the composition 45 mol % ZnO-(55-X) mol % B<sub>2</sub>O<sub>3</sub>-X mol % Fe<sub>2</sub>O<sub>3</sub>. X mol % is the concentration of iron and it is varied stepwise from 6 mol % to 14 mol %. The details of preparation of these glasses are given elsewhere<sup>4</sup>. The Mossbauer spectra were recorded on ECIL spectrometer in constant acceleration mode. All spectra were recorded at room temperature. For all the compositions studied, Mossbauer spectra exhibited well-resolved quad-

rupole doublet having large linewidth which is a characteristic of amorphous solids. The isomer shift ( $\delta$ ) and the quadrupole splitting ( $\Delta$ ) values decreased smoothly as the iron concentration was increased. The variation of these values with iron concentration is shown in figure 1.

The isomer shift and the quadrupole splitting values<sup>5</sup> for Fe<sup>3+</sup> in tetrahedral coordination are of the order 0.3 mm sec<sup>-1</sup> relative to Fe metal and 0.7 to 1 mm sec<sup>-1</sup> respectively. Based on these values it is suggested that iron is in Fe<sup>3+</sup> state and tetrahedrally coordinated in this glass system. Also, the decrease in ( $\delta$ ) indicates an increase in the covalency of Fe-O bond and the decrease in ( $\Delta$ ) indicates an increase in the tetrahedral symmetry at Fe<sup>3+</sup> ion, as the Fe<sub>2</sub>O<sub>3</sub> concentration is increased. A detailed report on the present investigation is in preparation.

3 March 1985

1. Raman, T., Rao, G. N., and Chakraborty, D., *J. Non-Cryst. Solids*, 1978, **29**, 85.
2. Tricker, M. J., and Thomas, J. M., *J. Mat. Sci.*, 1974, **9**, 1115.
3. Sekhon, S.S., and Kamal, R., *J. Non-Cryst. Solids*, 1978, **28**, 189.
4. Anavekar, R. V., Devaraj, N. and Ramakrishna, J., *Bull. Mater. Sci.*, 1984, **6**, 1009.
5. Kurkjian, C. and Sigety, E. A., *Phys. Chem. Glasses*, 1968, **9**, 73.

A NOVEL APPROACH IN THE STUDY  
OF CHEMICAL OSCILLATORS

R. RAMASWAMY and S. MOHAN

*Department of Chemistry, Indian Institute of Technology,  
Madras 600036, India.*

THE oscillatory behaviour of the iodate-hydrogen peroxide system (Briggs-Rauscher or BR reaction) with four different substrates is presented. The subsystems have been studied earlier employing malonic acid and methyl malonic acid as the substrates<sup>1,2</sup>. The consideration of the rate of electron exchange at the platinum indicator electrode in the potentiometric

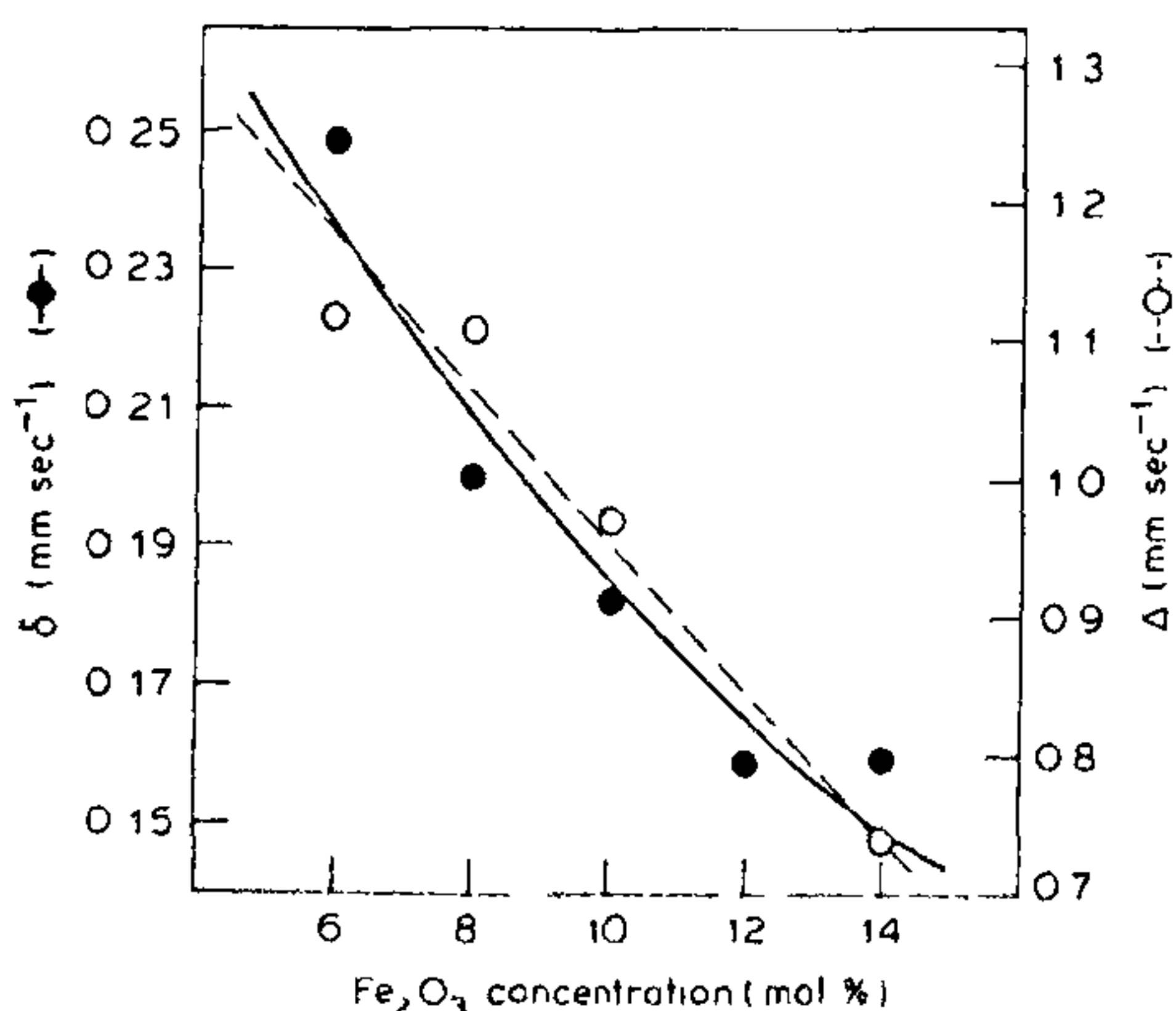


Figure 1. Variation of ( $\delta$ ) and ( $\Delta$ ) with iron concentration.

follow-up has provided deep insight into the mechanism of the reaction in the uncatalysed and catalysed bromate systems<sup>3-5</sup>.

The potentiometric follow-up of the reaction with a platinum indicator electrode provides valuable information regarding the species causing oscillations. The addition of the last constituent (hydrogen peroxide) to a mixture of all other constituents kept well stirred and thermostated in a polythene beaker triggers off the oscillations. The oscillations were recorded on a Siemens Kompensograph by connecting to it the cell formed between the indicator and saturated calomel electrode (SCE). The concentration conditions employed in a typical set of experiments are presented in table 1.

The oscillatory characteristics under comparable concentration conditions referred in table 1 are given in table 2.

**Table 1** Concentration conditions (temperature 32°C)

Substrate employed	Concentration (M)				
	Potassium iodate	Sulphuric acid	Hydrogen peroxide	Manganous sulphate	Substrate
Ethyl-acetoacetate (EAA)	0.04	0.04	0.4	0.004	0.04
Malonic acid (MA)	0.04	0.04	0.4	0.004	0.40
Acetyl-acetone (AcAc)	0.04	0.40	0.4	0.004	0.04
Diethyl-malonate	0.04	0.16	1.2	0.040	0.16

**Table 2** Oscillatory characteristics

Substrate employed	Induction time (min)	Oscillating time (min)	No. of oscillations	Potential range (V vs. SCE)	Amplitude (mV)
EAA	0.6	7.3	4	0.55 to 0.85	300
MA	1.4	0.9	3	0.55 to 0.63	80
AcAc	0.1	3.8	7	0.55 to 0.8	250
DEM	1.5	9.0	22	0.65 to 0.75	100

The solution is blue in the base potential region caused by the formation of iodine-starch complex. The concentration of hydrogen peroxide employed has invariably been of a large magnitude (1.2 M). Under these conditions, formation of Mn(III) during the oscillatory reaction evaded experimental identification even by ESR technique<sup>6</sup>.

In the present investigation the presence of Mn(III) at the peak potential region could be seen by the dark brown colour of the solution with lower concentration of hydrogen peroxide. The recordings obtained with the four substrates and the concentration conditions employed are presented in figure 1. The solution is dark blue at A. There is a gradual decrease in the intensity of blue as the potential decreases. The solution is colourless at B. The potential rapidly increases from B to C with simultaneous formation of red brown colour due to Mn(III). The fall of potential from C to D is also rapid synchronising with the fading of red brown colour and intensifying of blue colour.

Thus the sequence of reactions in all the four substrates is the same despite minor differences in the oscillatory pattern. The values of exchange current density at a concentration of  $10^{-3}$  M are<sup>7,8</sup>:

Pt/I<sub>2</sub>, I<sup>-</sup>  $10^{-2}$  amp/cm<sup>2</sup>,

Pt/Mn(III), Mn(II)  $10^{-5}$  amp/cm<sup>2</sup>.

At point A, the concentration of iodine is sufficient to control the potential. The decrease in the iodine concentration leads to a corresponding decrease in the potential (A to B). Concentration of iodine lower than  $10^{-5}$  M does not develop blue colour with starch. At B the concentration of iodine is too low ( $<10^{-6}$  M) to control the potential. The potential is now controlled by other species present namely Mn(II), Mn(III) couple. Point C represents the maximum Mn(III), Mn(II) ratio. The colour of the solution is intense red brown. From C to D, the fading of red brown and formation of blue colour correspond to the consumption of Mn(III) and formation of iodine. At D the potential is again controlled by iodine which is now present in sufficient concentration.

Two sets of simultaneous recordings with ethyl acetoacetate as the substrate under identical conditions are provided in figure 2. The potentiometric recordings with a platinum indicator electrode presented at the top and the spectrophotometric recordings at a wave length of 480 nm substantiate the above observations. The peak of the spectrophotometric recording corresponds to the lowest point in the base region of the potentiometric recording. The base region in the spectrometric recording corresponds to

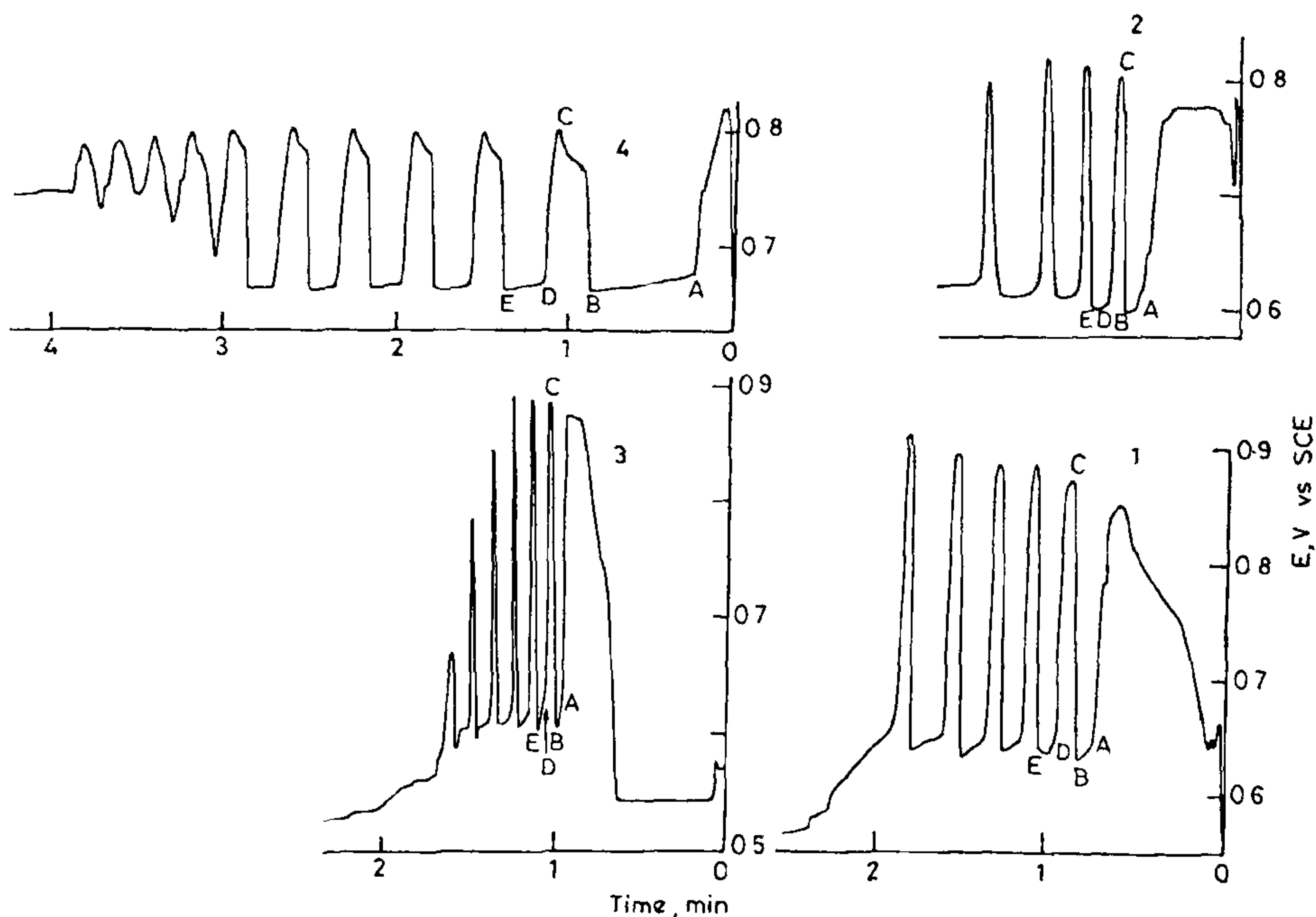


Figure 1. Oscillatory behaviour of different substrates

T 32°C	[H <sub>2</sub> O <sub>2</sub> ] M	[KIO <sub>3</sub> ] M	[Mn <sup>2+</sup> ] M	[H <sub>2</sub> SO <sub>4</sub> ] M
1 [EAA] = 0.1 M	0.2	0.062	0.003	0.1
2 [MA] = 0.04 M	0.4	0.062	0.006	0.04
3 [AcAc] = 0.09 M	0.2	0.035	0.005	0.4
4 [DEM] = 0.26 M	1.2	0.048	0.02	0.16

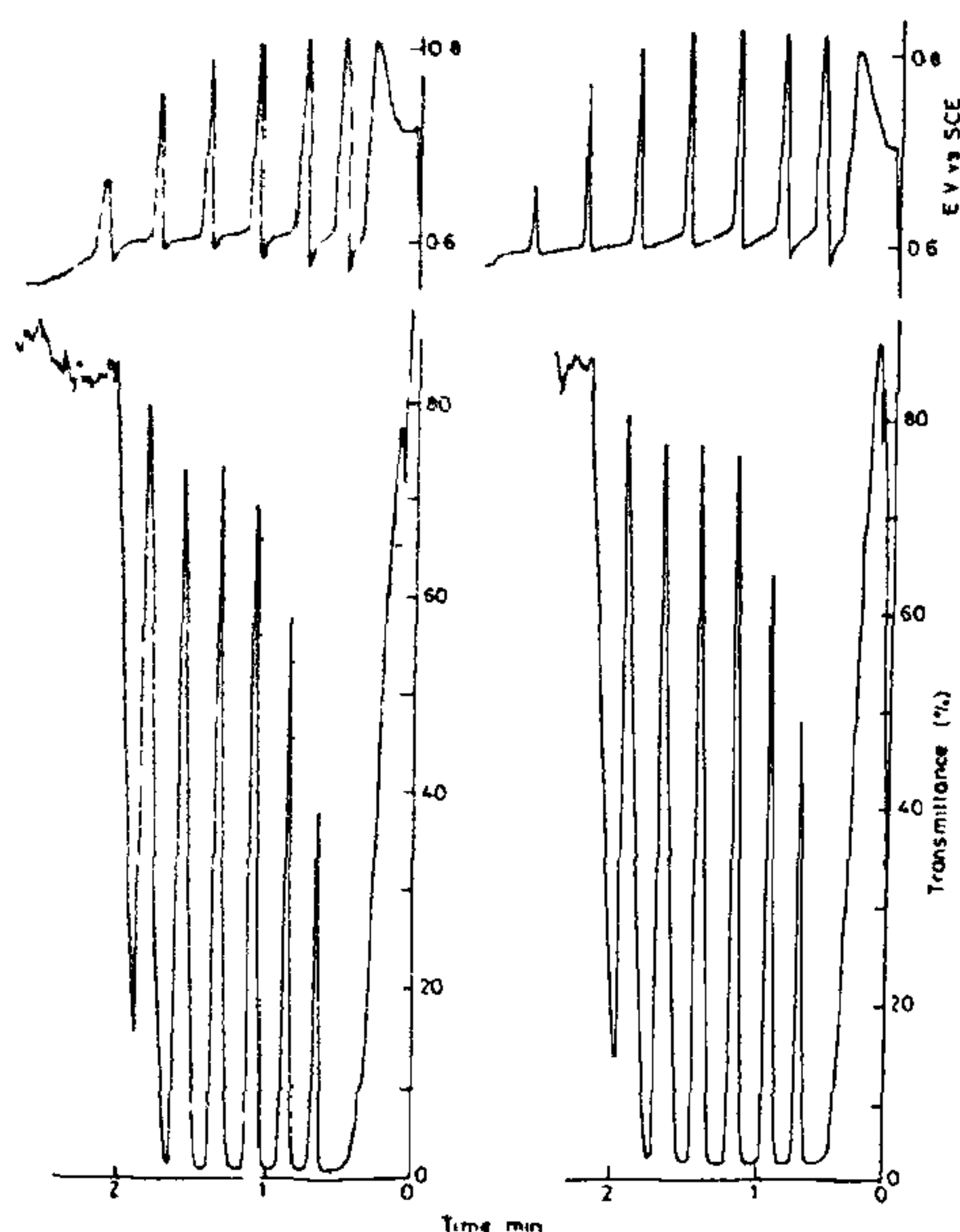
A = [I<sub>2</sub>]max; AB = [I<sub>2</sub>]consumption; B = [I<sub>2</sub>]min; BC = Mn(III) build up; CD = [I<sub>2</sub>] build up and Mn(III) consumption; D = [I<sub>2</sub>]max; E = [I<sub>2</sub>]min

maximum colour intensity of the solution with a large time lag.

The oscillations obtained with platinum indicator electrode with four different substrates provide vital information regarding the sequence of reactions taking place. This would provide a common scheme for all the four reactions and difference in oscillation characteristics can be attributed to difference in the reactivity of the substrate with special reference to the rate of iodine consumption.

9 May 1985; Revised 28 June 1985

1. Noyes, R. M. and Furrow, S. D., *J. Am. Chem. Soc.*, 1982, **45**, 104.
2. Furrow, S. D. and Noyes, R. M., *J. Am. Chem. Soc.*, 1982, **42**, 104.
3. Ramaswamy, R., *Proc. of the Symposium on interactions at electrode-electrolyte interface*, DAE-I.I.T. Madras, Dec. 1982, p. 30.
4. Ramaswamy, R. and Ramanathan, S., *Curr. Sci.*, 1983, **52**, 638.
5. Ramaswamy, R. and Ramanathan, S., *Proc. Indian Acad. Sci., (Chem. Sci.)* 1984, **93**, 813.
6. Dekepper, P. and Epstein, R., *J. Am. Chem. Soc.*,



**Figure 2.** Spectrophotometric ( $\lambda = 480\text{ nm}$ ) and potentiometric (Pt electrode) oscillations in EAA –  $\text{Mn}^{2+}$  –  $\text{H}_2\text{SO}_4$  – iodate system concentration conditions:  $[\text{EAA}] = 0.1\text{ M}$ ,  $[\text{Mn}^{2+}] = 0.003\text{ M}$ ,  $[\text{H}_2\text{SO}_4] = 0.1\text{ M}$ ,  $[\text{KIO}_3] = 0.058\text{ M}$ ,  $[\text{H}_2\text{O}_2] = 0.5\text{ M}$ . Temperature  $27^\circ\text{C}$ .

1982, 104, 49.

7. Tanaka, N. and Tamamushi, R., *Electrochim Acta*, 1964, 9, 963.
8. Vetter, K. J., *Trans. Symp. Electrode Processes*, (ed.) Ernest Yeager, John Wiley, N.Y. 1959, p. 47.

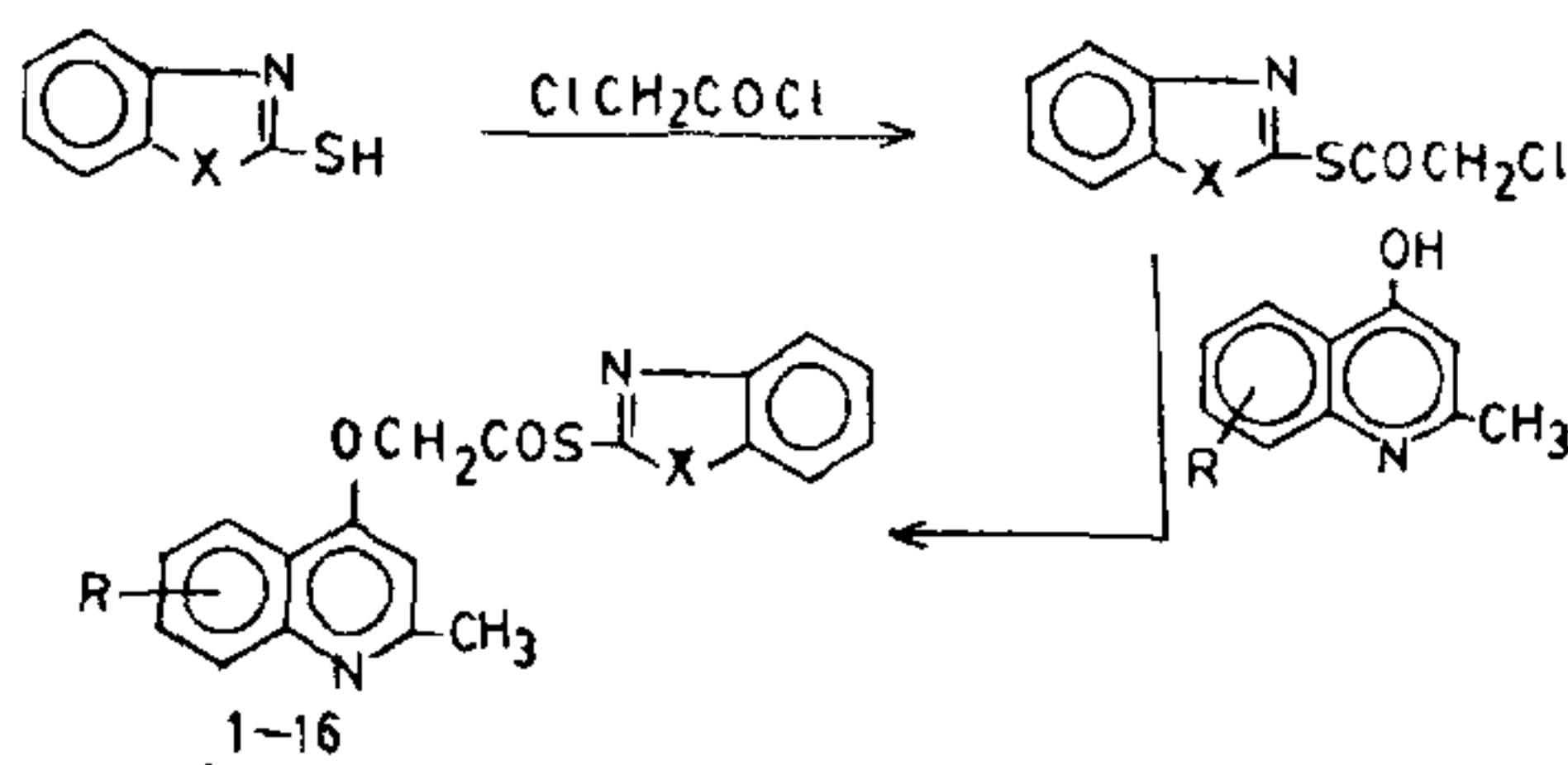
### SYNTHESIS OF 2-METHYL 4-[2'-(MERCAPTOACETOXY)BENZIMIDAZOLYL/BENZOXAZOLYL]-6-or 7-SUBSTITUTED QUINOLINES AS POTENT ANTIMALARIALS

J. S. SHUKLA and V. K. AGARWAL  
Chemistry Department, Lucknow University,  
Lucknow 226 007, India.

DRUGS of quinoline<sup>1-4</sup> type are known for their activity against erythrocytic stages of the malarial

parasite. Benzimidazoles<sup>5,6</sup> and benzoxazoles<sup>7,8</sup> are also well established as biologically active agents. An attempt has been made to develop new agents that would structurally include systems related to quinoline along with benzimidazole/benzoxazole and hopefully this may result in compounds having better anti-malarial activity.

2-Mercapto-benzimidazole/benzoxazole on chloroacetylation gave 2-chloroacetylmercapto-benzimidazole/benzoxazole which on condensation with 2-methyl-6 or 7-substituted quinolines, yielded 2-methyl-4-[2'-(mercapto acetoxy)benzimidazolyl/benzoxazolyl]-6 or 7-substituted quinolines.



Scheme-1

All m.p.s were recorded in an open capillary and are uncorrected. The IR spectra of the compounds were taken in Perkin-Elmer 137 and 177 spectrophotometer in KBr pellets ( $\nu_{\text{max}}$  in  $\text{cm}^{-1}$ ) and PMR on varian A-60D and Perkin Elmer R-32 spectrometer, using TMS as internal reference. The mass spectra of the compounds were taken in Jeol-JMS-D-300 instrument.

2-Chloroacetylmercaptobenzimidazole and 2-chloroacetylmercaptobenzoxazole were prepared according to the methods reported earlier<sup>9</sup>. 2-Methyl-4-hydroxy 6- or 7-substituted quinolines were also prepared as described in literature<sup>10</sup>. 2-Chloro-acetylmercapto-benzimidazole (2.26 g; 0.01 mol) and 2-methyl 4-hydroxyquinoline (1.6 g; 0.01 mol) were refluxed in 15 ml pyridine for 4 hr. The residue after distilling pyridine was poured in a mixture of conc. HCl and ice. The solid separated was filtered and recrystallized with methanol. m.p.  $134^\circ\text{C}$ ; yield: 2.16 g (62.6%). Anal. for  $\text{C}_{19}\text{H}_{15}\text{N}_3\text{O}_2\text{S}$ , Calc.: N, 12.1%; C, 65.3% & H, 4.3%; found N, 11.8%; C, 65.0% and H, 3.1%; IR (KBr)  $\text{cm}^{-1}$  1610 (C=N), 1620 (C=O), 3250–3300 (NH), 1235 (C—O—C), 650 (C—S); PMR ( $\text{CDCl}_3$ );  $\delta$  2.5 (s, 3H,  $\text{CH}_3$ ), 3.82 (s, 2H,  $\text{OCH}_2$ ) 8.0–8.4 (br, 1, NH), 6.7–7.34 (m, Ar-H); Mass:  $\text{M}^+$  at m/e 349.

Other compounds of the series were prepared similarly and the results are shown in table 1.