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Kinetic Studies on Resorcinol–Bromate–Manganese(II) Ion Oscillator with and without Additives[1]

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Abstract—The present work pertains to the effect of temperature on the oscillatory behavior of bromate driven, Manganese (II) ion catalyzed BZ reaction with aromatic substrate i.e. resorcinol under batch conditions in 1.3 M sulfuric acid as aqueous acid medium. In order to study the effect of methyl ketones as additives (co-substrates), acetone is added to the aforesaid reaction system and the oscillations of the mixed substrate systems were studied at different temperatures. Further the effect of temperature with respect to ternary systems comprising of acetone with other ketones like butanone, pentanone, hexanone and acetyl acetone in 1:1 (v/v) ratio is also studied. It is found that temperature has a marked influence on the reactivity of the reaction systems, with and without methyl ketones and at all concentrations of the additives. Moreover, the rate of enolization of ketones also affects the oscillatory parameters like t_{in} and t_p. Although the exact values of enolization constants for the methyl ketones are not known to us, but by studying the oscillatory behavior, a trend can be predicted. Further the formation of end products in the ternary systems is influenced due to hydrophobic interactions of the ketones.

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INTRODUCTION

The phenomenon of oscillations [1], traveling waves and chaos in reacting chemical reactions began as curiosities but now support an active research field. Oscillatory chemical reactions are related to important processes in biology, like nerve signal transmission [2], cardiac arrhythmias [3, 4] and animal coat patterning [5]. The study of these reactions has been dominated by Belousov–Zhabotinsky (BZ) reaction [6], which being a complex reaction involves a large number of species, categorized as reactants, products and intermediates. It is the concentration of intermediate species that undergo oscillations in time as a result of chemical kinetics [7, 8]. Well established mechanism for such a reaction involving a variety of substrates like malonic acid (FKN mechanism) [9] involving 10 steps and GTF mechanism [10, 11] which has 80 reaction steps can be generalized with the following core reactions:

$$BrO_3^- + HBrO_2 + H^+ \rightleftarrows 2Br_2 + H_2O, \qquad (I)$$

$$2Br_2 + M_{red} + H^+ \rightarrow HBrO_2 + M_{ox}. \qquad (II)$$

Here M_{red} and M_{ox} are the reduced and the oxidized forms of a metal ion respectively such as Ce(III)/Ce(IV), or Fe(II)/Fe(III), or Mn(II)/Mn(III) couple or the like. The overall stiochiometry of the above two equations can be depicted as under:

$$BrO_3^- + HBrO_2 + 3H^+ + 2M_{red} \rightarrow 2HBrO_2 + 2M_{ox} + H_2O. \qquad (III)$$

In the present system, the Mn(II)/Mn(III) couple gave good results in terms of rate constant as compared to Ce(III)/Ce(IV) and Fe(II)/Fe(III) couples. A detailed study of the BZ reaction with aliphatic compounds like oxalic acid [12], malonic acid [13], citric acid [6], glucose [14], gallic acid [15], hydroxybenzoic acid [16] and ketones viz., cyclohexanone [17], and acetone [18] in wide range of concentrations of the substrates have been reported, but the effect of binary mixtures of ketones on the BZ system containing aromatic substrates is not studied so far. Although it is reported that oscillations exhibit remarkable change with increasing or decreasing concentrations of ketones, e.g., increasing or decreasing the concentration of acetone causes the concentration of Br_2 to be either very low or else high [19]. Removal of Br_2 by reaction with acetone is competitive with its formation as very little BrO_3^- was present after the formation of Br_2. Enolization of acetone is the rate determining step for its bromination [20]. The varying concentration of acetone affects the induction period [21], time period as well as the rate of reaction. Further temperature is one of the external factors that have a pronounced effect on the kinetics of bromate driven oscillators. Temperature dependence for a variety of cata-

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Table 1. Effect of temperature on the oscillatory parameters on the systems without ketone (parent system) and with 10 vol % acetone, [Resorcinol] = 0.0225 mol l^{-1}, [BrO^{3-}] = 0.1 mol l^{-1}, [Mn^{2+}] = 4×10^{-3} mol l^{-1}, [H_2SO_4] = 1.3 mol l^{-1}

Temperature, °C	Induction period, t_{in}, s		Time period, t_p, s	
	without ketone	acetone	without ketone	acetone
25	250	320	140	95.0
30	130	190	110	65.0
35	90	135	85	45.0
40	70	100	65	37.5
45	55	80	50	28.5

Table 2. Effect of temperature on the oscillatory parameters for the system containing 1 : 1 solutions of acetone with butanone, pentanone, hexanone each separately added to the system: [Resorcinol] = 0.0225 mol l^{-1}, [BrO_3^-] = 0.1 mol l^{-1}, [Mn^{2+}] = 4×10^{-3} mol l^{-1} and [H_2SO_4] = 1.3 mol l^{-1}

Temperature, °C	Induction period, t_{in}, s			Time period, t_p, s		
	butanone	pentanone	hexanone	butanone	pentanone	hexanone
25	290	280	275	62.5	58.75	62.5
30	210	200	170	50.0	42.50	50.0
35	160	140	155	40.0	35.00	30.0
40	110	90	100	30.0	27.25	25.5
45	90	65	80	22.5	20.0	12.5

lyzed and uncatalyzed bromate driven oscillators have been characterized [22–28].

In the present investigation, the effect of temperature on oscillatory behavior of the system comprising of resorcinol as the chemical oscillator (substrate), bromate ion as the oxidant and manganese (II) ion as catalyst has been studied. The reaction was performed in 1.3 mol l^{-1} sulfuric acid with and with out acetone and mixed methyl ketones as additives (co-substrates) and thus a comparative trend was observed between single, binary and ternary systems.

EXPERIMENTAL

All reagents used were either analytical grade chemicals or else of high purity. The reagents used were resorcinol 99% (Himedia, AR), potassium bromate 99% (Merck), acetone 99% (Ranbaxy), butanone 99% (Qualigens), pentanone 99% (Himedia), hexanone 99% (Himedia), acetyl acetone 99% (Himedia), manganese (II) sulfate monohydrate (Merck). All desired solutions of the reagents were prepared in 1.3 mol l^{-1} sulfuric acid 98% (Merck LR).

The ion analyzer (ELICO LI-126) having pH as well as mV option was calibrated in ORP mode with the standard solutions, using Platinum electrode and Calomel (SCE) as indicator and reference electrodes respectively. The equipment was hooked to two half cells, one containing any of the reaction systems under investigation into which Platinum electrode was dipped as indicator electrode. The another half cell was filled with 2.5×10^{-4} mol l^{-1} solution of potassium chloride and the calomel electrode was dipped into it as reference electrode. The two half cells were connected through salt bridge and thermostated to a range of temperatures from 25 to 45 ± 0.1°C in a Siskin Julabo water bath. All the solutions used in the reaction systems were first kept under thermostatic conditions at desired temperatures for about ten minutes in order to maintain uniform temperature in the reagents. The reaction started after the addition of 2 ml 0.1 mol l^{-1} solution of potassium bromate to a solution containing 2 ml each of 0.0225 mol l^{-1} resorcinol, 1 : 1 binary mixture of ketones and 0.004 mol l^{-1} manganese (II) sulfate monohydrate.

RESULTS AND DISCUSSION

The nature of oscillations observed in the single substrate system, i.e., with resorcinol only as the organic substrate is shown in Fig. 1. Although the oscillatory of this system has already been reported [29], but the objective of the present investigation is to monitor the effect of temperature and single (acetone) as well as the mixed methyl ketones as co-substrates, on the oscillatory characteristics of the system which is now a binary system with acetone and ternary system with mixed methyl ketones. In the single substrate system (Fig. 1), the bromine controlled [30] oscillations appear only after an induction period (t_{in}) and with increasing temperature the induction period as well as the time period (t_p) decrease. The amplitude and the frequency of the oscillations are well pronounced at 30 ± 0.1°C. In the mixed substrate system (binary), considerable changes in the oscillatory parameters are observed with varying concentration of acetone as the co-substrate (Fig. 2). At 30 ± 0.1°C and with 10 vol % acetone, the number and amplitude of oscillations is found greater than with any other concentration of acetone (Fig. 2b) and thus further investigations of the binary system were carried out with 10 vol % acetone and the oscillatory parameters of this system obtained at various temperatures are recorded in Table 1 and the nature of oscillations depicted in Fig. 3.

For the ternary reaction systems containing a mixture of acetone with butanone, pentanone, or hexanone, we obtained data similar to those plotted in Figs. 1 and 3. The data on oscillatory parameters and the typical potential-time plots pertaining to the ternary reaction systems are shown in Table 2 respec-

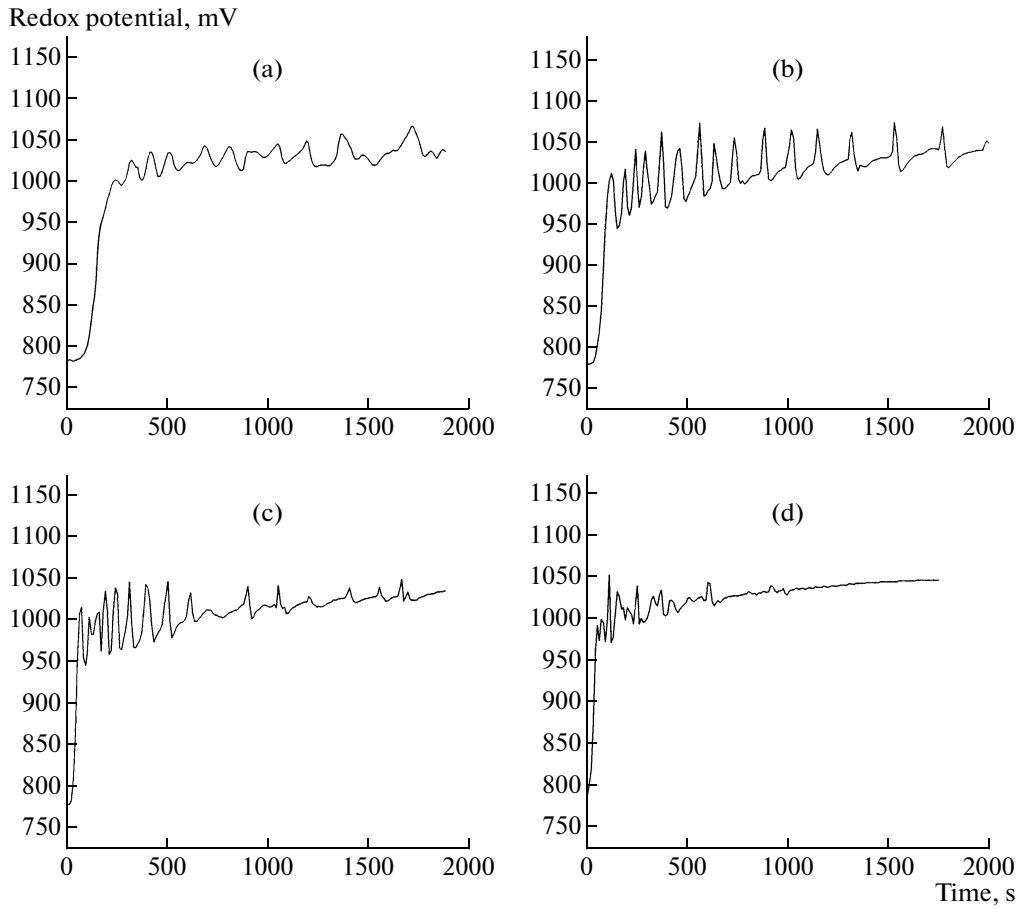


Fig. 1. Potential (mV) versus time (s) plots showing dependence of oscillatory characteristics on temperature variations. System: [Resorcinol] = 0.0225 mol l^{-1}, $[BrO_3^-] = 0.1$ mol l^{-1}, $[Mn^{2+}] = 4 \times 10^{-3}$ mol l^{-1}. (a) 25 ± 0.1°C, (b) 30 ± 0.1°C, (c) 35 ± 0.1°C, (d) 40 ± 0.1°C.

tively. The ternary reaction systems comprise of resorcinol as the main organic substrate with 1 : 1 binary mixtures (v/v) of acetone + butanone, acetone + pentanone, acetone + hexanone and acetone + acetylacetone. For all the three types of reaction systems, viz., single, binary and ternary, it is found that temperature has a marked effect on the magnitude of oscillatory characteristics and thus on the rate of reaction. As such, the oscillatory characteristics like time of induction (t_{in}) and time period (t_p) can be correlated with rate constant (k) as:

$$t \propto k, \quad (1)$$

$$t = \text{constant} \times k. \quad (2)$$

Substituting (1) and (2) in Arrhenius equation, we have:

$$k = A\, e^{-E/RT}, \quad (3)$$

or

$$t = \text{constant} \times e^{-E/RT}, \quad (4)$$

or

$$\log t = \log\text{constant} - (E/R)(1/T). \quad (5)$$

From Eq. (5), it is apparent that temperature (T) is inversely related to time of induction/time period, which is in turn directly proportional to the rate constant of the reaction. E, A, and R stand for effective activation energy, pre-exponential factor and molar gas constant respectively.

The order of reactivity of binary and ternary reaction systems, i.e., resorcinol + acetone and resorcinol + 1 : 1 mixtures of acetone with other methyl ketones as mixed substrate systems with respect to t_{in} and t_p show a varying trend at lower, high and higher temperatures. e.g., at lower temperature like 25 ± 0.1°C, the order follows as:

acetone > acetone–butanone > acetone–pentanone > acetone–hexanone (w.r.t t_{in}).

At high temperatures like 30 and 35 ± 0.1°C, the order of reactivity is:

acetone–butanone > acetone–hexanone > acetone–pentanone > acetone (w.r.t t_{in}),

while as, at higher temperatures like 40 and 45 ± 0.1°C, the order of reactivity is:

acetone–butanone > acetone = acetone–hexanone > acetone–pentanone (w.r.t t_{in}).

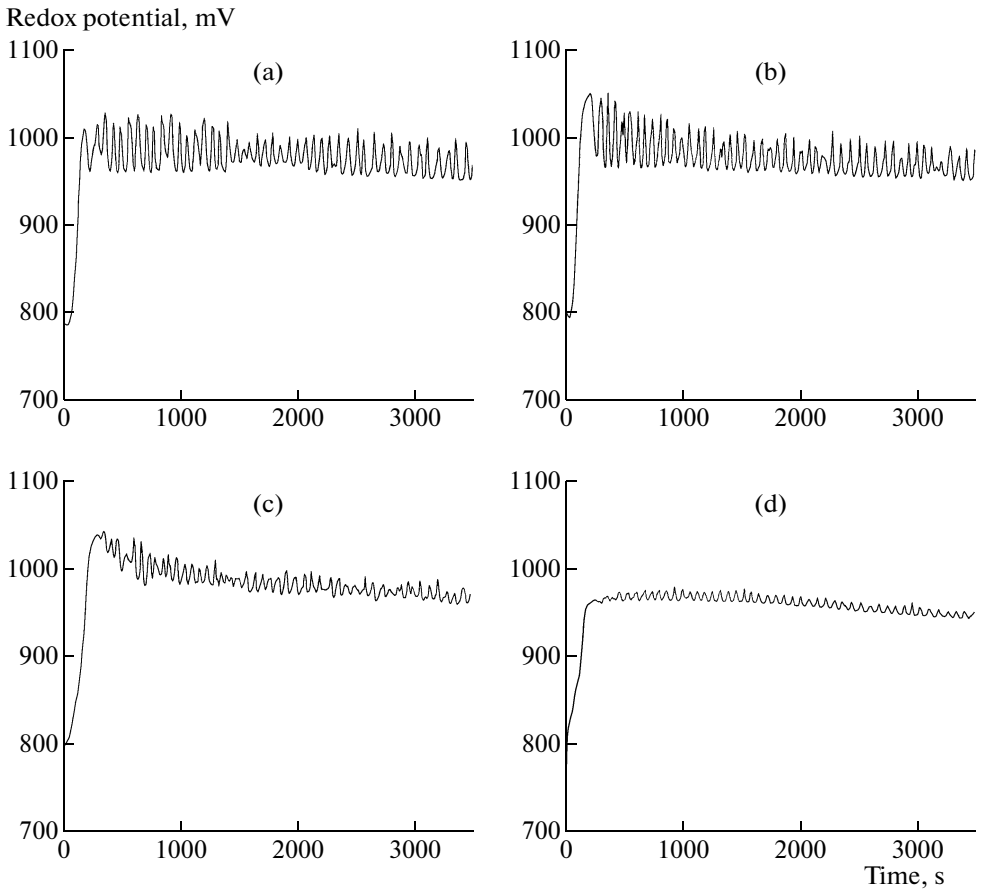


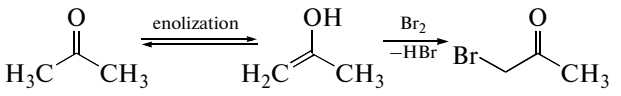
Fig. 2. Potential (mV) versus time (s) plots showing variation of oscillatory characteristics for the system containing [Resorcinol] = 0.0225 mol l^{-1}, $[BrO_3^-]$ = 0.1 mol l^{-1}, $[Mn^{2+}] = 4 \times 10^{-3}$ mol l^{-1}, $[H_2SO_4]$ = 1.3 mol l^{-1}. [Acetone]: (a) 5%, (b) 10%, (c) 15%, (d) 20%. Temperature = 30 ± 0.1°C.

Similarly, the order of reactivity with respect to time period, at lower (25, 30 ± 0.1°C) and higher temperatures (35, 40, 45 ± 0.1°C) is respectively shown as under:

acetone > acetone–butanone = acetone–hexanone > acetone–pentanone (lower *T*)

acetone > acetone–butanone > acetone–pentanone > acetone–hexanone (higher *T*)

The reactivity of the reaction systems is related to rate of enolization of ketones like:



keto form enol form bromo derivative

The enol form acts as a nucleophilic site for bromide attack and form bromo acetone as reaction intermediate. The bromo acetone/bromoketone derivative accounts for the decrease in induction period and time period. As suggested by FKN mechanism, the bromo derivative acts as positive feedback for the bromination of resorcinol. As the mechanism suggests that induction period corresponds to the saturation of the system with bromoderivative (autocatalyst), which is apparent in this experiment visually. However, the discrepancy in the order of reactivity with respective to t_{in} and t_p at lower and higher temperatures is because of the influence of both enolization constant as well as hydrophobic interactions. At lower temperatures, the hydrophobic interactions are dominant, in additions to other bromination reactions. While as, at higher temperatures, rate of enolization of ketones increases with increase in temperature [31], which favors the bromination, which in turn decreases the induction as well as time period of oscillations. Thus, for the ternary systems, it is the additive effects of ketones which influence the oscillatory parameters.

It is reported [32] that acetylacetone is the scavenger for HOBr and Br_2 and the minimal oscillations shown are purely radical controlled at higher concentrations of ketone. The main oscillator in the present system is resorcinol which being aromatic compound gets precipitated out at the end point as bromoderivative. The use of co-substrates like ketones increases the solubility of the end product and can show more oscil-

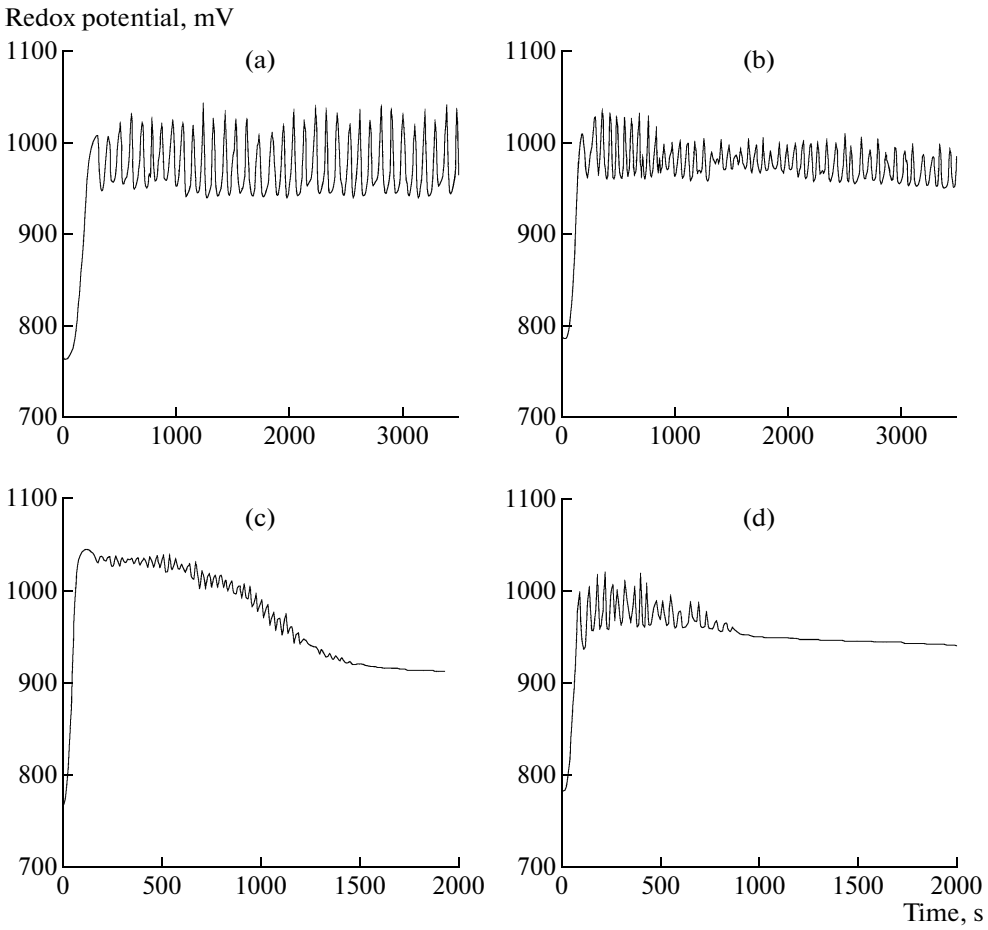


Fig. 3. Potential (mV) versus time (s) showing variation of oscillatory parameters with change in temperature for the system containing 10% acetone (v/v), [Resorcinol] = 0.0225 mol l^{-1}, $[BrO_3^-]$ = 0.1 mol l^{-1}, $[Mn^{2+}] = 4 \times 10^{-3}$ mol l^{-1}. (a) 25 ± 0.1°C (b) 30 ± 0.1°C (c) 35 ± 0.1°C (d) 40 ± 0.1°C.

lations by taking the reaction to the initial steps. But the increase in chain length of the ketones goes on increasing the non polar character (hydrophobic nature) of the reaction mixture. In this context, the reported values of dielectric constants [33] for acetone, butanone, pentanone, hexanone and acetyl acetone are 20.7 (25°C), 18.5 (20°C), 15.4 (20°C), 14.6 (15°C), and 23.1 (20°C) respectively. It is observed that the particles of precipitate formed are smaller with the lower ketones, but for the 1 : 1 binary mixture of acetone and hexanone larger crystals are formed, though in a small quantity. This may be due to the energy prevalent in the system owing to the higher hydrophobic of the hexanone. However, it needs further investigations on similar type of systems to probe into the mechanism. It is presumed that the higher hydrophobic nature of hexanone (lower dielectric constant of the reaction medium) provides the energy for the larger particles to form. This effect needs further investigations to carry out for the same and like systems. Amongst the ternary systems the system with resorcinol + 1 : 1 binary mixture of acetone with acetylacetone (Fig. 4) did not show oscillations up to

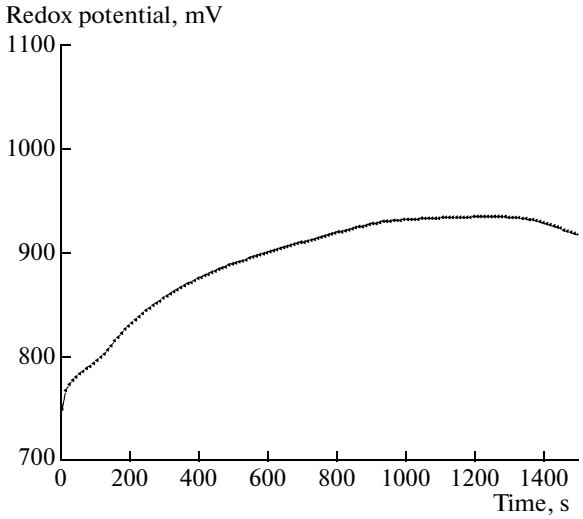


Fig. 4. Potential (mV) versus time (s) plot for the system containing 1 : 1 solution (v/v) of acetone and acetyl acetone at 30 ± 0.1°C. System: [Resorcinol] = 0.0225 mol l^{-1}, $[BrO_3^-]$ = 0.1 mol l^{-1}, $[Mn^{2+}] = 4 \times 10^{-3}$ mol l^{-1}, $[H_2SO_4]$ = 1.3 mol l^{-1}.

10% concentration range in 1 : 1 binary mixture with acetone and between 25 to 40 ± 0.1°C. It is also mentioned that the oscillatory parameters in the single substrate system (without methyl ketones) are found lower as compared to binary and ternary systems.

CONCLUSIONS

The oscillatory parameters like t_{in} and t_p are drastically affected by temperature. Mechanistically the rate of enolization of ketones as well as the stability of bromo ketones as reaction intermediates also effect the oscillatory parameters. Moreover, the oscillatory parameters in the ternary system vary due to the additive effect of methyl ketones. In ternary system, the hydrophobic interactions affect the quality of end product, i.e., with higher ketones larger crystals are formed due to the increase of non polar character in the reaction mixture. The appearance of heterogeneity in BZ reaction owing to decrease in dielectric constant opens new dimensions in catalyzed BZ reactions for probe.

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