liter[2]. The oscillation parameters are influenced to the greatest degree by the initial concentrations of sulfuric acid and cysteine hydrochloride; consequently, changes in these concentrations may be an important factor in regulating the periodic regime in the potassium iodate – hydrogen peroxide – cysteine hydrochloride – sulfuric acid system.

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OSCILLATIONS OF BROMINE CONCENTRATION IN BELOUSOV – ZHABOTINSKII REACTION

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Free bromine may play an important role in the mechanism of the Belousov – Zhabotsinkii oscillating chemical reaction, which takes place in a system consisting of bromate, malonic acid, cerium(III, IV), and sulfuric acid. The information available in the literature relative to the presence of a perceptible concentration of free bromine in this oscillating reaction is contradictory. Franck and Geiseler [1] believe that the oscillations of optical density in the 500 nm region that are observed in the reaction of bromate – malonic acid – cerium(III, IV) are due mainly to oscillations of free bromine concentration. In the oscillating reaction of bromate – malic acid – cerium(III, IV), free bromine can be extracted with chloroform, which cannot be done successfully when the malic acid is replaced by malonic [2]. From these observations it has been concluded that there is no free bromine present in the reaction with malonic acid. In [3], oscillations of optical density that were registered in the 400-600 nm region in the reaction of bromate – malonic acid – cerium(III, IV) were attributed to oscillations in the concentration of cerium(IV) ions and $BrO_2^{\cdot}$ radicals. However, in the calculations it was assumed that free bromine does not contribute to the oscillations of optical density in the 401 nm region. It was shown in [4] that the experimental absorption spectrum in the 400-550 nm region that is obtained in the process of the oscillating reaction of bromate – malonic acid – cerium(III, IV) is not consistent with the absorption spectrum of $BrO_2^{\cdot}$ radicals, but with the absorption spectrum of free bromine, the concentration of which was found to be $1 \cdot 10^{-4}$ mole/liter.

The goal of the present work has been to determine the amplitude of bromine concentration oscillations and to find the dependence of the amplitude on the initial concentrations of bromate and malonic acid.

The bromine concentrations were determined spectrophotometrically, using a Specol spectrocolorimeter combined with a magnetically stirred titration unit and recording the amplitude of the oscillations in optical density at a wavelength of 500 nm. The sensitivity of the unit was approximately 0.005 units of optical density per scale division (2 nm) of the strip chart of the KSP-4 automatic potentiometer that was used to register the oscillations of optical density. The potentiometer scale was calibrated on solutions with known concentrations of free bromine and cerium(IV) ions. In determining the amplitude of bromine concentration oscillations, the amplitude of oscillations of the total optical density was recorded at a wavelength of 500 nm; and from this value, there was deducted the amplitude of oscillations of optical density due to oscillations of the cerium(IV) ion con-

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TABLE 1. Positions of Absorption Band Maxima and Corresponding Molar Extinction Coefficients of Colored Products from Reducation of Bromate

Compound	λ_{max}, nm	ε, liter · mole^{-1} · cm^{-1}	Medium	Literature reference
$BrO_2^{\cdot}$	475	$2 \cdot 10^3$	10^{-2} mole/liter BrO_3^-, pH=7	[5]
$BrO^{\cdot}$	350	—	—	[5]
Br_2	400	194	0,5 mole/liter $HClO_4$	[6]
	395	178	KBr soln., —	[7]
Br_2^-	365	$(7,8 \pm 2) \cdot 10^3$	mole/liter pH=5—9	[8]
	700	420	10^{-3} mole/liter KBr, pH=7	[9]
Br_3^-	267	$(3,47 \pm 0,01) \cdot 10^4$	—	[10]
	270	$5,5 \cdot 10^4$	—	[7]

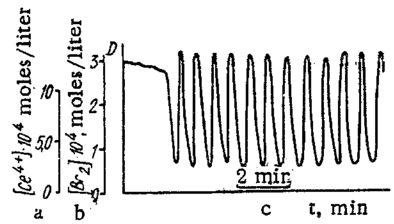

Fig. 1

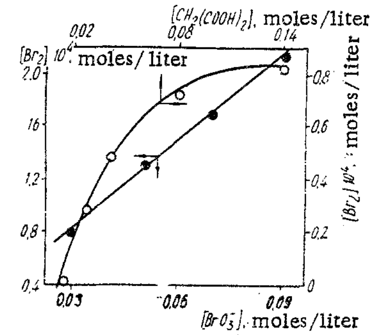

Fig. 2

Fig. 1. Calibration data for automatic potentiometer scale on 500 nm wavelength with respect to concentration of cerium(IV) ion (a) and free bromine (b); graph c shows the oscillations of total optical density at 500 nm in the reaction of sodium bromate (0.09), malonic acid (0.14), cerium (III) (0.001), and sulfuric acid (1.5 moles/liter).

Fig. 2. Bromine concentration oscillation amplitude as a function of original concentrations of bromate and malonic acid. Initial concentrations of reactants: cerium(III) 0.001, sulfuric acid 1.5, sodium bromate 0.035, malonic acid 0.14 mole/liter.

centration. The magnitude of the amplitude of oscillations in cerium(IV) concentration was determined at a wavelength of 320 nm, where the contribution of bromine to the optical density of the solution is insignificant (less than 1%). The sensitivity of determination of bromine and cerium(IV) concentrations at a wavelength of 500 nm was $1.2 \cdot 10^{-5}$ and $5.3 \cdot 10^{-5}$ mole/liter, respectively. When using this method, the accuracy in determining the amplitude of bromine concentration oscillations will depend on the reproducibility of the amplitude of cerium(IV) concentration oscillations. With a 10% change in the amplitude for cerium, the error in determining the amplitude of bromine concentration oscillations amounts to 2-3%.

All of the solutions used in this work were prepared from accurately weighed samples of reagents with a quality grade no lower than "ch. d. a." [pure, for analysis], with subsequent dilution. The measurements were performed in 30-ml cuvettes with a lightpath of 2 cm; the reaction mixture volume was 20 ml.

In Fig. 1 we show calibration data for the potentiometer scale, indicating the sensitivity of determination of cerium(IV) and bromine concentrations at 500 nm wavelength; also shown are the oscillations of total optical density at this wavelength. The amplitude of the cerium(IV) concentration oscillations in this system (Fig. 1) is $2.8 \cdot 10^{-4}$ mole/liter, that of bromine $2.1 \cdot 10^{-4}$ mole/liter. For such concentrations of cerium(IV) and bromine, the experimentally determined contribution of bromine to the total optical density of the solution at 500 nm is 77%, at 320 nm 0.3%, and at 401 nm 13%. This means that the assumption made in [3] that the contribution of bromine to the total optical density at 401 nm is insignificant is an erroneous assumption.

When the amplitude of bromine concentration oscillations is determined in the same manner for the reaction with malic acid, with the solution composition the same as in [2], malic acid 0.26, sodium bromate 0.07, cerium(III) 0.001, and sulfuric acid 1.5 moles/liter, the value that is obtained is approximately the same as in the reaction with malonic acid, specifically, $1.9 \cdot 10^{-4}$ mole/liter. The amplitude of cerium(IV) ion concentration oscillations in this reaction is $2.2 \cdot 10^{-4}$ mole/liter.

It is known that in successive one-electron reduction of bromate, the following compounds may be formed: $BrO_2\cdot$, $HBrO_2$, $BrO\cdot$, HBrO, $Br\cdot$, Br_2, Br^-, Br_2^-, Br_3^-. Of these products from the reduction, the following will absorb light in the visible region: Br_2, Br_2^-, Br_3^-, $BrO_2\cdot$, $BrO\cdot$ (Table 1), and probably the radical $Br\cdot$. Br_2^- anion-radicals are formed in the pulse radilysis of solutions containing a fairly high concentration of bromide ions [8, 9]; the formation of this species in the course of the oscillatory reaction is very improbable. In view of the fact that free bromine is formed very rapidly through the reaction

$$HOBr + Br^- + H^+ \rightleftarrows Br_2 + H_2O, \tag{1}$$

the equilibrium constant of which $K = [HOBr][Br^-][H^+]/[Br_2] = 4 \cdot 10^{-9}$ [11], for a bromine concentration of $2 \cdot 10^{-4}$ mole/liter and the time-coincident [4] minimal concentration of bromide ions in the course of the oscillating reaction approximately 1×10^{-6} mole/liter [12], we can estimate the maximal equilibrium concentration of HOBr, which proves to be $\sim 1 \cdot 10^{-7}$ mole/liter. The optical density of such an HOBr solution in the 260 nm region is approximately 10^{-5} mole · liter^{-1} · cm^{-1}; λ_{max} (HOBr) =262 nm, ε =100 [13].

Analogously, we can estimate the maximum concentration of the anion Br_3^-. Starting with the value of the equilibrium constant for its formation reaction $K = [Br_3^-]/[Br_2][Br^-] = 16.2$ [11], along with the above-listed concentrations of bromine and bromide ion, the Br_3^- concentration is approximately $3 \cdot 10^{-9}$ mole/liter. The optical density of such a Br_3^- solution in the 270 nm region is $\sim 10^{-4}$ mole · liter^{-1} · cm^{-1}. It is difficult to determine the concentrations of HOBr and Br_3^- in the course of the oscillating reaction by spectrophotometric analysis. As possible evidence that the light absorption in the 500 nm region is caused, apart from the cerium(IV) ion, by free bromine and not by $BrO_2\cdot$ radicals, we may offer the relationships we found between the bromine concentration oscillation amplitude and the original concentrations of bromate and malonic acid (Fig. 2).

According to the mechanism accepted in the literature for the oscillating reaction [14], bromine is formed as a result of reaction (1) and

$$BrO_3^- + Br^- + 2H^+ \rightleftarrows HOBr + HBrO_2, \tag{2}$$

$$HBrO_2 + Br^- + H^+ \rightleftarrows 2\,HOBr, \tag{3}$$

and is consumed in brominating the malonic acid

$$Br_2 + CH_2(COOH)_2 \rightarrow BrCH(COOH)_2 + Br^- + H^+. \tag{4}$$

The main source of bromide ions is the reaction

$$BrCH(COOH_2) + Ce^{4+} + H_2O \rightarrow CHOH(COOH)_2 + Br^- + H^+ + Ce^{3+}; \tag{5}$$

and bromide ions are also formed as a result of direct reduction of bromate by malonic acid [12]. It has been established experimentally that an increase in the initial bromate concentration in the oscillating reaction leads to an increase in the critical concentration of bromide ions and also an increase in the minimal ("background") concentration of bromide ions [12, 15]. As can be seen from the examination of reactions (1)-(3), this may lead to an increase in the bromine concentration oscillation amplitude. As the malonic acid concentration is increased, the rate of bromine consumption through reaction (4) increases. However, from the bromide that is thus formed, an equivalent quantity of bromine is formed immediately. Also, as the malonic acid concentration is increased, the minimal concentration of bromide ions increases as a consequence of reduction of bromate directly by malonic acid [12], which tends to increase the bromine concentration. On the other hand, an increase in the malonic acid concentration leads to an acceleration of the reaction of hypobromous acid consumption

$$HOBr + CH_2(COOH)_2 \rightarrow CHBr(COOH)_2 + H_2O \tag{6}$$

and a retardation of bromine accumulation through reaction (1). Therefore, the experimentally determined amplitude of the bromine concentration oscillations is actually the resultant of many competing reactions; when the initial malonic acid concentration is increased, the amplitude increases only up to a certain limit (Fig. 2). It should be noted that with a low initial concentration of malonic acid (0.014 mole/liter, Fig. 2), no bromine is detected in the course of the oscillating reaction.

According to the mechanism described for the oscillating reaction, the amplitude of the $BrO_2\cdot$ radical concentration oscillations should decrease with increasing initial malonic acid concentration, since this will give an increase in the bromide ion concentration, these ions inhibiting the autocatalytic reaction of $BrO_2\cdot$ radical accumulation. The amplitude of cerium(IV) concentration oscillations will also decrease, and the amplitude of optical density oscillations, after deducting the contribution from the cerium(IV) ions, will increase; this means that the increase in oscillation amplitude is not due to BrO_2^- radicals but rather to bromine. As cerium(IV) ions accumulate, bromide starts to accumulate rapidly through reaction (5), leading to inhibition of the oxidation of cerium(III) by bromate and a "switching" of the catalyst oxidation cycle to a catalyst reduction cycle [14]. However, as can be seen from experimental data reported in [4, 16], the oxidation of cerium(III) is interrupted at that instant at which the bromide ion concentration is minimal and the bromine concentration reaches a maximum. This means that bromine may serve as an inhibitor for the reaction of cerium(III) oxidation by bromate at this particular instant of time. It is known from the literature that free bromine lengthens the induction period of the cerium(III)–bromate reaction and retards the reaction rate, beginning at a bromine concentration of $1 \cdot 10^{-5}$ mole/liter [17].

The results from our studies have shown that in the course of the Belousov–Zhabotinskii reaction, oscillations of bromine concentration occur, the amplitude increasing with increasing initial concentrations of bromate and malonic acid, reaching $2 \cdot 10^{-4}$ mole/liter. The periodically accumulated bromine, together with bromide ions, may serve as a "switching agent" of the oscillating reaction.

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