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Determination of the Rate Constants from Phase Delay Effect in Chemical Reactions[1]

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Abstract—A new method for the determination of rate constant k of a reaction of the type $A + X \longrightarrow P_1 + P_2$ is presented. The method is based on the phase delay between the oscillatory inflow of the parent substance X into the reaction medium and the concentration of the parent substance in the field changing as a result of the reaction, which can be expressed as $\tan\phi = \frac{2\omega}{kA}$. A method was used for the determination of the rate constant of the saponification of ethyl acetate (reactant A) with sodium hydroxide (reactant X) at 17°C. Reactant A was used in excess with respect to reactant X, which ensured its constant concentration.

INTRODUCTION

Chemical reactions are usually studied by determining changes in the concentrations of reactants in time, from which the reaction rate constant is found. The most common chemical methods for the determination of rate constants are stopping reaction flow, flow methods, mirror techniques, and others [1, 2]. The physical methods used for the same purpose are flash photolysis, relaxation techniques, the measurement of the total pressure of gas, and electric and optical methods [1, 2]. Moreover, some mixed techniques such as dilatometric, calorimetric, and thermal ones are used. Mass spectroscopy and optical spectroscopy make it possible to study unstable reaction intermediates and the kinetics of complex systems [1]. For paramagnetic reactants, the EPR technique can be applied [3].

In chemical reactions, one or more reactants are constantly flowing into a reactor. If the inflow is oscillatory, concentrations of the reactants in the reaction medium can be expected to be oscillatory. However, because of the finite rate of the reaction, these oscillations will be delayed with respect to the inflow. The delay should depend on the rate of the reaction. This intuition and the ensuing possibility of determining the reaction rate constant on the basis of the delay have stimulated this work.

This study was aimed at checking if this intuitive point of view can be realized in practice. A detailed solution will be presented for a simple chemical reaction of the type $A + X \longrightarrow P_1 + P_2$. We assume that reactant A is in great excess, and, therefore, its concentration does not change with the reaction time, while X is supplied to the system in an oscillatory manner. In this case, it is possible to get an exact solution to the kinetic equation from which a time dependence $X(t)$ is obtained. For experimental verification of this relation, we chose the reaction of the saponification of ethyl acetate with sodium hydroxide. Kinetic data on this reaction can be found, for example, in [2, 4]. This reaction occurs at a low rate and has been well recognized. We have chosen this reaction because reactant concentration can be determined in an easy way by conductivity measurements. For this reaction, the literature data on the rate constant most frequently refer to temperatures of 25°C [4, 5] or 30°C [2].

THEORY

The subject of our consideration will be a relatively simple irreversible chemical reaction of the type

$$A + X \xrightarrow{k_1} P_1 + P_2 . \qquad \text{(I)}$$

We assume that component A is in considerable excess and that the concentration of A is constant during the reaction. The reaction of the decomposition of X is characterized by the rate constant k_1. In the kinetic model, we assume that the inflow of the parent substance X into the reactor is periodically variable in time and expressed by the function

$$I_X(t) = \alpha\cos^2\omega t = \frac{1}{2}\alpha(1 + \cos 2\omega t), \qquad (1)$$

where α and ω are the amplitude and frequency of this inflow, respectively. The kinetic equation describing the

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time changes of the X concentration for simple reaction (I) is as follows:

$$\frac{dX}{dt} = -k_1AX + \alpha\cos^2\omega t. \tag{2}$$

Kinetic equation (2) can be solved analytically. After integration, Eq. (2) becomes the following equation for the concentration of parent substance X:

$$X(t) = \frac{\alpha}{2k_1A} + \frac{\alpha}{2(k_1^2A^2+4\omega^2)} \times (k_1A\cos2\omega t + 2\omega\sin2\omega t) + c\exp(-k_1At), \tag{3}$$

where preexponential factor c is

$$c = X_0 - \frac{\alpha}{2k_1A} - \frac{\alpha k_1A}{2(k_1^2A^2+4\omega^2)}, \tag{4}$$

and X_0 is the initial concentration of the parent substance.

The sum of the two trigonometric functions in brackets can be replaced by a single trigonometric function after introdusing an auxiliary angle ϕ defined as

$$\tan\phi = \frac{2\omega}{k_1A}. \tag{5}$$

After substitution into Eq. (3) and some mathematical transformations, we obtain

$$X = \frac{\alpha}{2k_1A} + \frac{\alpha k_1A}{2(k_1^2A^2+4\omega^2)}\frac{1}{\cos\phi} \times \cos(2\omega t-\phi) + c\exp(-k_1At), \tag{6}$$

where the angle

$$\phi = \arctan\left(\frac{2\omega}{k_1A}\right) \tag{6a}$$

is called the shift angle.

The concentration of $X(t)$ changes from the initial value X_0 to the equilibrium value $\frac{\alpha}{2k_1A}$. The time of reaching equilibrium depends on the time constant $\tau = \frac{1}{k_1A}$, which is called the relaxation time. Putting τ into Eq. (6), we obtain

$$X(t) = \frac{\alpha\tau}{2} + b\cos(2\omega t-\phi) + c\exp\left(-\frac{t}{\tau}\right), \tag{7}$$

where b is the amplitude of oscillations which, after the elimination of $\cos\phi$ by means of the trigonometric relation $\cos\phi = \frac{1}{\sqrt{1+\tan^2\phi}}$, can be written as

$$b = \frac{\alpha}{2\sqrt{k_1^2A^2+4\omega^2}} = \frac{\alpha\tau}{2\sqrt{1+4\omega^2\tau^2}} \tag{7a}$$

and c from (4) as

$$c = X_0 - \frac{\alpha\tau}{2}\left(1+\frac{1}{1+4\omega^2\tau^2}\right). \tag{7b}$$

The time dependence of the concentration of the parent substance inflow $I_X(t)$ according to (1) and changes in the parent substance concentration $X(t)$ in the reactor forced by the inflow and described by Eq. (7) are shown in Fig. 1. Instead of the frequency ω, we introduced the oscillation period T which is related to ω through the relation $T = \frac{2\pi}{\omega}$. We assume that the variable inflow is described by the amplitude $\alpha = 6$ and $T = 10$ (Fig. 1, I) or 5 (Fig. 1, II) in arbitrary units. The time dependences of the parent substance concentration are shown in Fig. 1, Ib and Fig. 1, Ic, or Fig. 1, IIb and Fig. 1, IIc. According to Eq. (7), the oscillations of the parent substance concentration $X(t)$ of the amplitude b and frequency ω take place with respect to the average value which changes from the initial value $X_0 = 1$ to a steady state value of $\frac{\alpha\tau}{2}$. The time of the stabilization of the oscillations depends on the relaxation time of the system τ and is relatively long and well perceptible when τ is comparable to the oscillation period T (Fig. 1, Ib and Fig. 1, IIb). When $\tau \ll T$ (Fig. 1, Ic and Fig. 1, IIc), the oscillations are stabilized immediately. As follows from Fig. 1, the most interesting fact is the shift (delay) of the concentration $X(t)$ of the parent substance in the reaction medium compared to the same inflow $I_X(t)$ of X to the system. It is easily seen from a comparison of the maximum or minimum values of $X(t)$ and $I_X(t)$. After reaching a maximum, $I_X(t)$ decreases, whereas the parent substance concentration still increases for some time before it reaches a maximum. The time of this delay δ is related to the shift angle ϕ through $\delta = \frac{T}{2\pi}\phi = \frac{\phi}{\omega}$. Because according to Eq. (5), ϕ cannot exceed $\frac{\pi}{2}$, δ must be less than $\frac{T}{4}$. The time delay of the system response to the oscillatory inflow of the parent substance is determined by the shift angle ϕ, which is related to the $\frac{\tau}{T}$ ratio as $\phi = \arctan\frac{4\pi\tau}{T}$. This is evidenced by a comparison of the curves Ib and Ic or IIb and IIc in Fig. 1. For $T \gg \tau$, the shift angle is low, and for $\tau = T$, $\phi = 85°27'$ (Fig. 1, IIb). Thus we conclude that the angle ϕ takes high values when T is comparable with τ. The amplitude b (see Eq. (7a)) depends on the frequency of oscillations ω and the relaxation time τ.

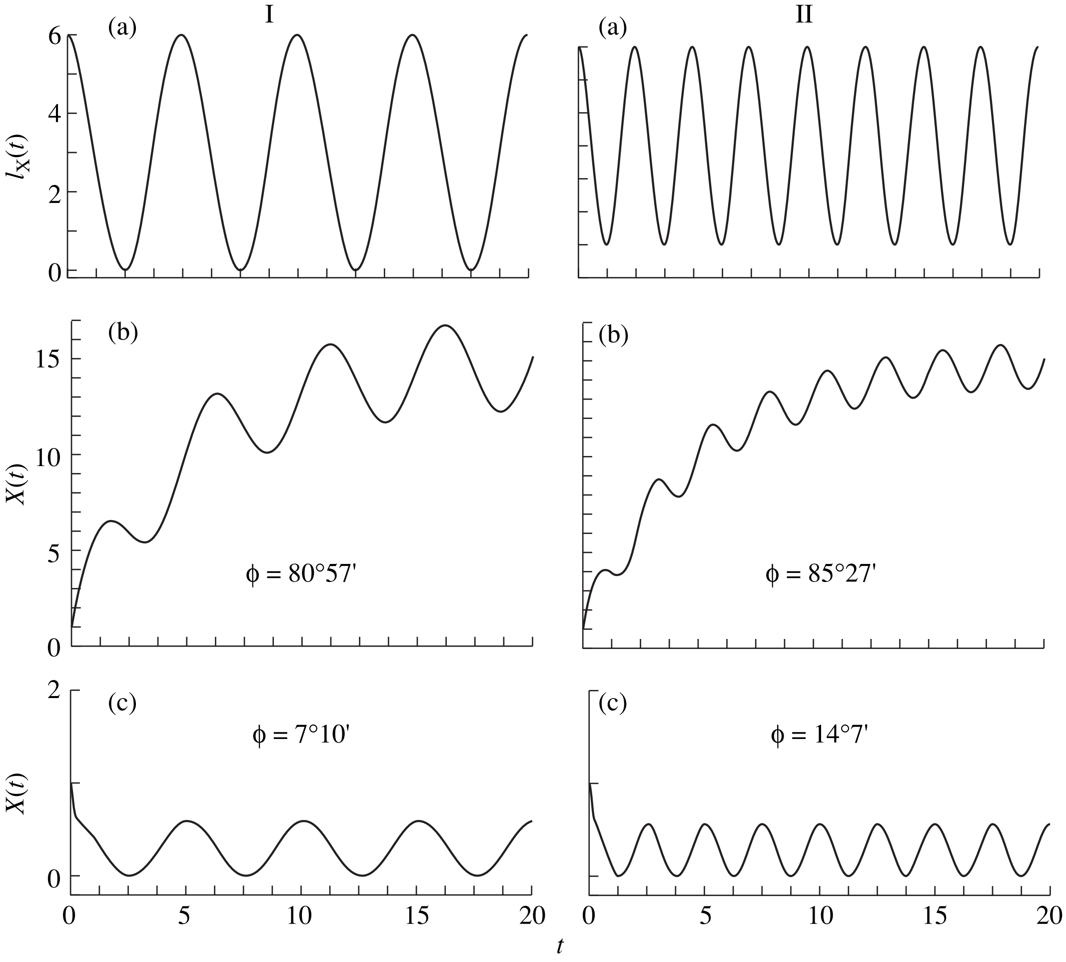

Fig. 1. Oscillatory inflow $I_X(t)$ of the reactant X for the amplitude $\alpha = 6$ and two periods of oscillations: $T = 10$ (I) and $T = 5$ (II) (arbitrary units of time) (a) and time changes in the concentration $X(t)$ in the reactor for two values of the relaxation time: $\tau = 5$ (Ib and IIb) and $\tau = 0.1$ (Ic and IIc) (arbitrary units of time).

The amplitude b increases with increasing τ tending to $\frac{\alpha}{4\omega}$ as follows from Eq. (7a). The value of the amplitude b decreases with increasing frequency ω and becomes zero for $\omega = \infty$.

A similar procedure is applied for the reversible reaction

$$\mathrm{A} + \mathrm{X} \underset{k_2}{\overset{k_1}{\rightleftarrows}} \mathrm{P}_1 + \mathrm{P}_2, \tag{II}$$

for which the solution to the kinetic equation has the following final analytical form:

$$X(t) = k_2P_1P_2\tau + \frac{\alpha\tau}{2} + b\cos(2\omega t - \phi) + c_1\exp\left(-\frac{t}{\tau}\right), \tag{8}$$

where $c_1 = c - k_2P_1P_2\tau$.

The amplitude of oscillation b and the shift angle ϕ are defined as before. Equation (8) differs from the analogous equation for the irreversible reaction (I) by an additional term: $k_2P_1P_2\tau$.

EXPERIMENTAL

To observe the course of a reaction type (R1) with oscillatory inflow of reactant X described by Eq. (7), we have chosen the slow reaction of the saponification of ethyl acetate with sodium hydroxide,

$$\mathrm{CH_3COOC_2H_5 + NaOH} \longrightarrow \mathrm{CH_3COONa + C_2H_5OH}.$$

The reaction was conducted in an aqueous medium in a reactor, from which the reaction products were not removed. Ethyl acetate (reactant A) was in a great excess with respect to NaOH (reactant X), so that it could be assumed that the concentration of A did not change in time, as assumed in the model. The reactant X was supplied in an oscillatory manner: $\alpha\cos^2\omega t$, which was realized by using an automatic burette, at equal time intervals depending on the period of dosage

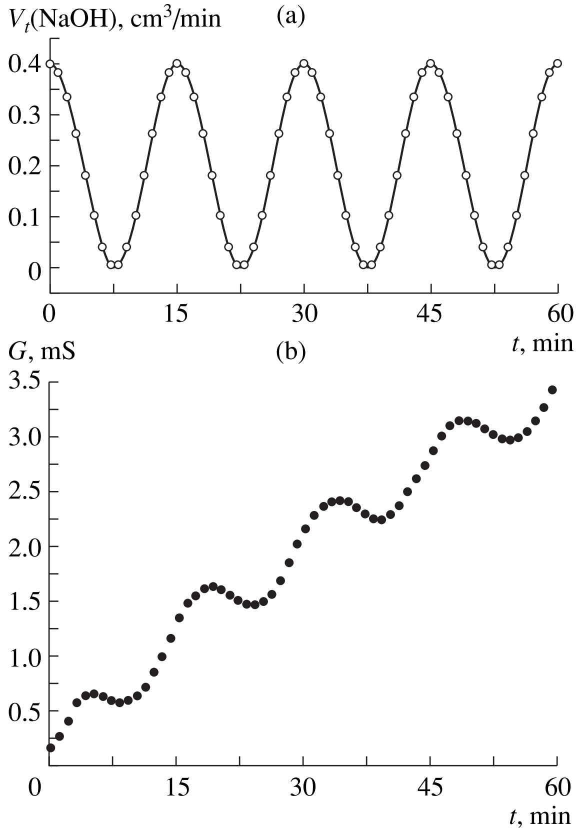

Fig. 2. (a) The changes in volume (at 1 min time intervals, open circles) of the periodically added 0.1 mol/l solution of NaOH with $T = 30$ min, according to the function assumed $\alpha\cos^2\omega t$ (the solid line). (b) Time changes in conductivity of the solution of ethyl acetate caused by oscillatory inflow of NaOH as described in (a); the each experimental point (the solid circles) is the average value of three measurements.

$T = \frac{2\pi}{\omega}$. The reaction was performed at 17°C; the reactor was thermostated and the reaction mixture stirred to ensure its thermal homogeneity and no concentration gradients. The choice of experiment temperature of 17°C was made to create better conditions for the observation of the phase delay effect, because reaction rate is lower at a lower temperature. Time changes in the system in response to the oscillatory inflow of NaOH were monitored by the measurements of the system conductance G, which was mainly determined by OH^- ions in the reaction mixture.

The measurements were carried out separately for aqueous solutions of both reactants with concentrations of 0.1 and 0.2 mol/l for different periods T characterizing the inflow of X. For $T = 10$ min, NaOH was supplied every 0.5 min, for T = 20, 30, 40 and 50 min, every 1 min, and for T = 60, 80, 100, 120 min, every 2 min. The amount of NaOH supplied was described by the function $\alpha\cos^2\left(\frac{2\pi}{T}t\right)$, where the amplitude α corresponded to the greatest amount of reactant X and was equal to 0.4 cm^3/min, except for the case of $T = 10$ min for which the amplitude was 0.6 cm^3/min. Measurements were always performed with 100 ml ethyl acetate, and conductivity was always measured in a protective atmosphere of nitrogen. Each measurement was repeated three times, and the average value was assumed as a final result. The differences between the results of measurements were small and fell within the experimental error.

RESULTS

Figure 2b shows the time changes of the averaged value of conductivity in the period of $T = 30$ min (lower part). Figure 2a presents the changes in volume (per unit of time) of the periodically added solution of NaOH according to the function assumed. The phase shift between the oscillations of the solution conductivity relative to those of the stream of the NaOH added is clearly marked. Moreover, the oscillations superimpose the monotonous increase in the solution conductivity, which is a result of additional conductivity owing to the accumulation of the reaction product formed P_1, sodium acetate, which undergoes hydrolysis. The acetate ion enters a reversible interaction. The latter reaction results in the formation of molecules of acetic acid and OH^- ion. Therefore, the number of ions contributing to conductivity, in particular OH^- ions, increases, which is manifested as a systematic increase in the conductivity. This fact is not reflected in Eq. (7), which should be supplemented with a term describing the contribution to the conductivity coming from the product. Let us consider a change in the product P_1 concentration in time in a reaction type (I) expressed by the following kinetic equation:

$$\frac{dP_1}{dt} = k_1AX = \frac{1}{\tau}X. \tag{9}$$

Putting Eq. (7) as X, we obtain

$$\frac{dP_1}{dt} = \frac{\alpha}{2} + \frac{\alpha}{2\sqrt{1+4\omega^2\tau^2}}\cos(2\omega t - \phi) + \frac{c}{\tau}\exp(-t/\tau), \tag{10}$$

where c is a constant equal to (7b).

Assuming that the initial concentration $P_1 = 0$, integration of this equation gives the expression describing the time changes of P_1 concentration $P_1(t)$:

$$P_1(t) = \frac{\alpha}{2}t + \frac{\alpha}{4\omega\sqrt{1+4\omega^2\tau^2}}\sin(2\omega t - \phi) - c\exp(-t/\tau) + c + \frac{\alpha\sin\varphi}{4\omega\sqrt{1+4\omega^2\tau^2}}, \qquad (11)$$

According to (11), the concentration of $P_1(t)$ increases in time due to the first linear term and the course of this increase is disturbed by the relaxation term and the oscillation term, which is delayed in phase by $\pi/2$ with respect to the oscillations of the parent substance X amount in the reaction medium (Eq. (7)).

The solution conductivity G is determined both by added NaOH and by the product P_1 formed in the solution. The contribution of the parent substance to the total conductivity of solution is proportional to the concentration of unreacted NaOH. The parent substance conductivity changes according to the function $X(t)$ (7) multiplied by a constant factor w, which is the specific conductivity of OH^- ions. The contribution to the conductivity from the increasing concentration of the product P_1 is a more complex matter because a part of the acetate ions react with water. To solve this problem we introduced a factor h, which is the ratio of the specific conductivity of product P_1 to the specific conductivity of sodium hydroxide (product X) and can be considered constant as the first approximation.

However, as the product accumulates in the solution and its concentration increases, the time changes of the conductivity reveal a certain nonlinearity (Fig. 2), which must be taken into account. In the first approximation, we introduce a correction proportional to the concentration of P_1 and multiply the term $wP_1(t)h$ by $[1 - gP_1(t)]$, where g characterizes the magnitude of the correction. Taking into account the above circumstances, we find that a good fit to the observed time dependence of the conductivity is obtained by the function $G(t)$:

$$G(t) = w\{X(t) + P_1(t)h[1 - gP_1(t)]\}. \qquad (12)$$

The factor w can be determined from measurements of the conductivity of an aqueous solution of NaOH as a function of its concentration. To do that, 0.2 ml of 0.1 mol/l solution of NaOH was added to 100 cm^3 of distilled water at equal time intervals, and the conductivity of the solution was measured. By extrapolation of the linear dependence valid for dilute solutions, this coefficient was found to be

$$w = (525 \pm 0.2)\ \text{mS l mol}^{-1}.$$

The results obtained for different periods T at which the reactant was added were fitted to the function (12) by the least-squares method, with h and g being the parameters of the fit. The other two parameters of the fit were the phase shift angle ϕ and the oscillation amplitude α. Figure 3 exemplifies such a procedure for T = 60 min, for two concentrations of A: 0.1 and 0.2 mol/l. The solid line shows the function of the fit (12). The values of the parameters ϕ, the time constants $\tau = \frac{T}{4\pi}\tan\phi$ (Eq. (5)), and the reaction rate constants $k = \frac{1}{\tau A}$ are given in Table 1. The values of the next parameters h, α, and g are collected in Table 2.

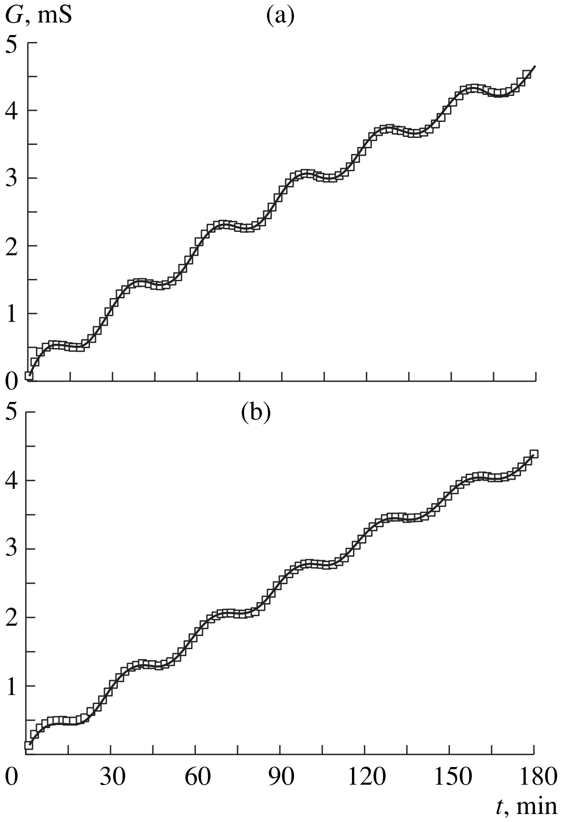

Fig. 3. Time changes in conductivity of the ethyl acetate solution caused by the oscillatory inflow of NaOH with T = 60 min, according to the function $\alpha\cos^2\omega t$ (squares) for two concentrations of ethyl acetate: (a) 0.1 and (b) 0.2 mol/l. Solid line shows the fit of (12) to the experimental points by the least squares method.

Our values of k, calculated from experimental data obtained at 17°C, as well as data from [2] (30°C) and [4, 5] (25°C) are collected in Table 3. For the sake of comparison, the data obtained at 30 and 25°C were converted to 17°C using the Arrhenius equation. Assuming that the preexponential factor is independent of temperature, the Arrhenius equation can be expressed in the form

$$k_1 = k_2\exp\left[\frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)\right],$$

where k_1 is the rate constant at T_1 = 17°C, k_2 is the rate constant at T_2 = 30 or 25°C, R is the gas constant, and

Table 1. The value of the phase shift ϕ (included in the function (12)), as well as the relaxation time τ and the rate constant k, calculated from ϕ. Standard deviations of the last digits are given in parentheses

t, min	ϕ, rad		τ, min		k, l mol^{-1} min^{-1}	
	A = 0.1	A = 0.2	A = 0.1	A = 0.2	A = 0.1	A = 0.2
10	1.339(12)	1.131(18)	3.45(10)	1.69(18)	2.90(8)	2.96(32)
20	1.186(32)	0.819(52)	3.93(36)	1.70(18)	2.54(23)	2.94(31)
30	0.990(25)	0.644(36)	3.64(20)	1.79(14)	2.75(15)	2.79(22)
40	0.791(25)	0.497(32)	3.22(16)	1.73(14)	3.11(15)	2.89(23)
50	0.724(21)	0.389(22)	3.52(15)	1.63(11)	2.84(12)	3.07(21)
60	0.593(33)	0.335(57)	3.22(23)	1.66(31)	3.11(22)	3.01(56)
80	0.507(36)	0.252(31)	3.54(30)	1.64(21)	2.82(24)	3.05(39)
100	0.375(25)	0.217(54)	3.14(23)	1.76(45)	3.18(23)	2.84(72)
120	0.340(27)	0.182(31)	3.38(29)	1.76(32)	2.96(25)	2.84(52)

Note: A is a concentration of ethyl acetate, mol/l.

Table 2. The values of parameters fitted to the function (12): α, h and g (see text). Standard deviations are given in parentheses

t, min	$\alpha \times 10^4$, cm^3/min		h		g, l/mol	
	A = 0.1	A = 0.2	A = 0.1	A = 0.2	A = 0.1	A = 0.2
10	4.99(8)	10.59(19)	0.516(7)	0.462(9)	13.60(42)	8.66(21)
20	4.88(15)	4.13(17)	0.494(15)	0.567(22)	11.03(53)	10.50(58)
30	4.82(9)	7.22(27)	0.491(11)	0.486(18)	10.55(32)	4.94(26)
40	4.15(9)	4.04(15)	0.514(11)	0.526(20)	12.02(37)	10.50(5)
50	3.56(8)	6.93(21)	0.593(11)	0.520(18)	14.02(32)	5.36(21)
60	2.17(8)	2.00(19)	0.581(19)	0.558(51)	13.39(53)	10.4(10)
80	2.08(9)	2.23(19)	0.524(21)	0.527(49)	9.61(47)	9.56(95)
100	1.77(8)	1.85(25)	0.495(19)	0.572(73)	10.50(5)	10.50(16)
120	2.30(11)	2.46(17)	0.518(25)	0.729(53)	11.39(58)	8.30(63)

Note: A is a concentration of ethyl acetate, mol/l.

E_a = 14.2 kcal/mol [7] is the activation energy for this reaction. On the basis of the comparison of data compared in Table 3, one can conclude that the values of the rate constant obtained by the phase shift method are in good agreement with those obtained in another way.

Figure 4 compares the phase shift angles determined in the experiment with the plot of the function (6a) for different periods T of oscillations of parent substance X inflow and for its two concentrations, 0.1 and 0.2 mol/l. The values of the measured phase shift angle fall on the theoretical curve within the experimental error. This confirms that the method based on the determination of the phase shift can be used in the study of the kinetics of chemical reactions, in particular for the determination of the reaction rate k and the relaxation time τ.

DISCUSSION

The results obtained for the reaction of ethyl acetate with periodically added NaOH confirmed the results of theoretical calculations. The dependence of the phase delay angle on the period of oscillations in the parent substance X inflow and the parent substance A concentration is in agreement with Eq. (6a). For different periods of NaOH inflow to the reaction medium, the reaction rate constant k takes approximately the same value (within the experimental error). This result indicates that the method based on the measurement of the phase shift angle can be applied to the determination of the reaction rate constant k. This conclusion holds for the reaction type (I) described by the kinetic equation (2). When the concentration of reactant A does not change in time, these reactions are characterized by the exponential disappearance of the reactant involved in the chemical conversion, and the time constant of the reaction τ is related to the rate constant k_1 by the relation $\tau = \frac{1}{k_1 A}$. This description is valid for first-order reactions. For higher order and autocatalytic reactions, a simple solution to the kinetic equation for the case of oscillatory inflow of one of the reactants is impossible. However, the phase delay effect occurs for these reactions as well.

The proposed method for the determination of the reaction rate constant (as well as relaxation time) based on oscillatory disturbance and the phase delay effect which follows from this disturbance is obviously not the easiest one compared to the already existing methods of rate constant determination. It can, however, serve to verify data on reaction rate constants obtained by other methods, as exemplified in Table 3. It follows from this table that values obtained using the method presented by us are in better agreement with those given in [2] than with those found in [4, 5].

The effect of phase delay is also observed in a classic dumped harmonic oscillator excited with a resonance frequency ω_r, the amplitude of which is modulated with a low frequency $\Omega \ll \omega_r$. The modulated

Table 3. Comparison of the rate constant data k at 30 and 25°C found in [2, 4, 5] with our experimental data at 17°C.

Values of k, l mol^{-1} min^{-1}				
Data from [2]		Data from [5]		Data from our experiment carried out at***
30°C	17°C*	25°C	17°C*	17°C
7.71	2.68	6.66**	3.44	2.90
9.38	3.26	6.94	3.58	2.96
8.86	3.08	6.36	3.28	2.54
8.01	2.78	6.78	3.49	2.94
7.98	2.77	6.06	3.12	2.75
8.65	3.00	6.24	3.22	2.79
8.52	2.96	6.36	3.28	3.11
		6.42	3.31	2.89
		6.48	3.34	2.84
		6.54	3.37	3.07
				3.01
				2.82
				3.05
				3.18
				2.84
				2.96
				2.84
Average	2.93		3.39	2.92

* Data from the literature obtained at 30 and 25°C and converted to 17°C by using the Arrhenius equation (E_a = 14.2 kcal/mol [6]).

** From [4].

*** Errors are shown in Tables 1 and 2.

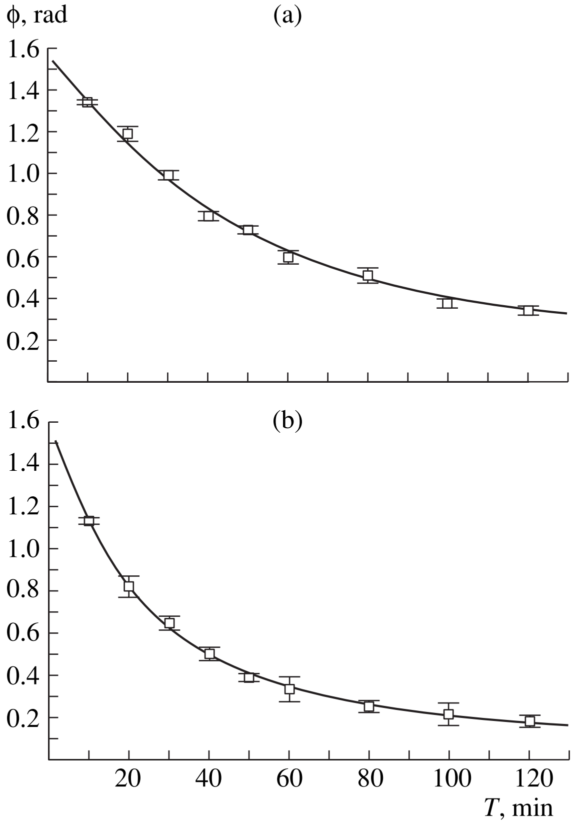

Fig. 4. The phase shift angle ϕ versus the period T of the oscillatory inflow of NaOH into the reaction medium containing ethyl acetate: (a) 0.1 and (b) 0.2 mol/l, respectively. The experimental points are given in Table 1. The solid line reproduces the function $\phi = \arctan\left(\frac{4\pi}{T}\tau_{av}\right)$ where τ_{av} is the mean value of rate constants determined for different periods (Table 1). (a) τ_{av} = 3.45 min and (b) τ_{av} = 1.71 min.

amplitude of vibrations of the harmonic oscillator reveals the phase delay ϕ described by the formula $\tan\phi = \Omega\tau$, where τ is the relaxation time known also as a lifetime. The method based on the measurement of the phase shift is used for the direct measurement of the lifetime of laser-excited particles [7].

The phase shift phenomenon is met in all relaxing systems. It is in agreement with the Le Chatelier–Braun principle, according to which a system under the influence of an external disturbance tends to eliminate its effects by the shift of the equilibrium state. In chemical reactions, it is manifested as a shift of the maximum or minimum concentration of reactant X and the modification of the amplitude of its inflow.

The system's response to a disturbance changing in time is an interesting subject for research, since it is commonly met in biological systems in which nonlinear processes (of the autocatalytic type and others) occur. In biological systems, situations with periodical inflow of a parent substance used in metabolic processes with some phase delay are frequently encountered. However, because of the effects of the transportation and diffusion of the components, describing these processes in real biological systems is much more complex and cannot be performed with the simple mathematical relations given in this work. It would require using equations in which the processes of diffusion are into account.

CONCLUSIONS

In chemical reactions with a time-dependent inflow of parent substance X, the concentration of this parent substance during a chemical reaction is delayed with respect to its inflow into the reaction medium. The delay depends on the reaction rate constant, the concentration of the other parent substance A taking part in the reaction, and the frequency of the inflow of X. Measurements of the phase delay can be an alternative method for the determination of a chemical reaction rate.

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