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KINETIC REGULARITIES OF THE EARLY STAGES OF SOL-GEL PROCESS IN TETRAETHOXYSILANE-BASED SYSTEMS

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Abstract. Kinetic peculiarities of the early stages of the processes of acid-catalyzed hydrolysis and condensation in sol-gel systems tetraethoxysilane (TEOS)–ethanol–water have been investigated by gas chromatography. Kinetic parameters of the process, evaluated using quantum-chemical calculations, satisfactorilly coincide with the ones determined experimentally.

Keywords: sol-gel process, tetraethoxysilane, kinetics, rate constant, activation energy.

1. Introduction

Nanocomposite materials find an increasing application in modern industry. Since filler nanoparticles and polymer matrix in such composites interact at nanoscale level it is possible to obtain a variety of materials, including nanomaterials with unique electrochemical, magnetic, thermosensitive, nonlinear-optical, insulating, and water-repellent properties, materials with controlled pore size, *etc*. [1, 2].

However, uniform nanophase distribution throughout composite volume can be hardly achieved, because the excess surface energy causes nanoparticles to aggregate. Besides, nanoparticles are chemically active and often loose their properties at interaction with other substances. Sol-gel technology, which allows to create composite nanostructure *in situ* during the process of synthesis, makes it possible to avoid these problems. Currently, this technology is considered as one of the most promising methods for nanochemistry [3, 4].

Sol-gel method includes hydrolysis, polycondensation of gel-precursor, nucleation and growth of particles with subsequent agglomeration. As precursors silicon alkoxides – tetramethoxysilane (TMOS), tetraethoxysilane (TEOS) and others – are commonly used. One of the important advantages of sol-gel synthesis is the ability to obtain materials with desired structure due to different conditions of process conducting. Understanding of the chemical reactions that occur in the early stages of sol-gel synthesis can provide the potential for better control of microstructural evolution in nanomaterials.

A series of articles is devoted to research of the stages of hydrolysis and polycondensation of precursors of sol-gel synthesis, however investigation of these processes with obtaining adequate kinetic models is a complicated task not only due to the number of chemical reactions in sol-gel system (three reactions – hydrolysis, water and alcohol condensation – occur almost simultaneously), but also due to a significant difference between their nature. Kinetics of the process is affected by many factors: choice and concentration of alkoxycompounds, amount of water, nature and amount of solvents that provide a homogeneous medium, temperature at which the processes are carried out, and even a sequence of components input and homogenization techniques. Additionally, at some stage of the processes development (in so-called percolation point) highly branched macromolecules are formed as the result of polycondensation reactions. Conformational volumes overlap, structuring the entire volume of sol-gel system. This leads to a drastic change in physical properties of the

system, particularly, in its viscosity, which may cause additional diffusion restrictions on the rate of chemical processes in sol-gel system.

D. Donatti and coauthors [5, 6] studied the process of acid hydrolysis in systems TEOS-H_2O-HCl under ultrasound stimulation by a calorimetric method. The exothermal peak, which arises due to the heat release of the hydrolysis reaction, was considered as a measure of reaction rate. The authors propose a kinetic model that includes equations of the process of water dissolution in TEOS and ethanol under ultrasound stimulation and reaction of TEOS hydrolysis as itself. This simplified model satisfactorily describes the experimentally found rate of the hydrolysis process as a function of acid concentration. For the temperature 312 K and $r = [H_2O]/[TEOS] = 4$ the rate constant of acid hydrolysis $k = 6.1$ l·mol^{-1}·min^{-1}·[H$^+$]$^{-1}$, being consistent with previous data.

In [7] the rate constant of acid hydrolysis of TEOS in dioxane at 293 K was found to be 3.06 l·mol^{-1}·min^{-1} [HCl]$^{-1}$ giving a value of 6.1 l·mol^{-1}·min^{-1} [HCl]$^{-1}$ taking into account the Arrhenius dependence of the reaction rate constant of hydrolysis and activation energy found by the authors (6.8 kcal·mol^{-1}). The authors of the above mentioned paper have also found that the value of the rate constant of hydrolysis varies slightly for different solvents.

The authors [8, 9] studied sol-gel process in the systems on the base of TEOS, ethyltriethoxysilane [EtSi(OEt)$_3$] and diethyldiethoxysilane [Et$_2$Si(OEt)$_2$]. The method ^{29}Si NMR was used to study the chemical reactions in these systems before gelation. This method allows to determine the concentration of intermediates of the process – silicon compounds with varying degrees of substitution of OH-groups and with varying degrees of condensation, *i.e.* the number of links that join silicon atoms. Silicon compounds may be denoted by their functionality: $Q_i^{\ j}$ – four-functional unit (tetraethoxysilane system), $T_i^{\ j}$ - three-functional unit (triethoxysilane system), $D_i^{\ j}$ – two-functional unit (diethoxysilane system). Indeces i and j denote the number of the bonds between silicon atoms, and the number of OH-groups joined to Si atom, *i.e.*, the degree of hydrolysis, respectively. Finding concentrations of $Q_i^{\ j}$, $T_i^{\ j}$ and $D_i^{\ j}$ from ^{29}Si NMR spectra makes it possible to draw conclusions about the kinetic behavior of the investigated sol-gel systems. A complete description of reaction kinetics in these systems requires determination of too many constants, therefore for simplification of this problem it has been assumed earlier that reactive ability to hydrolysis of ethoxy-groups and reactive ability to condensation of OH-groups do not depend on the type of the place on Si atom, to which these groups are attached, *i.e.* effects of substitution are excluded [10].

At the same time, the authors [8, 9] compared the rates of reaction of hydrolyzed intermediates TEOS, [EtSi(OEt)$_3$] and [Et$_2$Si(OEt)$_2$] at constant concentrations of initial water and catalyst. A significant effect of the first shell substitution – increase in reactive ability to hydrolysis and decrease in reactive ability to condensation of alkoxysilanes with more alkyl groups attached to silicon atom – has been revealed. Discovered kinetic trends may be explained by inductive and steric effects.

In [11] it was assumed that hydrolysis and condensation are irreversible. Condensation of two OH-groups, *i.e.* water-forming condensation, was suggested to be considered as the only reaction that occurs with a noticeable rate before gelation. It was subsequently confirmed experimentally for TEOS at moderate concentrations of water, at least at the beginning of the process [12]. In the latter article the second order of dimerization reaction was revealed. These assumptions allow to use a kinetic model that includes only two constants: for reactions of hydrolysis and water-forming condensation.

Assink and Kay [10, 13, 14] have used ^{1}H and ^{29}Si NMR to determine rate constants of three reactions: hydrolysis (k_h), water condensation (k_{cw}) and alcohol condensation (k_{ca}) during the initial stages of acid-catalysed hydrolysis of tetramethoxysiylane. ^{1}H NMR was used to measure concentration of methoxy-groups as a function of reaction time. The rate constant of hydrolysis $k_h = 0.2$ l·mol^{-1}·min^{-1} was determined for the limiting case when the initial rate of hydrolysis is much greater than the sum of condensation reaction rates, and [SiOH] is equal to the expense of H_2O in the process of hydrolysis. The rate of formation of chemical bonds ≡Si-O-Si≡ was determined by ^{29}Si NMR method. Two limiting cases were considered: (i) if k_{cw} significantly exceeds k_{ca} the rate of condensation is proportional to [≡ SiOH]^2; (ii) if k_{cw} is much less than k_{ca} the rate of condensation is proportional to [≡SiOH] [≡SiOR]. For the initial stage of the process, when the concentration of ≡Si-O-Si≡ is insignificant as compared with the initial concentration of functional methoxy-groups $k_{cw} = 0.006$ l·mol^{-1}·min^{-1} and $k_{ca} = 0.001$ l·mol^{-1} min^{-1} have been defined.

The authors [15] studied kinetics and mechanisms of reactions of hydrolysis and condensation of tetrametoxysilane, tetraethoxysilane and tetrapropoxysilane in some alcohol solvents (methanol, ethanol, 1-propanol and 2-propanol) using ^{29}Si NMR method. The influence of water concentration on the rate of the process was studied. Hydrolyzability of silanes in acidic medium was found to decrease in a series TMOS > TEOS > TPOS. The effect of alcohols in order methanol > ethanol, 1-propanol > 2-propanol on the rate of hydrolysis of each silane is caused by the difference in degree of dissociation of catalyst (HCl) in various alcohols.

Authors [16] have modeled kinetics of sol formation from water-alcohol solutions of TEOS with addition of tin(IV) chloride by a system of differential equations, generated from reaction equations. The reaction rate constants were taken from the experimental data of studying the process kinetics by conductometry at varying $SnCl_4$ concentration. The possibility of forming of condensation intermediates (dimers $(C_2H_5O)_3Si–O–Si(C_2H_5O)_3$, trimers $(HO)_3Sn–O–Si(OH)_2–O–Sn(OH)_3$, tetramers $(HO)_3Sn–O–Si\ (OH)_2–O–Sn(OH)_2–O–Si(OH)_3$ *etc.*, pentamers $(HO)_3Sn–O–Si(OH)_2–O–Sn(OH)_2–O–Si(OH)_2–O–Sn(OH)_3$ *etc.*) was calculated by quantum-chemical method.

As one can see, sol-gel process on the base of alkoxysilanes is a subject of a lot of researches, but kinetic peculiarities of these processes under different conditions require both further experimental study and development of kinetic models that satisfactorily summarized experimental data. The present work is devoted to experimental studies of the early stages of sol-gel process in tetraethoxysilane-based systems and quantum-chemical calculations of kinetic parameters of this process.

2. Experimental

Reagents for investigations were of analytical grade. Tetraethoxysilane $(C_2H_5O)_4Si$ was obtained from "EKOS-1" (Russia) with the following characteristics: FW 208.33, mp 355 K, bp 442 K, d^{20} 0.9335, n_D^{20} 1.3830, purity ≥ 99 %. Ethanol C_2H_5OH (bp 351 K, d^{20} 0.789, n_D^{20} 1.3614) and orthophosphoric acid H_3PO_4 (d^{20} ~ 1.6) were used as solvent and catalyst, respectively.

Sol-gel systems were prepared by mixing of TEOS, ethanol, water and orthophosphoric acid in proper ratio. The general system volume was 10 ml.

Quantitative analysis of sol-gel components was carried out using gas chromatograph "LHM-80" equipped with thermal conductivity detector. Columns (1.8 m×0.3 cm) filled with adsorbents – POLYSORB-1 and CHROMATON N-AW, washed by acid and coated with stationary phase SILICONE SE 30 (5 %), were used for determining TEOS and water concentrations, respectively. The flow rate of carrier gas argon was 20 ml/min. Tests were conducted at the operating temperatures of columns – 393 K, of evaporator – 408 K, of detector – 393 K. Current of katharometer bridge was 70 mA.

3. Results and Discussion

Chemical transformations occurring in sol-gel systems based on alkoxycompounds can be described by three overall reactions – hydrolysis↔esterification (1), water condensation↔hydrolysis (2), alcohol condensation↔alcoholysis (3):

– hydrolysis to form silanols

$$(RO)_3Si–OR + HOH \leftrightarrow (RO)_3Si–OH + ROH \quad (1)$$

– condensation to form latent water at silanol interaction

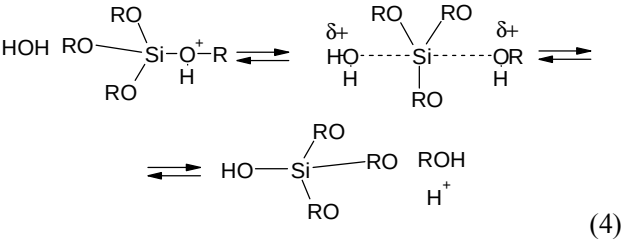
$$\equiv Si\text{-}OH + HO\text{-}Si \equiv \leftrightarrow \equiv Si\text{-}O\text{-}Si \equiv + HOH \quad (2)$$

– alcohol condensation at interaction between silanols and alkoxycompounds

$$\equiv Si\text{-}OH + RO\text{-}Si \equiv \leftrightarrow \equiv Si\text{-}O\text{-}Si \equiv + ROH \quad (3)$$

where R is alkyl group C_xH_{2x+1}.

Acid-catalyzed hydrolysis proceeds *via* bimolecular nucleophilic displacement reaction S_N^2. Mechanism involves protonation of alkoxide group, electron density is withdrawn from silicon, making it more susceptible to attack by water. Then transition state is formed: the water molecule attacks from the rear and acquires a partial positive charge. The positive charge of the protonated alkoxide is correspondingly reduced making alcohol a better leaving group (4).



(4)

To analyze the kinetics of the early stages of these reactions in investigated sol-gel systems chromatographic method was proposed to be used. This method allows monitoring of the progress of reactions on changing TEOS and water concentrations.

TEOS concentration was measured for 1 h on the column filled by the adsorbent CHROMATON N-AW. Sol-gel process was carried out at different temperatures, different catalyst and TEOS concentrations. The results are shown in Fig. 1 in the form of concentration dependence of unreacted TEOS on time.

On the next stage of the study an analysis of current water concentration in sol-gel system was conducted. Water concentration was measured using a column with the adsorbent POLYSORB-1. Changeable output parameters of sol-gel system were TEOS and catalyst concentrations, and temperature. The main results obtained are shown in Fig. 2.

As it can be seen, all the kinetic curves have a typical shape: they consist of two sections. The first one indicates a rapid decrease in water concentration due to its consumption in reaction of hydrolysis (1), the second section of the kinetic curve shows relatively slow increase in water concentration in sol-gel system, testifying that the rate of polycondensation reaction (2) is higher as compared to the rate of hydrolysis reaction (1). It is possible to suggest that at minimal water concentration the rates of reactions (1) and (2) are equal.

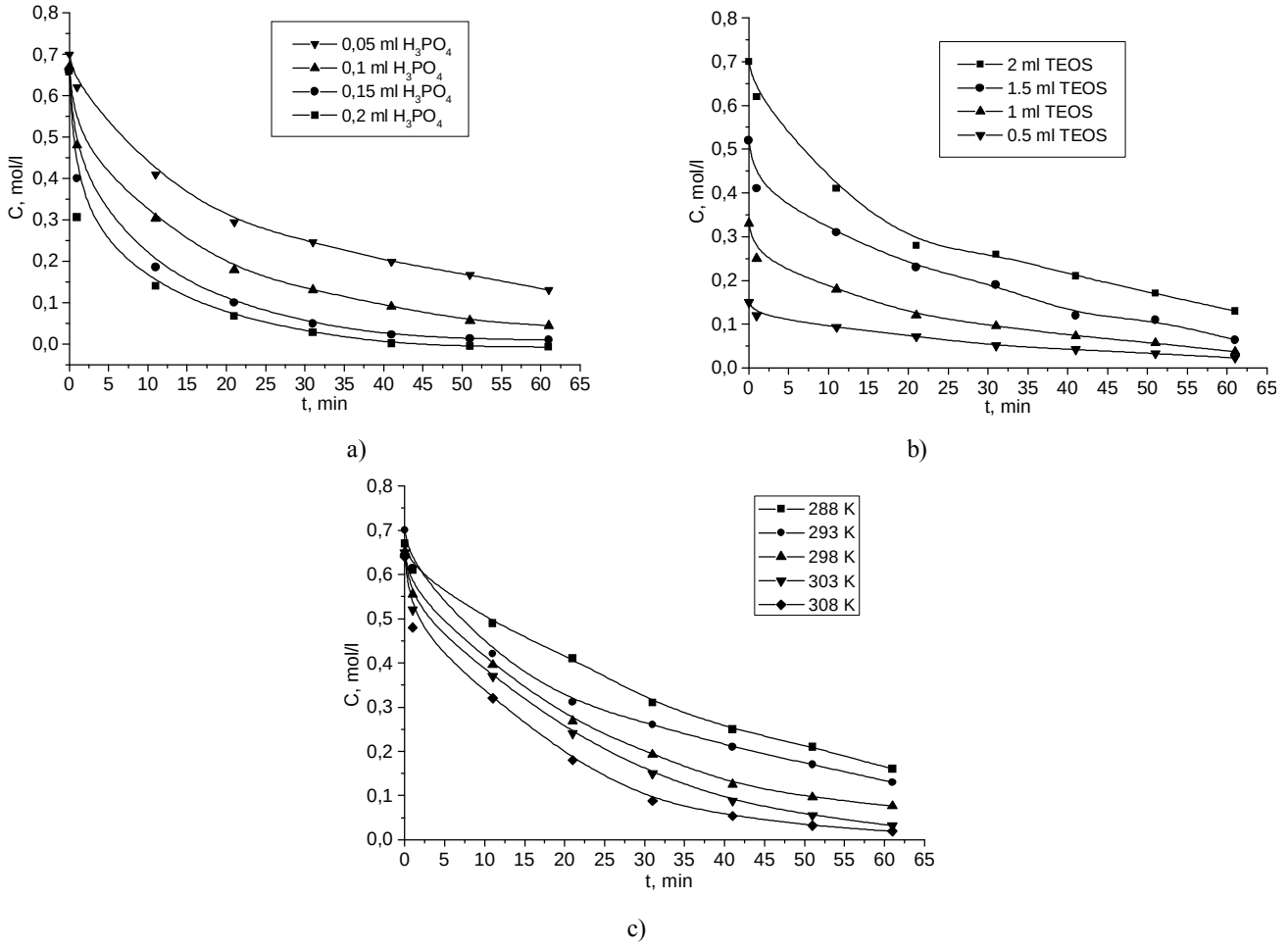


Fig. 1. Kinetic curves of TEOS hydrolysis: at different catalyst concentration (a); at different TEOS concentration (b) and at different temperatures (c)

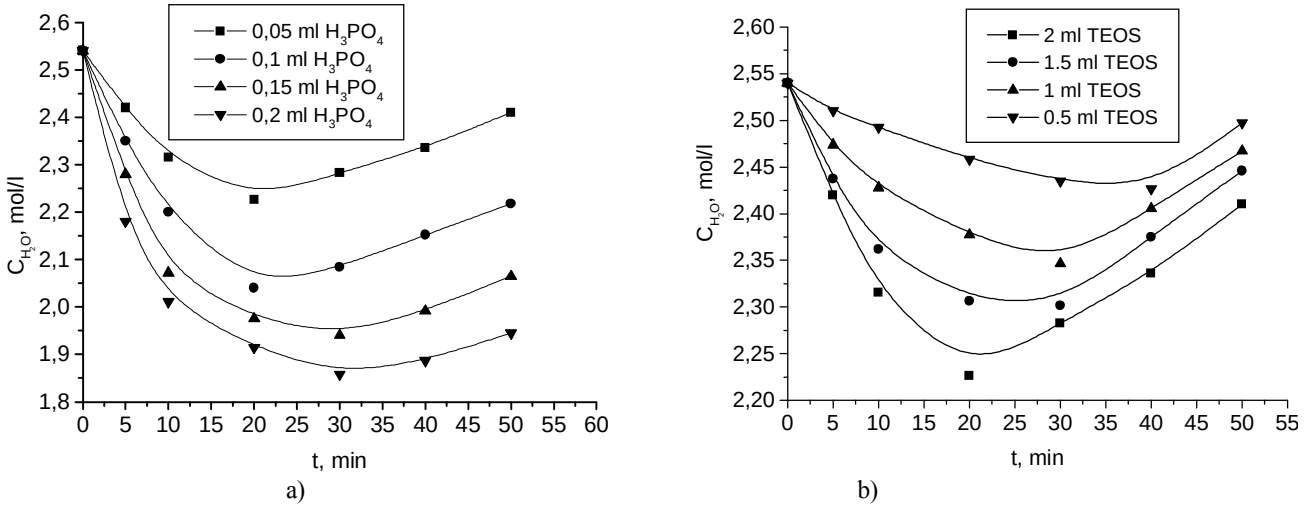
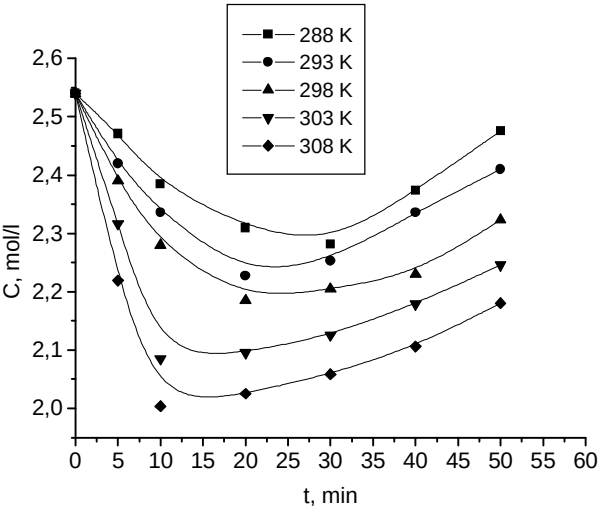
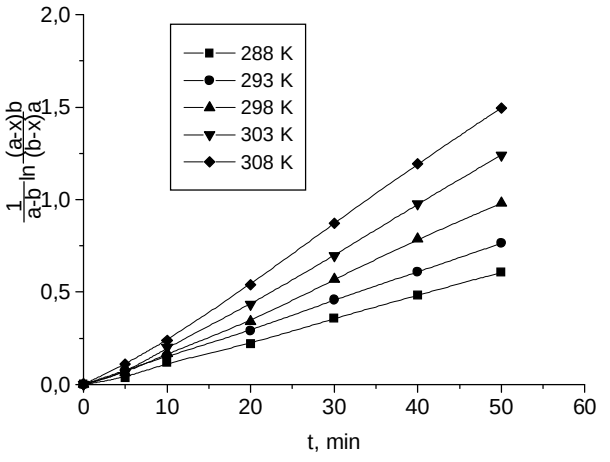


Fig. 2. Water concentration change in time: at different H_3PO_4 concentrations (a); at different TEOS content (b) and at different temperatures (c)

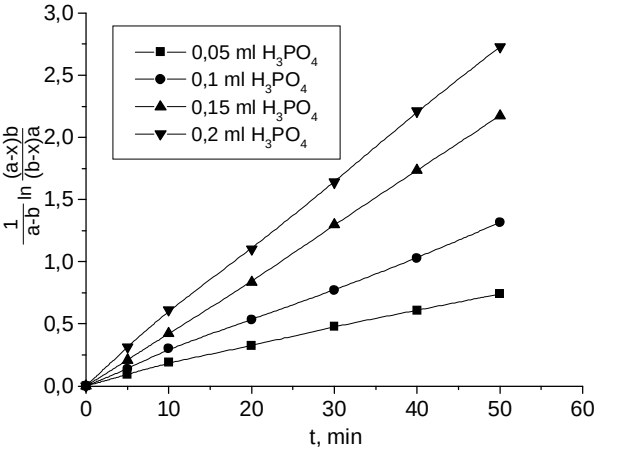


c)

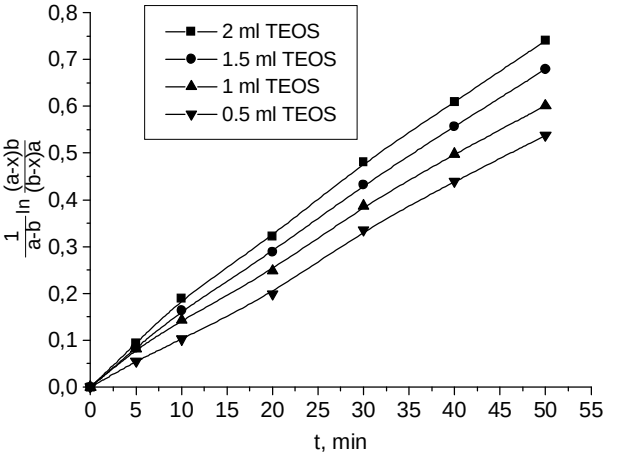
Fig. 2. *(Continued)* Water concentration change in time: at different H_3PO_4 concentrations (a); at different TEOS content (b) and at different temperatures (c)



a)



b)



c)

Fig. 3. The change of reaction rate in time: at different temperatures (a); at different content of catalyst (b) and at different concentration of TEOS (c)

Table 1

Kinetic parameters of TEOS hydrolysis in sol-gel systems

TEOS:H_2O:H_3PO_4, ml	T, K	$k_h \cdot 10^2$, $l \cdot s^{-1} \cdot mol^{-1}$
2:0.5:0.05	288	1.20
	293	1.57
	298	1.95
	303	3.00
	308	5.00
2:0.5:0.2	293	5.40
2:0.5:0.15	293	4.35
2:0.5:0.1	293	2.58
1.5:0.5:0.05	293	1.41
1:0.5:0.05	293	1.29
0.5:0.5:0.05	293	1.11

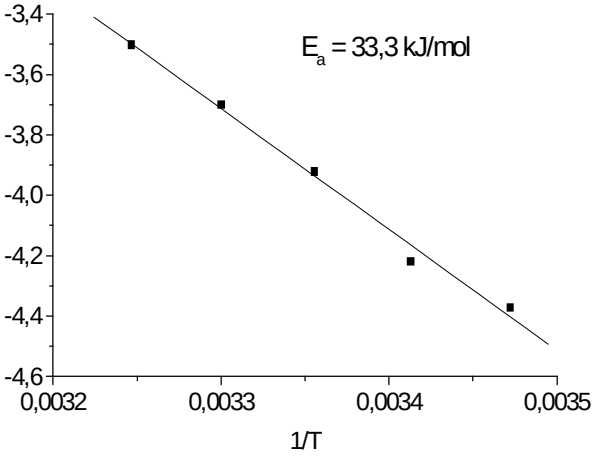


Fig. 4. Dependence of the rate constant of TEOS hydrolysis on temperature in the Arrhenius coordinates

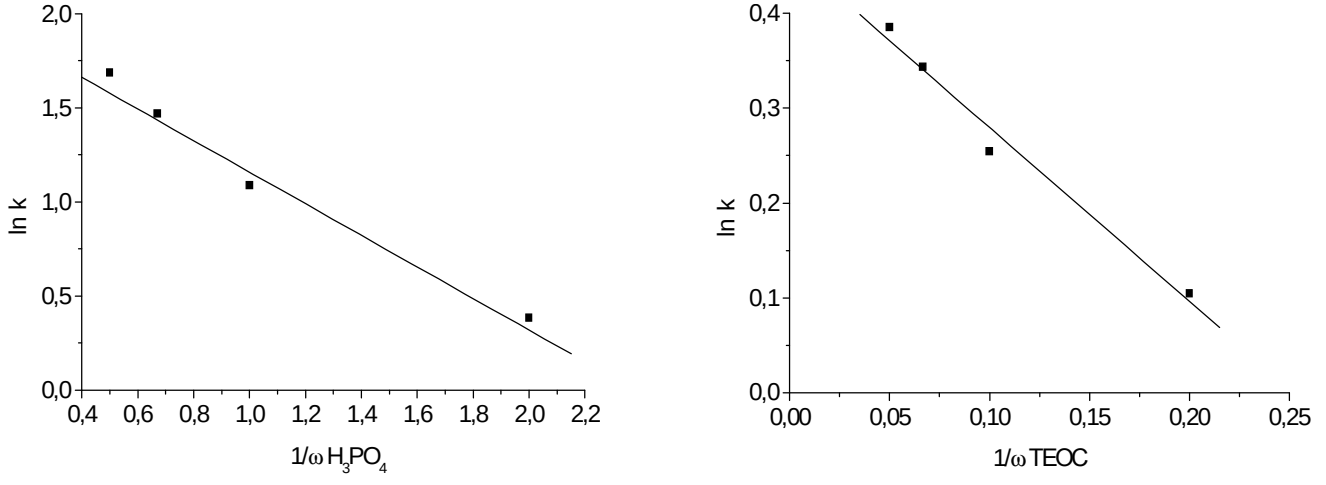


Fig. 5. Dependence of the reaction of TEOS hydrolysis rate constant on H_3PO_4 (a) and TEOS (b) concentration

The reaction of TEOS hydrolysis was found to be of the second order (Fig. 3). The reaction rate increases notably in the investigated temperature interval (288–408 K), as well as at increase in TEOS and H_3PO_4 concentrations (Fig. 3).

The experimental temperature dependence of the reaction of TEOS hydrolysis rate constant in the Arrhenius equation coordinates (ln*k vs* 1/T) was found to be a straight line. Using this dependence the Arrhenius equation parameters were determined: activation energy E_a = 33.3 kJ·mol^{-1} and preexponential factor $k_o = 1.354 \cdot 10^4$ l·s^{-1}·mol^{-1} (Fig. 4, Table 1).

The dependence of the rate constant on TEOS and H_3PO_4 concentration in the studied concentration range also was found to be a straight line in the coordinates ln$k$–1/ω, where ω is a volume fraction of TEOS or H_3PO_4 in the system (Fig. 5).

The rate constant of the reaction of water condensation can be calculated by equating the reaction rates of hydrolysis and of water condensation at the moment when the lowest concentration of water in the system is observed. According to the earlier investigations the rate of the alcohol condensation reaction is negligible compared to the rates of the above mentioned reactions, hence, this reaction may be neglected. The degree of TEOS conversion was accepted as concentration of silicon specimens with functional groups –OH. The calculated constants are presented in Table 2.

The dependence of rate constants on temperature allows to estimate activation energy – 76.8 kJ/mol.

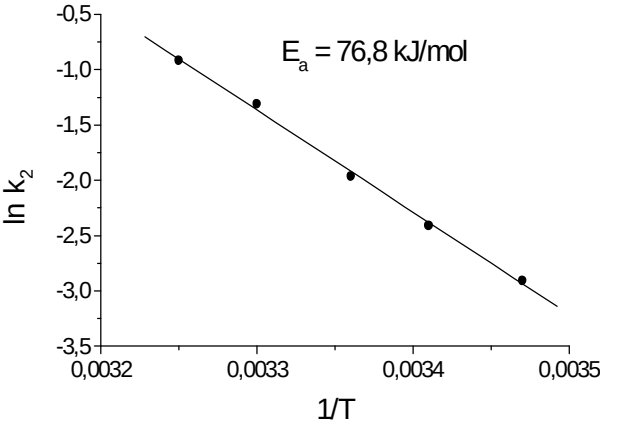


Fig. 6. Dependence of the rate constant of water condensation on temperature in the Arrhenius coordinates

Theoretical investigation of the early stage of sol-gel process in this system using quantum-chemical method of calculation was conducted at the assumption that only one $–OC_2H_5$ group of TEOS is hydrolyzed.

The mechanism of reactions in sol-gel process is defined by peculiarities of electronic and geometric structure of TEOS molecule, which are crucial for determination of thermodynamic and kinetic parameters of its interaction in reactive medium. So first of all characteristics of TEOS electronic structure were studied using quantum-chemical calculation method PM6 [17] (Table 3).

Table 2

Kinetic parameters of water condensation reaction in sol-gel systemsx

TEOC:H_2O:H_3PO_4, ml	T, K	$k_{cw} \cdot 10^2$, l·s^{-1}·mol^{-1}
2:0.5:0.05	288	5.5
	293	9.0
	298	14.0
	303	27.1
	308	40.0

Table 3

Characteristics of TEOS electronic structure

Interatom			Electron density on O atom, e	Orbital energy, eV	
distance, ºA		angules, degree			
SiO	CO	SiOC		HOMO	LUMO
1.6832	1.3640	118.48	1.3614	10.5632	14.8677

To calculate the reaction between TEOS molecule and hydroxonium H_3O^+ in aqueous medium under acid hydrolysis, TEOS molecule was placed into so-called cage that included 216 molecules of H_2O. As a result small changes in positions of energy levels of HOMO and LUMO take place, namely HOMO = 10.2615 eV, LUMO = 14.2318 eV. Calculation of TEOS acid hydrolysis reaction was carried out using the scanning of reaction coordinate in the dependence: heat of system formation (ΔH) – distance (r) between O (from TEOS) and H^+ under normal conditions. The curve of this interaction is shown in Fig. 7.

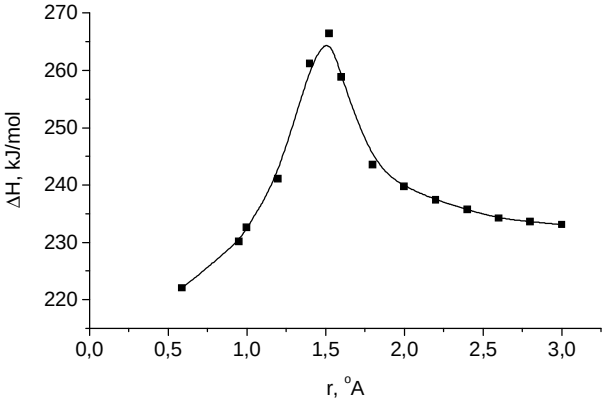
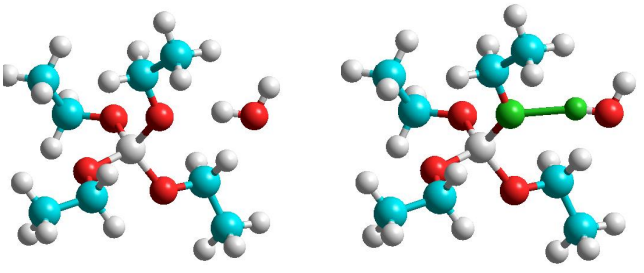


Fig. 7. The dependence ΔH–r for the reaction of interaction between TEOS and H_3O^+ molecules

The activation energy of the above mentioned reaction was determined as the difference between energies of reactants and intermediates. It was found to be E_a = 266.5 - 221.4 = 45.1 kJ·mol^{-1}, which is in good agreement with experimentally determined activation energy. Then the statistic sum of vibrations in TEOS–H^+ system and the power matrix have been calculated, which allowed to evaluate preexponential factor – $1.85 \cdot 10^4$ l·s^{-1}·mol^{-1}. Theoretical result is satisfactory as compared with the experimental value ($1.354 \cdot 10^4$ l·s^{-1}·mol^{-1}).

Fig. 8 shows the structure of TEOS and H_2O molecules and $(OC_2H_5)_3Si$–O–H in transition state in PM6 approximation.



a) b)

Fig. 8. Structure of TEOS and H_2O molecules (a) and $(OC_2H_5)_3$ Si–O–H in transition state (b) in PM6 approximation

Then we calculated the next step – two $Si(OC_2H_5)_3OH$ molecules condensation in frames of semi-empirical method PM6:

$$Si(OC_2H_5)_3OH + HO(OC_2H_5)_3Si \rightarrow$$
$$\rightarrow Si(OC_2H_5)_3–O–(OC_2H_5)_3Si + H_2O \quad (4)$$

In Fig. 9 the route of reaction of interaction between two hydrolyzed TEOS molecules, leading to $((OC_2H_5)_3Si)_2O$ and H_2O molecules formation, is presented. The activation energy of this process was estimated to be equal 90.4 kJ·mol^{-1}.

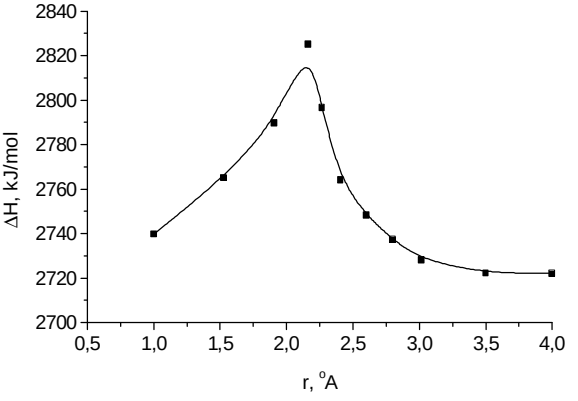
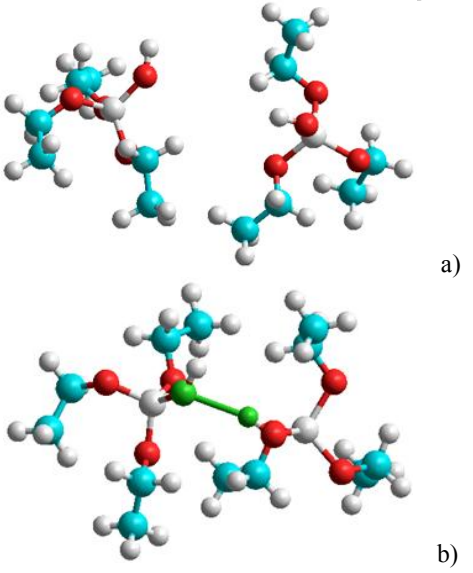


Fig. 9. The dependence ΔH–r for the reaction of interaction between two $Si(OC_2H_5)_3OH$ molecules

In Fig. 10 the structure of two partly (by one group –OC_2H_5) hydrolyzed molecules TEOS and $Si(OC_2H_5)_3$–O–$(OC_2H_5)_3Si$ molecules in transition state is presented.



a)

b)

Fig. 10. Structure of $Si(OC_2H_5)_3OH$ molecules (a) and $Si(OC_2H_5)_3$–O–$(OC_2H_5)_3Si$ molecule in transition state (b) in PM6 approximation

4. Conclusions

Kinetics of the early stage of sol-gel transformation in the system on the base of TEOS has been studied using gas chromatography. The proposed method of analysis

(parallel analysis of unreacted TEOS and water concentrations in the system) makes it possible to determine the rate constants of the reactions of TEOS hydrolysis and water condensation of hydrolyzed TEOS at the assumption that the rate of alcohol condensation may be neglected in the early stage of the process. The calculation of kinetic parameters of these reactions by means of semiempirical quantum-chemical method PM6 has shown satisfactory agreement of the experimental and the calculated results.

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КІНЕТИЧНІ ЗАКОНОМІРНОСТІ ПОЧАТКОВИХ СТАДІЙ ЗОЛЬ-ГЕЛЬ ПРОЦЕСУ В СИСТЕМАХ НА ОСНОВІ ТЕТРАЕТОКСИСИЛАНУ

Анотація. *Досліджено кінетичні особливості початкових стадій процесів кислотного гідролізу та конденсації в золь-гель системах тетраетоксисилан–етанол–вода методом газової хроматографії. Кінетичні параметри процесу, оцінені з використанням програми квантово-хімічних розрахунків, задовільно співпадають з визначеними експериментально.*

Ключові слова: *золь-гель метод, тетраетоксисилан, кінетика, константа швидкості, енергія активації.*