

Investigation of the Sol-Gel Transition by Rheological Methods

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Abstract: - In this paper the rheological study of gelation processes were carried out. Developed measurement complex allows obtaining rheological kinetic curves, from the beginning of sol-gel transition until complete conversion of the sol into a gel. Critical shear stresses in a wide range were measured. It showed that the starting sol is a Newtonian liquid, and after the beginning of gelation process is converted into a Bingham body, and has the character of the phase transition of the 2nd kind. Using the developed device has allowed to establish the form of the initial part of rheological curve and develop the correct method for determining the gelation time. New phenomenon was discovered which is that the kinetic curves in coordinates of Avrami-Erofeeva-Bogolubov's equation have an inflection point that divides the kinetic curve into two parts initial and final. Numerical treatment of rheological curves showed that the constant in this equation is independent of temperature and is the same as for the initial and final part of the kinetic curve. It depends only on the chemical nature of the reacting system. It is shown that for the initial part of the rheological curves, the value of the power index in the in this model amounted $n = 23.4 \pm 2.8$ and in contrast to the final part of rheological curve does not depend on temperature. The observed behavior of the kinetic curves due to the change process and the mechanism of reducing the number of possible directions of fractal aggregates growth.

Key-Words: - Sol-gel process; Rheology; Non-Newtonian fluid; Avrami-Erofeev-Bogolubov's equation; Phase transition of the 2nd kind

1 Introduction

The basis of the sol-gel technology is the most important feature of colloidal solutions (sols) - ability to form a gel. Gelation allows wide application of colloidal solutions as binders in the preparation of composites, catalyst supports, adsorbents, etc.

The induction period is preceded by the formation of gels. During this period, in the properties of the colloidal system are no significant changes. After the induction period, abruptly increases the viscosity of the colloidal system, after which there is the loss of fluidity. The duration of the induction period is also commonly called the gelation time, and refers to the kinetic characteristics of the process. During the induction period in colloidal solutions, as a result of the aggregation process, the new phase nuclei are formed, then takes place their growth and coagulation. These processes are preceded by the formation of "endless" aggregate which is a gel.

Sol-gel transition associated with the formation of spatial chains which permeate the whole volume of the sol. The emergence of the spatial grid is accompanied by a significant increase in the

viscosity of the system. It has a number of new physical properties: elasticity, critical shear stress, the ability to preserve shape. Colloidal system loses its fluidity under the influence of its own weight and small external stresses.

The viscosity and yield stress - are two integral macroscopic characteristics of Newtonian (sol) and Bingham (gel) media, which are included in the rheological equations. There are many different methods for measuring viscosity, which can be grouped as follows: a) methods of capillary viscosimetry; b) methods of rotational viscosimetry; c) methods of vibration viscosimetry; d) the falling ball method; e) methods of plastometry. A fairly complete description of the methods for measuring the viscosity and the instruments used for this purpose is contained in [1].

Various methods for determining the gelation time are also known. For example, methods of "falling sticks", falling ball, displacement of the meniscus, which consists in the visual observation of the pour point of the sol and cannot give satisfactory accuracy and reliability of measurement the gelation time. Determination of the gelation time is usually accomplished by measuring the critical shear stress. For this purpose, usually used method

of tangential shear of the plate [4], implemented by means of devices such as Weiler-Rebinder [2,3], but there are several other methods.

One such example is the capillary immersion method [5]. This method can be measured relatively small quantities of critical shear stress. The disadvantage of the method is possible to consider the need for thorough degreasing of the inner surface of the capillary. Evolution critical shear stress with time can be determined using a rotational viscometer, but due to the low sensitivity of the device, the initial portion of rheological curve cannot be determined. Method tangential shear corrugated plate does not include careful degreasing operations, and its sensitivity is determined by the sensitivity of weighing-machine used and the area of the corrugated plate.

2 Experimental section

2.1. Methods of investigation

For rheological investigations the gelation process, measuring complex has been designed by us. It consisted of the following units:

- three measuring cells such as Weiler-Rebinder;
- unit for the automatic changing composition of the medium;
- thermal stabilization unit.

This system is designed to measure the dependence of the critical shear stress on the time since the start of the sol-gel transition until complete conversion of the sol into a gel. The measuring cell consists of a heating jacket, the indicator and the dynamometer, which is used as torsion scales. The unit of automatically changing medium composition includes an ionomer with electrodes, interface unit and an automatic burette. The indenter is made of a rectangular aluminum plate, 0.1 mm thick attached to a rod which is made of fibers composed of boron nitride.

Scheme developed device is shown in Figure 1. Block 1 includes the devices a, b, c, d: a – ionomer; b - interface unit; c - automatic burette; d - thermostatic cuvette in which the pH of the sol is automatically changed to a p redetermined value. Block 2 is composed of thermostat (t), connecting pipes and jackets for temperature control of three cuvettes (k, l, m). The measuring unit 3 consists of three devices, such as Weiler-Rebinder with different sensitivity (f, g, h); three modernized torsion balance and three thermostatically controlled cuvettes. The presence of three measuring cells is necessary for complete coverage of all of the

measuring range of the critical shear stress. The first cell (f) has a range, $\tau_0 = (0.05 \div 10.0) \text{ dynes/cm}^2$, the second (g) - $\tau_0 = (5.0 \div 1000) \text{ dynes/cm}^2$, and the third (h) - $\tau_0 = (500 \div 50000) \text{ dyne/cm}^2$. The measuring complex developed by us, allows determining the critical shear stresses in the range $\tau_0 = (0,05 \div 50000) \text{ dyne / cm}^2$ [6].

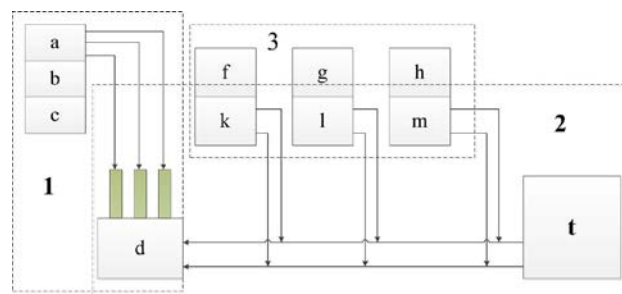


Figure 1. Scheme of the device for measuring the critical shear stress. (The description is in the text).

2.2. Reagents

For testing the measuring complex for gelation process research by rheological methods, as a model, we used the silica sol with a concentration of 2% SiO₂, obtained by ion-exchange method described in [11]. To stabilize the silica sol used in its composition was added concentrated hydrochloric acid to pH 1.8. The constancy of the sol properties was monitored throughout the experiment. To initiate the process of gelation, the sol portion of volume 100 ml destabilized by the addition of 1.0 N NaOH solution to pH 6.0. The process was carried out at different temperature values of the reaction medium. In the experiments, we were maintained constant the following parameters: pH, concentration and shape of the sol particle size distribution function.

2.3. Measurement methods

When the vertical displacement of the corrugated thin plates, which surface area, is equal to S, under the force F, the magnitude of the tangential shear stress in a viscous medium determined by the expression:

$$\tau = \frac{F}{S} \quad (1)$$

When pulling the plate indenter from the gel, we will gradually increase the magnitude of the applied force, starting from zero value, and then the shift will occur at some critical value of this force F^* . In

this case, the obtained value of shear stress τ_0 , it makes sense to critical shear stress:

$$\tau_0 = \frac{F^*}{S} \quad (2)$$

Where: F^* - the minimum value of the applied force, above which, there is destruction of the contact plate-gel; S — plate area.

In the case of an ideal body Bingham, it is sufficient to make the shift of the plate at an infinitely small distance, and then there is the destruction of the contact plate - gel. In a real experiment is impossible to achieve such conditions. In addition, the situation is complicated by the fact that the gel has certain elasticity, and destruction of the contact occurs when the plate is moved to a certain finite distance, which depends on many factors. These influencing factors are the stage of sol maturity, sol concentration, the amount of ionic strength, temperature, pH of the medium, etc. In order to overcome these difficulties, we have investigated the dependence of the shear stress value of the length of the moving plate (r) (Figure 2).

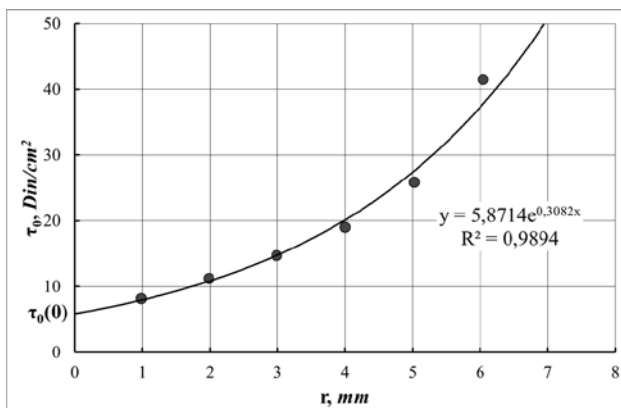


Figure 2. The magnitude of shear stresses for the indenter plate, depending on the length of its displacement.

As shown by experiment, regardless of the surface area of the plate, curve $\tau_0(r)$ can be described by equation:

$$\tau_0 = A \exp(B \cdot r) \quad (3)$$

Having determined in this equation coefficients A and B , we can calculate the value of τ_0 at zero displacement of the indenter ($r = 0$). The obtained value is the meaning of critical shear stress or yield point of the medium.

In [1] to determine the gelation time used the device of Weiler-Rebinder type with the sensitivity $\Delta=10$

dyn/cm^2 . In order, in such sensitivity, the instrument error does not exceed 5%; the critical shear stress should be measured starting with 200 dyn/cm^2 (see Figure 3). However, when the value of critical shear stress equal to $5 \div 10 \text{ dyn/cm}^2$, flow loss of sol can already be determined visually, for example, by displacement of the meniscus. Thus, for a detailed study of rheological curve it was necessary to have the device, which has a lower limit of measurement of the critical shear stress about 0.05 dyn/cm^2 . Thus sensitivity of the device should not be worse than $\Delta \leq 0,005 \text{ dyn/cm}^2$. The threshold of device sensitivity is determined by lower limit of the measuring force ($P_{min} = 0.25 \text{ dyn}$). These parameters have been achieved on the device, developed by us. It is characterized by a torsion balance type used and the surface area of the indenter ($S = 50 \text{ cm}^2$). These parameters have been achieved in our developed device. From this stable measurements of the critical shear stress is achieved, in accordance with the formula (1), when the sensitivity threshold value is less than the relative measurement error $\delta < 10\%$.

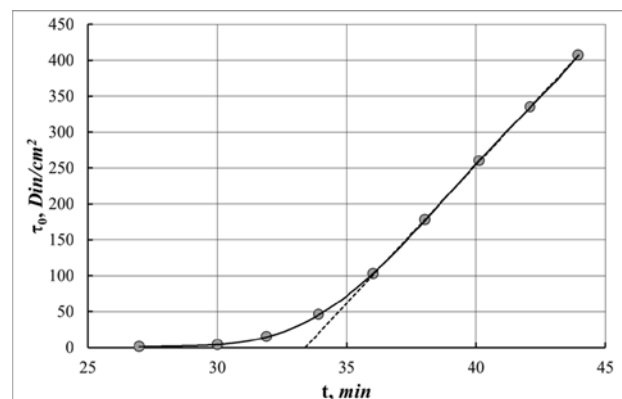


Figure 3. Type the initial segment of rheological curve $\tau_0(t)$ during gelation of dilute sols.

An important aspect of such rheological experiments is a technique for determining start time of gelation. Thus, in [4] gelation time was determined by the point of intersection of the tangent to the linear part of the curve $\tau_0(t)$ with the x -axis.

As shown by experiments conducted on the developed device, the initial segment of the curve $\tau_0(t)$ has the form shown in Figure 3 (solid line). The initial segment of the experimental dependence $\tau_0(t)$ is well described by the equation:

$$\tau_0 = B \exp(C \cdot t) + D \quad (4)$$

Parameters B , C , D in equation (4) can be determined numerically by the method of least

squares from the experimental values $\tau_0 = f(t)$. The gel time t^* is determined from the expression (4), provided $\tau_0=0$:

$$t^* = \frac{1}{C} \ln \left(-\frac{D}{B} \right) \quad (5)$$

The above described method for determining the gelation time is more correct than the one described in [4]. Our use of the developed device has allowed to establish a more detailed view of the initial portion of the curve $\tau_0 = f(t)$ and to develop a methodology for a more precise definition of gelation time, which is important in the preparation of inorganic composites by sol-gel technology.

3 Discussion of research results sol-gel transition by rheological methods

This section focuses on the definition of gelation time using rheological methods. We have experimentally investigated the dependence of the critical shear stress and yield point at the time of silica sol gelation. In order to define the gelation time, is preliminary necessary discuss a range of conditions under which this definition would have the most simple form, and could be used by other experimenters.

When studying the dependence gelation time, of a parameter or to determine the gel time measurement errors, it is necessary to carry out a series of measurements for quite some time t' . Obviously, during this time the properties of the starting sol must be constant. For this purpose, various methods are stabilized sols, changing the pH, temperature, introducing chemical additives. In order to characterize the constancy or change the properties of sol, it is necessary to measure the time evolution of any of its integral macro parameter, for example, the effective viscosity [7].

With invariance properties of the sol should meet the following condition:

$$K = \frac{\eta(t') - \eta(0)}{\eta(0)} \ll 1 \quad (6)$$

Where: $\eta(0)$ — the effective viscosity of the starting sol; $\eta(t')$ — the effective viscosity of the sol, had been stored for the time t' .

For destabilization of certain amount of the starting sol, sometime t' is needed. The duration of this stage t' , It depends on the amount of destabilizing sol, its pH, titration rate using a correction solution and final pH of sol solution titrated. An important

question is the reference point when measuring the time of passing the gelation process. To use as a reference point the end of the titration is not quite correct. This is due to the fact that the change in pH to a predetermined value, especially at the end of titration occurs slowly. This effect creates an uncertainty in fixing the starting point of reference. Start of titration is a strictly defined point of time, and uses it as a point of origin is much more convenient. Some error occurred when it is a constant quantity and depends only on the volume of the experimental cell.

The gelation time is usually called a time interval measured from time, corresponding to the beginning of gelation; until the time when gelling sol would lose its fluidity.

Moment of fluidity loss is usually determined in various ways. For example, by tracking changes in the shape of the meniscus surface; by falling sticks; the viscosimetry methods at aspiration in the effective viscosity to infinity [7]; by the method of the tangential shear plate. In the last case is determined dependence of the critical shear stress of time $\tau(t)$.

At various times destabilization certain amount of the starting sol t' and $t' + \Delta t$, the curve $\tau_0(t)$ can be displaced by a certain time interval Δt . In determining gelation time, this time of Δt , we can be ignored if the following condition is:

$$\frac{\tau(t' + \Delta t) - \tau_0(t')}{\tau_0(t')} \ll 1 \quad (7)$$

Where: $\tau_0(t')$ - the critical shear stress at the time corresponding to the beginning of the linear part of the curve $\tau_0(t')$; $\tau(t' + \Delta t)$ - the critical shear stress at the displacement in time by Δt .

This condition is not always satisfied, so in order to experiment could be reproduced somebody, it is necessary, among other conditions, that the dependence was specified volume of titrated solution versus time, or dependence titration rate versus time. The typical form of these curves is shown in Figure 4. This type of titration curves realized only in case of automatic titration mode. The coefficient K in equation (6) does not exceed 0.04. Thus, for each portion sol the destabilization regime was maintained constant. For each value of the time measurements of all variables were performed minimum of three times. From the rheological curves the gelation time was determined using the method of least squares.

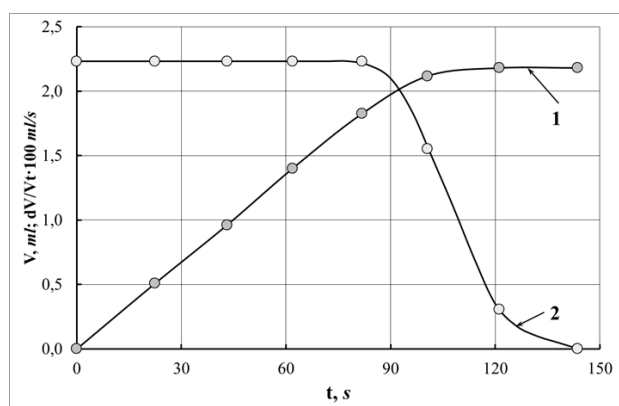


Figure 4. Dependence of volume (1) and dosing speed (2) of NaOH solution versus time.

Carried on the developed device, experiments have shown that the initial segment of the curve $\tau_0 = f(t)$ has the form shown in Figure 5.

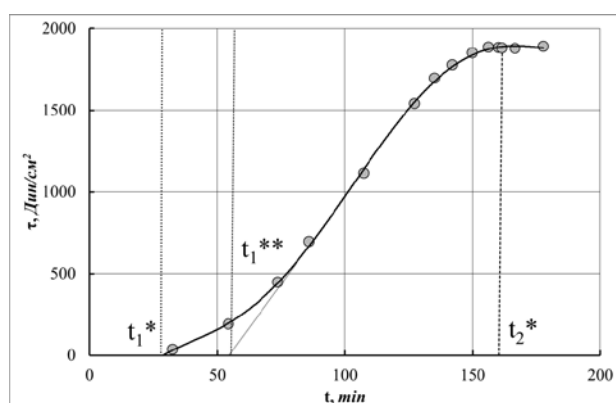


Figure 5. View the full curve of the critical shear stress versus time $\tau_0 = f(t)$ during gelation of silica sol with a concentration of 3% at pH 6.0 and $T = 20^\circ\text{C}$.

The obtained experimental dependence of the critical shear stress versus time can be divided into three segments - the zero, the initial and final. The zero segment accounted for the time interval from moment of initiation of gelation process, i.e. until the appearance in the system non-zero critical shear stress corresponding to time of the beginning of gelation t_1^* . In this segment, gelling sol is characterized as a classical Newtonian fluid. Initial segment rheological curve is located in the time interval from the beginning of gelation t_1^* to a point corresponding to the completion of gelation process. The final segment of rheological curve is located in the time interval from the completion points, of gelation process until to the point of full completion of the gelation process, accompanied by the hardening of the gel, and output rheological curve to

constant values of the critical shear stress. At the initial and final segments of rheological curve, the material is already characterized as a non-Newtonian fluid or Bingham body.

Experimental data for the initial section of dependence of the critical shear stress versus time is well described by the following equation:

$$\tau_0 = A_1 \exp(B_1 t) + C_1 \quad (8)$$

Empirical parameters A_1 , B_1 , C_1 in this equation can be determined numerically by the method of least squares. Time of gelation t_1^* is determined from the expression (11) when $\tau_0 = 0$:

$$t_1^* = -\frac{1}{B_1} \ln\left(-\frac{C_1}{A_1}\right) \quad (9)$$

Experimental data for the final segment of the dependence of the critical shear stress versus time is well described by the following equation:

$$\tau_0 = A_2 \ln(B_2 t) + C_2 \quad (10)$$

The coefficients A_2 , B_2 and C_2 can be defined similarly as for the initial segment. The complete conversion time of sol into gel, is t_2^* and it is determined from the expression (10) under the condition of equality $\tau_0 = \tau_{max}$:

$$t_2^* = \frac{1}{B_2} \exp\left\{\frac{\tau_{max} - C_2}{A_2}\right\} \quad (11)$$

At timing t_1^* , corresponding to the start of gelation, the cluster is formed in gelling sol, its edges touch the vessel walls, i.e. medium begins to be tough. Such cluster is called "infinite" aggregate. At this time, the reaction medium has a lot of smaller aggregates and individual particles of the sol, which over time join the "infinite" aggregate, which is accompanied by an increase in its strength. The point of t_2^* corresponds to the moment time at which the processes of formation and destruction of the bonds between the particles come to equilibrium. This moment comes when all possible small aggregates and particles had joined the "infinite" aggregate, and it is worth the time, the full transition of sol to gel. Further, after the point t_2^* is the area of the gel aging. As noted above, the process of initiating the sol-gel transition, in the silica sol was carried out by changing the pH from 1.8 to 6.0. In the system thus obtained, were measured the critical shear stress of time at various temperatures. The results of the measurements are shown in Figure 6.

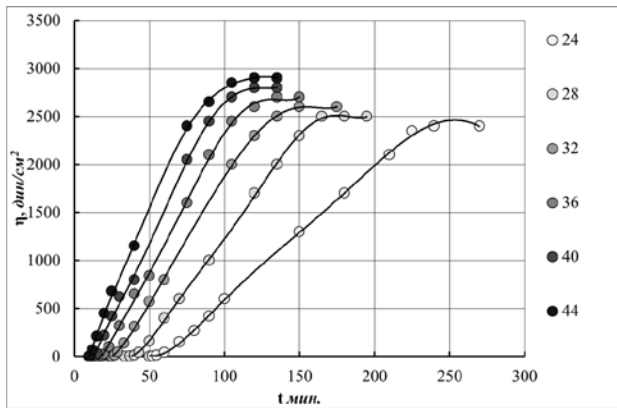


Figure 6. The measurement results depending on the critical shear stress on the time at different temperatures (°C).

Analysis of data obtained shows that the rheological curve can be described by the following equation during the sol-gel process flow:

$$\tau_0 = \begin{cases} 0, & 0 \leq t < t_1^* \\ A_1 \exp(B_1(t - t_1^*)) + C_1, & t_{l1} > t \geq t_1^* \\ A_l + B_l t, & t_{l2} > t \geq t_{l1} \\ A_2 \ln(B_2 t) + C_2, & t_2^* \geq t > t_{l2} \\ \tau_{max}, & t > t_2^* \end{cases} \quad (12)$$

From these dependencies can be seen that the time derivative of a rheological curve is $\tau_0 = f(t)$ current sense gel hardening speed, and can be written as the following expression:

$$\frac{d\tau_0}{dt} = \begin{cases} 0, & 0 \leq t < t_1^* \\ A_1 B_1 \exp(B_1(t - t_1^*)), & t_{l1} > t \geq t_1^* \\ A_l, & t_{l2} > t \geq t_{l1} \\ \frac{A_2}{t}, & t_2^* \geq t > t_{l2} \\ 0, & t > t_2^* \end{cases} \quad (13)$$

Below are the results illustrating the dependence t_1^* and t_2^* on the temperature (Fig. 7). The initial part of the experimental dependence of the critical shear stress versus time for each dependency was approximated by the expression (8). Coefficients, A_1 , B_1 , and C_1 were determined numerically by the method of least squares. The gelation time corresponding to these coefficients were obtained from the expression (9) (Figure 8). Time t_1^{**} was obtained by the intersection points of the linear parts of the curves $\tau_0 = f(t)$ with the abscissa (see Figure 5). The upper part of each curve $\tau_0 = f(t)$ has been approximated by the expression (10). Coefficients, A_2 , B_2 , C_2 are determined analogously. Time complete conversion

of the sol into a gel was obtained from the expression (11).

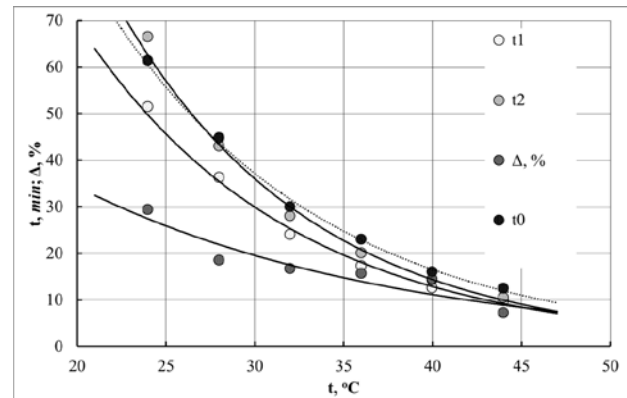


Figure 7. The results of determination of the gelation time at various temperatures.

t_1 - Time t_1^* determined by the method proposed by authors [6].

t_2 - Time t_1^{**} determined by the point of intersection of the tangent line to the linear part of rheological curve $\tau_0 = f(t)$ [4].

t_0 - time corresponding to the inflection point on the rheological curves shown in Figure 8, the dotted line.

Δ - Relative error in the determination of the gelation time, using different methods of its determination.

Temperature dependence of inverse values t_1^* and t_2^* in this temperature range can be described by the Arrhenius equation, and from which the value of activation energy can be obtained:

$$\frac{1}{t^*} = A \exp\left(-\frac{E}{RT}\right) \quad (14)$$

According to the results shown in Figure 7, it has been calculated the value of the activation energy. The results of these calculations are presented in Table 1.

Table 1.

The results of the calculations, the activation energy of the sol-gel process on the Arrhenius equation (17)

The segment of rheological curve	Kind of activation energy	The activation energy, kJ/mol
t_1^*	E_1	46.0±0.5
t_1^{**}	E_1	70±2
t_2^*	E_2	62±1

It is clear from the data obtained that the method of time determination of the beginning of the of sol-gel

transition with the point of intersection of the tangent to linear part of the curve $\tau_0 = f(t)$ [4], provides significantly distorted results in the direction of overstatement. Thus the time error reaches 30%, especially at low temperatures. The calculation of the activation energy of the process also gives an inflated value. Using the device described above is allowed to establish the form of the initial part of the curve $\tau_0 = f(t)$ and develop a methodology for a more accurate determination of gelation time.

In addition to the gelation time, another characteristic of sol-gel transition is the time of achieving the plateau, by dependence $\tau_0 = f(t)$, which is the time of complete transformation (see. Figure 5). The time point of gelation is usually associated with the formation of aggregate in the reaction medium, the dimensions of which are similar to the characteristic size of the reaction vessel. Such a aggregate is called "infinite aggregate". In the reaction medium, in addition to the large aggregate, contains a lot of smaller aggregates of different size, and individual sol particles, which are gradually join it, and which leads to increase of its strength. After all the smaller aggregates and free particles will join the "infinite aggregate," the rate of change of its strength will be significantly reduced. After that comes the stage of gel aging.

The magnitude of the critical shear stress, the degree of conversion at hardening of the gel may be represented as follows [8]:

$$\beta = \frac{\tau_0(t)}{\tau_{max}} \quad (15)$$

The dependence of the degree of conversion for each rheological curve $\tau_0 = f(t)$ can be described by the equation of Avrami-Erofeev-Bogolyubov:

$$\beta = 1 - \exp\left\{-k\left(\frac{t}{t_0}\right)^n\right\} \quad (16)$$

The results of the conversion of curves from Figure 6, in the coordinates of the Avrami-Erofeev-Bogolyubov's equation are shown in Figure 8. These data show that the kinetic curves in coordinates of the Avrami-Erofeev-Bogolyubov's equation are complex and have a point of inflection, which separates the kinetic curve into two parts, the initial and final. The presented data also allow estimating the constants of the Avrami-Erofeev-Bogolyubov's equation $k = (5,81 \pm 0,62) \cdot 10^{-2}$. The calculations show that this constant is independent of

temperature and is the same as for the initial and final part of the kinetic curve. This constant depends only on the chemical nature of the reacting system.

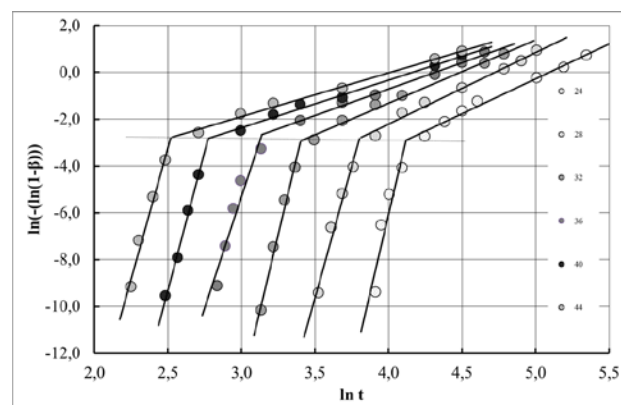


Figure 8. The sol-gel process can be described by equations of macrokinetic such as equations of Avrami-Erofeev-Bogolyubov. The dashed line goes through the inflection point on the presented dependencies. The numbers next to the symbols of the experimental points correspond to temperatures of the process.

To explain this behavior of the kinetic curves, consider possible options for the behavior of the system in terms of the Avrami-Erofeev-Bogolyubov theory. The basic assumption of the Avrami-Erofeev-Bogolyubov theory is that the limiting stage of the solid-state interaction is the formation and nucleus growth of the resulting product phase. The provisions of this theory can be successfully also apply to the process of sol-gel transition. The basic concept of the Avrami-Erofeev-Bogolyubov theory is a critical nucleus - the unit (cluster) composed of atoms, molecules or colloidal particles of the solid phase. In the process of its growth work (ΔG), which is spent on its formation is reaches its maximum value. Nucleus smaller size, called subcritical, they are unstable and quickly disintegrate after formation, while large, called supercritical and are continue its further growth.

The following options of nucleation process:

- an instantaneous nucleation;
- one-step nucleation;
- multistage nucleation.

Changing mechanism of nucleation process will change the values of the parameters in the Avrami-Erofeev-Bogolyubov's equation. The parameters of the Avrami-Erofeev-Bogolyubov's equation have the following physical meaning. β - degree of conversion; t - time; n - parameter which most often has a value from 2 to 4 and depends on the reaction mechanism, the rate of nucleation and geometry of

nuclei. The physical meaning of the parameter n , can be understood from the following expression:

$$n = \gamma + \lambda \tag{17}$$

where γ - the number of stages in the formation of aggregate (often equal to 1 or 0, and the last case corresponds to the instantaneous nucleation, or the case where the growing compact nucleuses completely cover the outer edge). The parameter λ is the effective number of directions nucleus growth (equal to 3 for spheres or hemispheres, 2 - disc or cylinder, 1 - for the one-dimensional growth). The parameter values obtained from the equations (16) and (17) are shown in Figure 9.

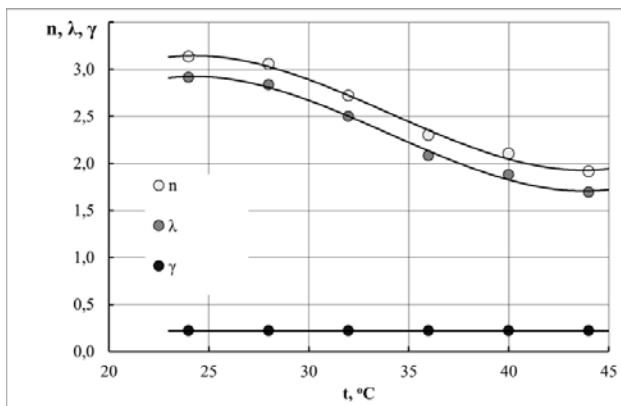


Figure 9. Dependence of the parameters n , λ and γ in equation (17) versus temperature for the final segment of rheological curve (Figures 6 and 8).

By definition, the parameter γ represents the number of steps in the aggregate formation. For this system, the calculated value of $\gamma = 0,221$, indicates that a compactly growing nuclei is coated surface of the growing aggregate, only in part. As noted above, the parameter λ , is the number of directions an effective growth of nuclei. Therefore Fig. 9 shows that as the temperature increases, there is mechanisms of the process change, and reduces the number of possible directions of growth. At the same time the process from three-dimensional direction of growth, gradually moving to a two-dimensional surface geometry, and even to one-dimensional linear geometry. This phenomenon is likely due to steric hindrance arising in the formed gel.

For the initial section of the rheological curves shown in Figures 6 and 8, this parameter has a significant amount $n=23,4 \pm 2,8$. In this part of rheological curve, in contrast to its end section (Figure 9), the parameter n , independent of temperature. In addition, too much of the value of this parameter can be interpreted as the average

number of growth areas for the fractal aggregate in the process of its growth. It is possible to make an analogy between the directions of a fractal aggregate growth, and regular polyhedron where each rising branch is located at the vertices of the polyhedron. Thus of the existing regular polyhedrons, most similar by number of vertices is the dodecahedron, which has 20 vertices. Given that the shapes of growing aggregates have stochastic nature, and the resulting polyhedron faces will have the wrong kind, and, respectively, polyhedrons themselves will have the form of the Voronoi polyhedron. Thus, the value of parameter n will depend primarily on the chemical nature of the sol particles involved in the process of gelation.

Figure 10 shows the coordinates of the inflection point on the rheological curves shown in Figure 8. See from these data that only the ordinate is temperature dependent. Recalculation of the value of the abscissas corresponding to the inflection point in the dimension of time allows us to get a parameter closer in magnitude to t_1^{**} , representing the point of intersection of the tangent to the linear part of rheological curve $\tau_0 = f(t)$. These data are also presented in Figure 7. The closeness of these values, however, does not mean they are equal, and we can assume that this point is the moment of formation, in fact, a solid gel phase. Thus, prior to the inflection point is observed free growth of aggregates without, geometric difficulties. After passing through this critical point of the process, there is a formation a continuous network consisting of coagulated particles, and arise steric hindrances in further growth of formed "infinite aggregate".

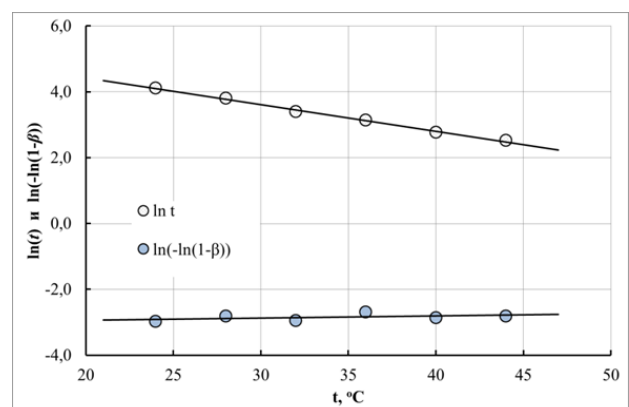


Figure 10. The coordinates of the inflection point on the curves of Avrami-Erofeev-Bogolyubov, presented in Figure 8.

Thus, the inflection in the flow curves presented in the coordinates of the Avrami-Erofeev-Bogolyubov can be explained as the point of completion of the

gelation process and the beginning of structural changes in formed infinite aggregate, or start point of the gel-hardening process.

The curves shown in Figure 9 can be approximated by the following equation:

$$\lambda = \frac{A}{T} + B \quad (18)$$

where $A = 6327$ and $B = -18,3$ empirical constants. The thus-obtained relationship is shown in Figure 11.

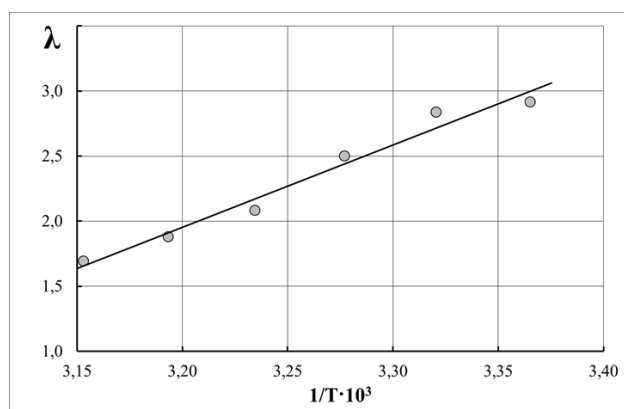


Figure 11. Dependence of the parameter λ in equation (21) versus the inverse temperature.

Based on these data can be stated that the gelation process is characterized by three critical points. First, there is actually point of sol-gel transition which is caused by the formation of aggregate of infinite, which is a cluster of particles and having dimensions commensurate with the dimensions of the reaction vessel. The second point is the point of completion of the process of gelation and beginning of structural reforms, in the formed infinite aggregate, or the start point of the gel-hardening process. The third critical point determines the completion of gelation process and the beginning of gel aging.

On the basis of general considerations, these critical points can be classified as a point of second order phase transitions. Phase transitions of the second kind are phase transitions, in which the second derivatives of the thermodynamic potentials, depending on the pressure and temperature are changed abruptly, then, as their first derivatives are changed gradually. It follows, in particular, that the energy and the volume of the substance in the phase transition of the second kind do not change, but are changed its heat capacity, compressibility, different susceptibilities, etc. Of the existing examples of phase transitions of the second kind, the most close

to the process of the sol-gel transition at its geometric essence are the processes of transition of amorphous material in glassy state.

The greatest development in recent years has received the fluctuation theory of phase transitions of the second kind. This theory works even outside the field of applicability of Landau theory, and finds the critical parameters and general patterns of phase transitions of the second kind [9, 10]. In this theory, the anomalous behavior of physical quantities near the phase transition point is associated with a strong interaction of fluctuations of the order parameter, the correlation radius of which grows without bound and tends to infinity at the point of phase transition. Consequently, the system cannot be divided into the statistically independent subsystems, and fluctuations on all scales are non-Gaussian. These phenomena we observe in the case of the sol-gel transition.

4 Conclusion

Sol-gel transition associated with the formation of spatial chains which permeate the whole volume of the sol. The appearance of the spatial grid is accompanied by a significant increase in the viscosity of the system. The sol-gel transition the colloid system loses its fluidity. It has manifested a number of new physical properties: elasticity, the critical shear stress, the ability to preserve shape. Viscosity and yield point - two macroscopic integral characteristics of Newtonian medium (sol) and Bingham medium (gel) that are responsive to changes in colloidal system, occurring in the process of gelation. Therefore, the study of these processes require of using special rheological methods.

In order to study rheology of gelation we have developed a measuring system, consisting of several measuring cells such as Weiler-Rebinder; the system of automatic control of medium composition; and thermal stabilization system. The measuring cell consists of a heating jacket, indenter and dynamometer. Automatic adjusting system of the medium composition is includes an ionomer with ion-selective electrodes, interface unit, and an automatic burette, for automatic dosing reagents for adjusts composition of the reaction medium. This measurement complex is designed to measure the dependence of the critical shear stress on the time, since the beginning of the sol-gel transition to the complete conversion of the sol into a gel. For the system we have developed, the range of the measured values of the critical shear stress is $\tau_0 = (0.05 \div 50000) \text{ dyne/cm}^2$.

Using the above device, it has allowed to establish the form of the initial part of the curve $\tau_0 = f(t)$, and to develop a methodology for a more accurate definition of gelation time. With the use of this method, it was found that the classical method of determining the start time of the sol-gel transition based on the determination of the intersection point of a tangent to the linear portion of rheological curve $\tau_0 = f(t)$, gives a much distorted results.

So the time error is 30%, especially at low temperatures. It was also found that the calculation of activation energy of the process, using the classical method, excluding the initial section of rheological curve also overestimates value. Carried out analysis of experimental data has allowed to find new phenomenon, which is that the kinetic curves in coordinates of the Avrami-Erofeev-Bogolyubov's equation, are complex and have a point of inflection. As has been shown, this point on the kinetic curve divides it into three parts, initial, middle and end. The constant in the Avrami-Erofeev-Bogolyubov's equation was defined, it amounted to value $k = (5.8 \pm 0.6) \cdot 10^{-2}$. It was found that this constant is not dependent on the temperature and the same for both the initial and final parts of the kinetic curve. It depends only on the chemical nature of the reacting system.

For the initial section of the kinetic curves, the value of the parameter n in the Avrami-Erofeev-Bogolyubov's equation amounted to $n=23.4 \pm 2.8$. It was also found that for the initial part of dependence parameter n , as opposed to the end part of dependence it does not depend on temperature. The large value of this parameter can be interpreted as the average number of growth directions, of a fractal aggregate. The value of this parameter depends on the chemical nature of the sol particles involved in the process of gelation. The observed behavior of the kinetic curves due to the change of the process mechanism, and decreasing the number of possible directions of fractal aggregates growth. At the same time, aggregate growth process is gradually moving from a three-dimensional growth to the two-dimensional surface geometry, and even to one-dimensional linear geometry. This behavior is due to steric hindrance arising in the aggregation of the sol particles in the formed gel.

A detailed study of the sol-gel process with the help of highly sensitive rheological methods will allow further control these processes in order to obtain new nanocomposite materials, which has a unique set of mechanical, physical and chemical, and other functional properties.

Acknowledgement

The author expresses his gratitude to Koltakov A.I., for its assistance in the creation of measurement system and carrying out relevant measurements. The author also expresses his thanks to Mr. Omer Yagel, VP Business Development and Training DigiSec Ltd., official representative of the company Maplesoft, branch of Waterloo Maple Inc. in Israel, for the opportunity to use the software product of the company, Maple program of analytical calculations.

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