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Kinetics of the exchange of water absorbed in silica hydrogel with ethanol: Modelling by Brouers and Sotolongo–Costa fractal kinetics

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Abstract: Isothermal kinetics of the exchange of absorbed water in a silica hydrogel (SH) with ethanol was examined. The isothermal kinetic curves of absorbed water exchange with ethanol were measured at the temperatures: $T = 297, 306$ and 316 K. The rate of the exchange was analysed as a function of time. The possibility of mathematical description of the kinetics of exchange by the Brouers and Sotolongo–Costa's (BS) fractal's kinetics model was examined. Parameter values (n, τ, β) of the model and their changes with temperature were calculated. By applying the method of Ozao, it was determined that the rate limiting step of the process of exchange was the rate of exchange of the absorbed water with ethanol. Values of the fractal dimension of the SH–ethanol interphase were calculated. The dependences of the effective time-dependent rate coefficient, activation energy and pre-exponential factor on time and degree of exchange were calculated and discussed. The proposed model of the mechanism of the exchange of absorbed water with ethanol was discussed.

Keywords: silica hydrogel; solvent exchange; kinetics; fractal dimension.

INTRODUCTION

Nanoporous materials of low density, large specific surfaces and high porosity are called aerogels.¹ Due to the unique properties of silica aerogels: extreme low density, $\approx 30 \text{ kg m}^{-3}$; high porosity, $>98 \%$; low thermal conductivity, $\approx 0.01 \text{ W m}^{-1} \text{ K}^{-1}$; high surface area, $>1000 \text{ m}^2 \text{ g}^{-1}$; low refractive index, 1.01–1.10; low dielectric constant, <2 ; optical transparency, $>95 \%$; and low sound velocity, 100 m s^{-1} ,² it could be expected that they would find numerous application, such

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as: excellent transparent thermal insulation materials,³ materials for acoustic barriers,⁴ catalytic support,⁵ absorption of oil,⁶ collectors,⁷ drug delivery carriers,⁸ sensors,⁹ *etc.*

The basic steps of the preparation of a silica aerogel are: formation of a silica sol in an aqueous solution, gelation of the silica sol, aging of gels, exchange of water with alcohol and supercritical drying of alcogels.¹⁰ Solvent exchange and modification (silylation) of the surfaces of the gel presents the essential processes for preserving the highly porous silica network structure during drying and obtaining aerogels with a high cumulative pore volume, high specific area, and extremely low density. Solvent exchange is a long-lasting and tedious process, because it mostly depends on the surface tension of the solvent and surface area of the gel.

Knowing the kinetics of exchange of the absorbed water from hydrogels is of extraordinary practical and scientific importance, since it enables mathematical modelling of the exchange process, which supports the design, optimization and scale-up of the processes, and development of novel technologies. To the best of our knowledge, there are no available literature data on the kinetics of the exchange of the absorbed water with a solvent. Nevertheless, there are only a few papers that investigated the exchange of absorbed water with a solvent. Rao *et al.*¹¹ investigated the effect of the solvent type (toluene, *n*-hexane, *n*-heptane) on the physico-chemical properties of silica aerogels prepared by the atmospheric pressure drying method.

The exchange of the water absorbed within a silica hydrogel with ethanol occurs at the interface between the silica hydrogel–ethanol phases. The spatial structure of the interface of the interaction is completely unknown in a dimensional and topological sense.¹² Bearing in mind the amorphous structure of a silica hydrogel, it is possible to assume that it is not ideal but disordered, irregular and non-homogeneous. Since the dimensional and topological heterogeneity of a system causes its chemical heterogeneity, the boundary surface of the interaction phase is probably also energetically heterogeneous. To describe the kinetics of processes which occur in such systems, the application of classical kinetic models, based on defined dimensional and topological properties, is not quite adequate.¹³

A fractal is an unregulated system, the disorder of which can generally be described with an innumerable value of the dimensionality of the system. A fractal object is fragmentable and can be divided into parts, with each part being a copy of the basic motif. Just for this reason, the assumption of the fractal nature of the boundary interaction surface is probably the most appropriate in describing the water absorbed–ethanol exchange kinetics, since it allows for the interaction, which occurs on the basic motif, to be reproduce on different time and duration scales.

Bearing this in mind, the present paper deals with the possibility of using a fractal kinetics model in investigating the kinetics of the exchange of water absorbed in silica hydrogel with ethanol, for the first time in the available literature.

Brouers and Sotongo–Costa fractal kinetics

In the works of Brouers and Sotongo-Costa¹⁴ and Brouers,¹⁵ the bases of fractal kinetics of chemical reactions and physicochemical processes are presented.

According to the Brouers and Sotongo-Costa (BS) fractal kinetics, the rate of chemical reaction is described by the fractional differential:

$$-\frac{dc_{n,\beta}(t)}{dt} = k_{n,\beta} [c_{n,\beta}(t)]^n \quad (1)$$

where the $c_{n,\beta}(t) / \text{g mL}^{-1}$ is the concentration of the reactant at time t , n – non-integer overall reaction order, β – fractional time index, $k_{n,\beta}(t) / \text{min}^{-\beta} \text{ mL g}^{-1}$ – effective time-dependent rate coefficient:

$$k_{n,\beta}(t) = \beta \frac{t^{\beta-1}}{\tau_{n,\beta}^\beta} \left[1 + (n-1) \left(\frac{t}{\tau_{n,\beta}} \right)^\beta \right]^{-1} \quad (2)$$

the $\tau_{n,\beta}^\beta / \text{min}^{-\beta}$ is a characteristic time of the complex kinetic, and is given by:

$$\tau_{n,\beta} = \left(c_0^{n-1} k_{n,\beta} \right)^{-\frac{1}{\beta}} \quad (3)$$

where $c_0 / \text{g mL}^{-1}$ is the initial concentration of the reactants. The solution of the differential Eq. (1) is given by:

$$c_{n,\beta}(t) = c_0 \left[1 + (n-1) \left(\frac{t}{\tau_{n,\beta}} \right)^\beta \right]^{-\frac{1}{(n-1)}} \quad (4)$$

In the case when fractal kinetics is used to describe the solvent exchange kinetics, Eq. (4) is transformed into:

$$c_{n,\beta}(t) = c_e \left\{ 1 - \left[1 + c_e (n-1) k_{n,\beta} t^\beta \right]^{-\frac{1}{(n-1)}} \right\} \quad (5)$$

where $c_e / \text{g mL}^{-1}$ is equilibrium concentration of the reactant (maximum quantity), and:

$$\tau_{n,\beta} = \left(c_e k_{n,\beta} \right)^{-\frac{1}{\beta}} \quad (6)$$

In the case when fractal kinetics is used to describe the solvent exchange kinetics, Eqs. (5) and (6) are transformed into:

$$c_{n,\beta}(t) = c_e \left\{ 1 - \left[1 + (n-1) \left(\frac{t}{\tau_{n,\beta}} \right)^\beta \right]^{\frac{1}{(n-1)}} \right\} \quad (7)$$

If the degree of exchange is defined by:

$$\alpha_{n,\beta}(t) = \frac{c_{n,\beta}(t)}{c_e} \quad (8)$$

then the conversion curve of exchange can be described by:

$$\alpha_{n,\beta}(t) = 1 - \left[1 + (n-1) \left(\frac{t}{\tau_{n,\beta}} \right)^\beta \right]^{\frac{1}{(n-1)}} \quad (9)$$

EXPERIMENTAL

The following materials were used to synthesize the silica hydrogel and to examine the kinetics of the change.

Soluble glass (sodium silicate solution), Silco 3.1, was purchased from A.D. Zeolite BSB, Probištip, North Macedonia. The chemical composition of soluble glass was as follows: silicon dioxide = 28.7 wt. %; sodium oxide = 8 wt. %; modul, $M = 3.30$; density = 1380 kg m^{-3} . For the exchange of sodium ions from a solution of soluble glass with hydrogen ions, a strong acid ion exchange resin IR-120, supplier Amberlite, USA, was used. Ammonium hydroxide and absolute ethanol 99.8 %, both *p.a.*, were purchased from Zorka Pharma, Šabac, Serbia. Distilled water was used to prepare the soluble glass solution.

Synthesis of silica hydrogels was performed according to the procedure described in detail by Rao.² In accordance with this procedure, the synthesis of silica hydrogels was carried out as follows. The soluble glass was diluted by adding distilled water to density = 1120 kg m^{-3} . The diluted soluble glass solution, at room temperature, was passed through a layer of ion exchange resin ($\phi = 2.54 \text{ cm}$, $h = 25 \text{ cm}$) at a flow rate of 1 mL min^{-1} in order to obtain the silica sol. The obtained silica sol was collected in a 250 mL beaker. Silica hydrogel was obtained by neutralisation of the silica sol ($V = 100 \text{ mL}$) with 0.4 mL of 1 M ammonium hydroxide solution. The hydrogel was formed after 15 min. In order to strengthen the silica network, the gel was left to age for 3 h at $50 \text{ }^\circ\text{C}$. After that, the gel was rinsed with water 3 times and kept in a closed vessel.

The water content in silica hydrogel, p / wt. %, was determined gravimetrically. A precise amount of the hydrogel, m_0 / g, was dried at a temperature of $T = 393 \text{ K}$, until its mass became constant, m_{TN} / g. Water content was calculated as:

$$p = 100 \frac{m_0 - m_{\text{TN}}}{m_0} \quad (10)$$

The water content in the used silica hydrogel was 91 wt. %. Determination of the degree of exchange of water absorbed on silica hydrogel with ethanol (α) was performed as follows.

In 250 mL of absolute ethanol preheated at a predetermined temperature, m / g of silica hydrogel wrapped in a meshed carrier was immersed. The reaction mixture was stirred by a magnetic stirrer at 400 rpm for a predetermined time.

The reaction mixture was sampled at predetermined time intervals in order to determine the water concentration in the reaction mixture. The water concentration exchanged, $c_{\text{H}_2\text{O}}$, in the samples, was determined by the Karl–Fischer's coulometric method. The titration was performed using a Metrohm 831 Karl–Fischer coulometer. The quantity of water exchange, q_t / g was determined by:

$$q_t = c_{\text{H}_2\text{O}} V_s \quad (11)$$

where: $c_{\text{H}_2\text{O}}$ / g mL⁻¹ is the concentration of water in the ethanol solution at time t / min, V_s / mL is the volume of the ethanol solution.

The degree of water exchange with ethanol, was calculated as:

$$\alpha = 100 \frac{q_t}{mp} \quad (12)$$

Determination of the parameters of the Brouers and Sotolongo–Costa Equation (n , τ , β) was performed by fitting the isothermal exchange conversion curves, using non-linear regression. The values of the equation parameters were determined using the OriginPro 9.0 64 Bit software. To evaluate the quality of fit, two criteria were used: the coefficient of determination, R^2 , and the reduced chi square coefficient, χ^2 .

RESULTS AND DISCUSSION

Fig. 1 shows the isothermal kinetic curves $c_{\text{H}_2\text{O}} = f(t)_T$ (Fig. 1a) and conversion curves (the dependence $\alpha = f(t)_T$, Fig. 1b) of the exchange of the absorbed water in the silica hydrogel with ethanol.

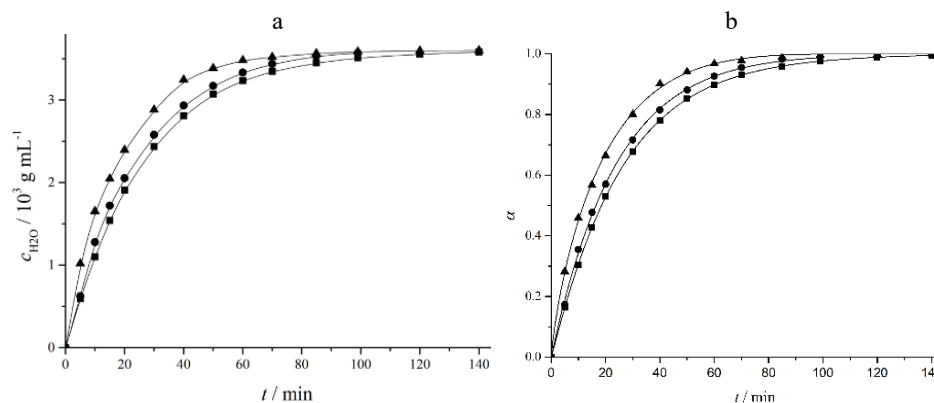


Fig. 1. Isothermal kinetic curves (a) and conversion curves (b) of the exchange of the absorbed water in ethanol–water mixtures as a function of time at: ■ 297, ● 306 and ▲ 316 K.

The kinetics and conversions curves of the water exchange have complex shapes. There are three characteristic and clearly noticeable shapes of increasing $c_{\text{H}_2\text{O}}$ with the extended exchange duration: a linear part, non-linear part and a pla-

teau. At short times of exchange, the concentration of water in ethanol increases almost linearly with extended duration of the exchange. Further increase in exchange time leads to a concave increase in $c_{\text{H}_2\text{O}}$, whereas with longer exchange time the maximum of $c_{\text{H}_2\text{O}}$ is achieved (plateau). With increasing temperature, the slope of the linear change in water concentration becomes steeper, and the equilibrium water concentration is reached sooner. The increase in the slope and the shortening of equilibration time indicates that the exchange process is thermally activated, and that the rate of exchange increases with temperature.

An attempt at determining the kinetics model of water exchange was made by analysing the shape of the curve of the exchange rate vs. time. The isothermal rate of water exchange vs. time is shown in Fig. 2.

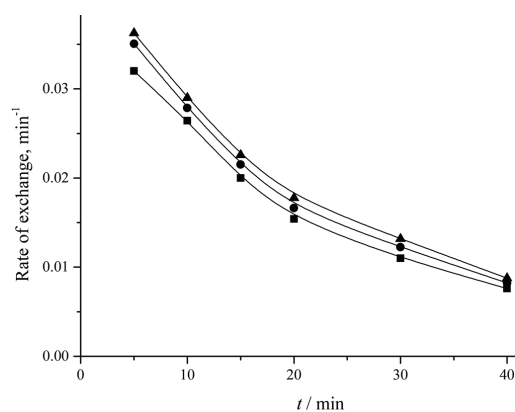


Fig. 2. Isothermal dependences of exchange rate vs. time at: ■ 297, ● 306 and ▲ 316 K.

At all the examined temperatures, the rate of exchange concavely decreases in a complex way with the time of exchange. The shape of dependence (da/dt) of the rate of exchange on time is significantly different than in cases of kinetically controlled chemical reactions (first and second order), and diffusion-controlled chemical reactions and processes, which implies a complex nature of this exchange kinetics.

With this complex dependence of the reaction rate on time in mind, and the complex structure of interface SH, the possibility of fitting isothermal conversion curves of change with the BS equation was investigated. The results of fitting the experimental conversion curves with the BS equation are shown in Fig. 1b (solid line). As shown, the experimental conversion curves, at all the investigated temperatures, are successfully fitted with the BS equation in the whole range, Fig. 1b.

The values of the BS equation parameters (n , β , τ) are given in Table I.

The values of fractal parameter n that characterizes the apparent order of the reaction are non-integer 1.05 to 0.8 and significantly deviate from the values for the reaction order of conventional chemical reactions, which confirms the fractal nature of the exchange kinetics. The parameter β varies from 1.05 to 0.82, with increasing temperature, which indicates that the mechanism of exchange does not

change with temperature, but that there is a change in the structure of the fractal interface of interaction of ethanol molecules with absorbed water on the hydrogel. The values of the characteristic time, τ , decrease with increasing temperature, which confirms the previous proposition that the specific rate of exchange increases with temperature.

TABLE I. Values of the Brouers and Sotongo-Costa fractal parameters for the isothermal kinetics

T / K	Fractal parameters	Value	$\chi^2 \times 10^6$	R^2
297	n	1.05	1.74	0.99998
	$\tau^{-1.05} / \text{min}^{-1.05}$	25.86		
	β	1.05		
306	n	0.98	0.638	0.99944
	$\tau^{-1.01} / \text{min}^{-1.01}$	23.84		
	β	1.01		
316	n	0.80	0.450	0.99955
	$\tau^{-0.82} / \text{min}^{-0.82}$	20.06		
	β	0.82		

The exchange of water absorbed on the silica hydrogel with ethanol is a heterogeneous chemical reaction which occurs continuously if there is a continuous molecular or convective diffusion of ethanol molecules to the reacting boundary surface of the hydrogel and a continuous diffusion of the altered water into the ethanol solution. In general, the rate of the exchange process is determined by the rate of the slowest stage of exchange. In the case where the rate of exchange is higher than the diffusion rate of ethanol, the kinetically limiting stage of the process is the diffusion rate of ethanol to interface. In contrast, when the rate of water exchange with ethanol is lower than the diffusion rate, the kinetically limiting stage is the rate of that exchange.

Ozao¹⁶ developed a method for determining the kinetically limiting stage of chemical reactions and physicochemical processes that can be described by fractal kinetics. According to this method, in case the kinetically limiting stage of fractal kinetics is the rate of the chemical reaction (process) at the interface, the dependence of $\ln (d\alpha/dt)$ on $\ln (1-\alpha)$, should be linear, and the slope N of this dependence is in a functional relationship with the fractal dimension D of the interface is given as:

$$N = \frac{D}{D-1} \quad (13)$$

The isothermal dependences of $\ln (d\alpha/dt)$ on $\ln (1-\alpha)$ are shown in Fig. 3. The dependence $\ln (d\alpha/dt)$ on $\ln (1-\alpha)$ is linear, which indicates that the kinetically limiting stage is the rate of exchange of absorbed water with ethanol.

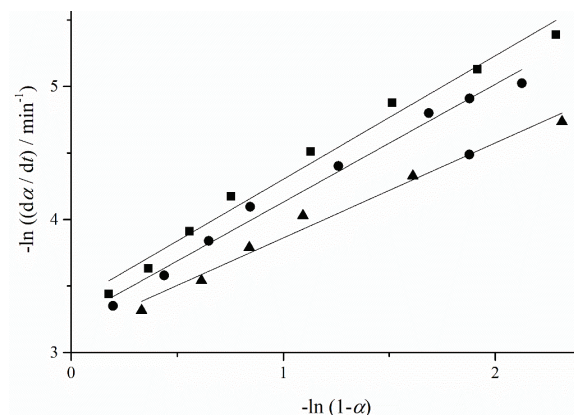


Fig. 3. Isothermal dependences of $\ln(d\alpha/dt)$ on $\ln(1-\alpha)$ at: ■ 297, ● 306 and ▲ 316 K.

The dependence of the slope and fractal dimension on temperature are given in Table II.

TABLE II. The effect of temperature on fractal dimension of the interface

T / K	N	D
297	0.93	1.93
306	0.88	1.88
316	0.71	1.71

As can be seen from Table II, an increase in the temperature of exchange leads to a decrease in the value of the fractal dimension from 1.93 to 1.71 of the interface interaction, which confirms the previously assumed assumption that a change in temperature leads to a change in the fractal structure of the interaction.

Upon knowing the isothermal values of the parameters (n , β , τ), the isothermal dependences of the effective time-dependent rate coefficient on time are calculated by Eq. (2). The isothermal dependences of the effective time-dependent rate coefficient on time are shown in Fig. 4.

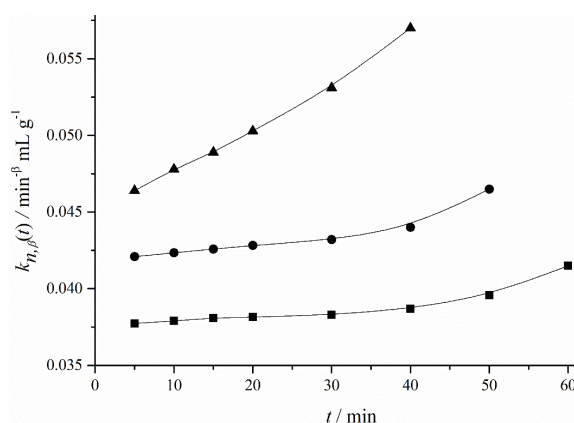


Fig. 4. Isothermal dependences of $k_{n,\beta}(t)$ on time, at: ■ 297, ● 306 and ▲ 316 K.

The effective rate coefficient of the exchange of water from silica hydrogel with ethanol is a time-dependent value. The values of the effective rate coefficient at all of the investigated temperatures, increase with the duration of the exchange process. At the defined times of exchange (isochronal conditions), the values of the effective time-dependent rate coefficient increase with temperature.

The time dependence of $k_{n,\beta}(t)$ is most likely due to the following points:

- a) the irregularities and the inhomogeneous interface in different phases of the interaction;¹⁷
- b) different rates of relaxation of the reacting species in the heterogeneous system;¹⁸
- c) the reaction rate exceeds the rate of internal rearrangement, which leads to regeneration of the distribution of reactant reactivity in disordered systems;¹⁹
- d) changing of the so-called reaction parameter, caused by the interface change during the reaction.²⁰

Bearing in mind the fractal structure of the water absorbed in silica hydrogel, it is presumed that the specific reaction rate is higher than the rate of internal rearrangement in the absorbed phase, which leads to the regeneration of the reactivity of the reactant, this being the main source of the time-dependency of k .

In fact, any exchange of a water molecule with an ethanol molecule has to lead to a structural reorganization within the absorbed phase, and due to this, the rate of internal rearrangement will change during the reaction, which will in turn change the specific reaction rate of this exchange. The increase in $k_{n,\beta}(t)$ with α indicates that the specific rate of reactivity regeneration decreases with time, since the structure of the absorbed phase is enriched with ethanol molecules

Knowing the mathematical dependence of the degree of exchange on time, the dependence of $k_{n,\beta}(t)$ on time can be transformed into dependence of $k_{n,\beta}(t)$ on the degree of exchange. The dependence of $k_{n,\beta}(t)$ on the degree of exchange is shown in Fig. 5.

At all of the examined temperatures, the $k_{n,\beta}(t)$ non-linearly increases with increasing degree of exchange. At a particular degree of exchange (isoconversional condition), the values of $k_{n,\beta}(t)$ increase with temperature in accordance with the Arrhenius equation. Thus, by applying the Arrhenius equation, the isoconversion values of the parameters of the exchange kinetics are calculated.

The isothermal dependence of E_a and $\ln A$ on the degree of exchange is presented in Fig. 6.

The values of kinetic parameters increase with α in a complex manner. This complex change of kinetic parameters with α confirms the complex fractal nature of the kinetics of exchange. The increase in the values of E_a with α indicates an enhancement of the interactions between the molecules of water in the absorbed phase with increasing degree of exchange, leading to structural changes in the absorbed phase.

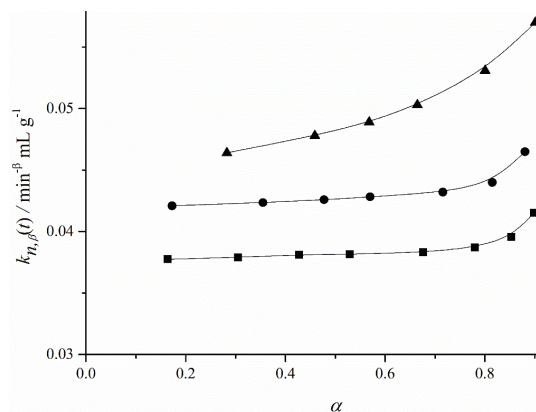


Fig. 5. Dependence of $k_{n,\beta}(t)$ on the degree of exchange at: ■ 297, ● 306 and ▲ 316 K.

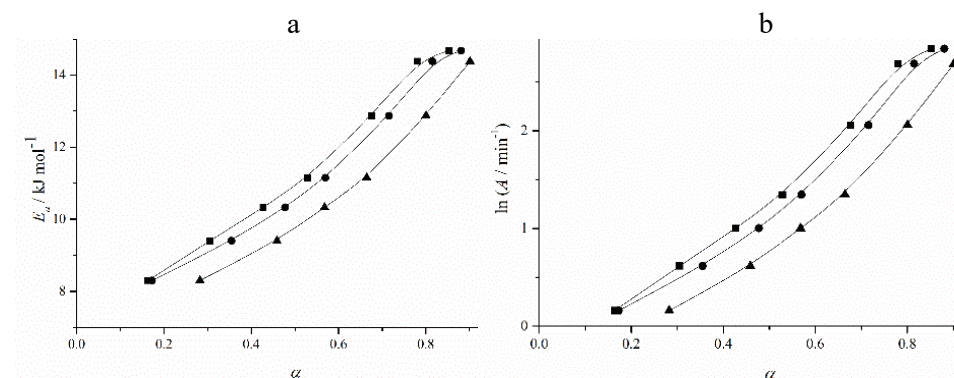


Fig. 6. Isothermal dependences of E_a on α (a) and $\ln A$ on α (b), at: ■ 297, ● 306 and ▲ 316 K.

Between the values of the kinetic parameters (E_a and $\ln A$) there is a correlation, *i.e.*, a compensation effect, which can be described by:

$$\ln A = 3.21951 + 040911E_a \quad (14)$$

The existence of a compensation effect confirms the complex nature of this kinetics, and leads to the assumption that it is the consequence of: a) the difference in the value of the effective time-dependent rate coefficient of exchange and the effective time-dependent rate coefficient of internal rearrangement in the absorbed phase; b) changes in the geometric (structural) conditions under which the process occurs.

The existence of the time-dependent values of k , E and $\ln A$ indicates that the value of the effective time-dependent rate coefficient of the exchange exceeds the rate of the internal rearrangement in the absorbed phase of the hydrogel. The increase in the value of the effective time-dependent rate coefficient of water exchange with time and degree of the exchange indicates that the effective time-dependent rate coefficient of structural transformation in the absorbed phase of

the hydrogel with the duration of the exchange and α decreases, due to the changes in the structural and aggregational properties of the absorbed water. It is confirmed with the increase in $\ln A$ with α , as seen in Fig. 6b.

CONCLUSIONS

The isothermal kinetics of the exchange of water absorbed in a hydrogel with ethanol is a kinetically complex process. The kinetics of the exchange can be completely described by the Brouers, Sotolongo-Costa fractal kinetics model. The values of the parameters of the Brouers, Sotolongo-Costa kinetic model decrease with increasing temperature of exchange. The kinetics limiting stage of the exchange process is the value of the surface area of the boundary phase of interaction. The value of the effective time-dependent rate coefficient of exchange at all the temperatures increases with the duration of exchange. The effective time-dependent rate coefficient at a specific time of exchange increases with increasing temperature. The activation energy of the exchange process increases with the duration of the exchange and with the increase in the degree of exchange. The values of $\ln A$ and the activation energy are interrelated *via* a compensation effect.

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ИЗВОД

КИНЕТИКА ИЗМЕНЕ ВОДЕ АПСОРБОВАНЕ У ХИДРОГЕЛУ СИЛИЦИЈУМ-ДИОКСИДА СА ЕТАНОЛОМ: МОДЕЛОВАЊЕ BROUERS И SOTOLONGO-COSTA ФРАКТАЛНЕ КИНЕТИКЕ

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Испитана је изотермна кинетика измене апсорбоване воде у хидрогелу на бази силицијум-диоксида (SH) са етанолом. Изотермне кинетичке криве измене воде са етанолом измерене су на температури: $T = 297, 306$ и 316 К. Анализирана је зависност брзине измене од времена. Испитана је могућност математичког описивања кинетике измене Brouers и Sotolongo-Costa (BS) моделима фракталне кинетике. Израчунате су вредности параметара (n, τ, β) модела и њихове промене са температуром. Применом Озао методе утврђено је да је брзина процеса измене лимитирана брзином измене апсорбоване воде етанолом. Израчунате су вредности фракталне димензије граничне фазе SH–етанол. Израчунате су и дискутоване промене временски зависног коефицијента брзине, енергије активације и предекспоненцијалног фактора током времена и степена измене. Разматран је предложени модел механизма измене апсорбоване воде са етанолом.

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