

Kinetics of Exchange of the Water Absorbed in Poly (Acrylic Acid) Hydrogel with Ethanol

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Authors' contributions

This work was carried out in collaboration between all authors. All authors read and approved the final manuscript.

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ABSTRACT

Isothermal kinetics of exchange of absorbed water with ethanol in poly(acrylic acid) hydrogel was investigated at different temperatures: 295 K, 303 K and 313 K. By applying isoconversional and model-fitting methods it was found that the exchange of absorbed water with ethanol is an elementary (single step) kinetic process which can be mathematically described with the kinetic model of Jander three-dimensional diffusion (3D). The values of kinetics parameters (rate constants (k_M), energy of activation $E_a = 18.8 \text{ kJ mol}^{-1}$, pre-exponential factor $\ln[A/\text{min}^{-1}] = 4.93$) and thermodynamics parameters of activated complex formation ($\Delta H^* = 16.5 \text{ kJ mol}^{-1}$, $\Delta S^* = -177 \text{ J K}^{-1} \text{ mol}^{-1}$, $\Delta G^* = 68.73\text{-}71.92 \text{ kJ mol}^{-1}$) of exchange were calculated. It was found that the value of ΔH^* corresponds to the energy of rearrangements of bound water around hydrophilic groups of polymeric network.

Keywords: Exchange; water; ethanol; kinetics; model-fitting method; Poly(Acrylic Acid) hydrogel.

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1. INTRODUCTION

Hydrogels are three-dimensional cross-linked hydrophilic polymer network capable of swelling in water and other “good” solvents and retaining a large volume of water (solvent) in the swollen state [1]. Hydrogels are also capable to undergo the changes in their actual volume (volume phase transition) in a response to various external stimuli, either physical (temperature, magnetic field, electric field, solvent composition, light, pressure, sound, etc) chemical or biochemical stimuli (pH, ions specific molecular recognition events, etc) [2-6]. The ability of hydrogels to undergo volume phase transitions in response to infinitesimal changes in environmental conditions enables us to exploit them as smart materials. In this framework, the investigation of volume phase transitions is of huge theoretical and applicative significance [7]. Investigations of the volume phase transitions in polymer network systems were initiated by Dusek and Patterson, who had predicted theoretically a discontinuous volume change for chemically cross-linked gels [8]. Later Tanaka et al. observed the critical behavior of cross-linked ionized polymer networks as a result of temperature or solvent composition variations, as well as the pronounced collapse transition. It was suggested that the volume phase transition in gels is analogous to the coil-to-globule transition in single polymer chains in poor solvents [9-11]. Wu et al. overviewed the models for description of hydrogel volume transition behaviours [1].

A. Hiroki et al. investigated the volume phase transitions of poly(acryloyl-L-proline methyl ester) gels in various water–alcohol composition [12]. A Hüther et al. investigated swelling of *n*-isopropyl acrylamide hydrogels in water and aqueous solutions of ethanol and acetone [13]. Kinetics of swelling and de-swelling of gelatin hydrogels in ethanol–water marginal solvent was investigated in the work of S. Boral et al. [14]. Volume phase transition and preferential alcohol adsorption of poly(N,N-diethylacrylamide) gel in water/alcohol mixtures was investigated in the work of B. Liu et al. [15].

The aerogels are ultra-porous (more than 90% of porosity) material with wide-ranging applications. The unique properties includes low density, high surface area, low thermal conductivity, low dielectric constant, low index of refraction, and so on. Owing to these unique properties, such aerogels have been studied extensively for use as catalysts and thermal insulators and in

applications related to adsorption and drug delivery systems [16]. Aerogels can be obtained by hydrogels drying (dehydration).

Textural properties of dehydrated hydrogels (xerogels) depend on the drying method. Three different methods of drying (dehydrations) are usually used: a) evaporation of the solvent at different temperatures b) exchange of water with the solvent and solvent evaporation above critical point c) freeze drying [17]. Evaporation of the solvent leads to the collapse of the primary structure of polymer chains in hydrogel while the other two methods allow preserving of the primary structure and formation of aerogel [18].

Since preservation of the primary structural properties of xerogels is very important for successful formation of aerogel and knowing that the kinetics of exchange of absorbed water with solvent is of crucial importance, in this investigation the kinetics of isothermal exchange of absorbed water with ethanol was thoroughly evaluated with the aim to determine the kinetic model, degree of kinetic complexity, activation energy E_a and pre-exponential factor $\ln(A/\text{min}^{-1})$.

2. MATERIALS AND METHODS

2.1 Materials

Acrylic acid (AA) was purchased from Merck-Darmstadt, Germany. Sodium persulfate ($\text{Na}_2\text{S}_2\text{O}_8$) and sodium thiosulfate ($\text{Na}_2\text{S}_2\text{O}_5$), both p.a. purity, were supplied from Merck. Hydrogen peroxide (H_2O_2 , 30%), was purchased from Zorka-Šabac, R. Serbia. N, N'-methylenebisacrylamide (NMBA) was purchased from Merck-Darmstadt, Germany. Ethylenediaminetetraacetic acid (EDTA), p. a., was purchased from Merck-Darmstadt, Germany. Sodium carbonate (Na_2CO_3), p.a. purity, was purchased from Zorka-Šabac, R. Serbia. Ethanol ($\text{C}_2\text{H}_5\text{OH}$) (99.9 w/w) was purchased from Carlo Erba, R. Italy. Bidistilled water was used in all experiments.

2.2 Synthesis of Poly (Acrylic Acid) Hydrogel

The poly(acrylic acid) hydrogel (PAA) was synthesized following the cross-linking free radical polymerization [19].

Hydrogel synthesis was performed in polymerization reactor in a nitrogen atmosphere equipped with magnetic stirrer, reflux condenser,

nitrogen income and a thermometer. A monomer solution was prepared from: 80 mL of melted glacial AA dissolved in 180 mL of distilled water, 0.8 g of NMBA, 0.08 g EDTA both dissolved in 60 mL of distilled water. This monomer solution was placed in the reactor, stirred and deoxygenated with nitrogen gas bubbling through the solution for 60 min. The initiator stock solutions were: sodium persulfate, sodium thiosulfate (2.5 g of each were dissolved in 22.5 mL bidistilled water) and hydrogen peroxide, 30%. When the deoxygenation time was finished, the initiator solutions were added to the following monomer solutions: 2.4 mL of sodium persulfate solution, 10 mL of hydrogen peroxide, and 1.2 mL of sodium thiosulfate solution. The reaction mixture was then slightly gradually warmed up to 50°C until there was a dramatic increase in the reaction mixture's temperature (gel-point) and then it was left for 4 h at the temperature of 80°C. The obtained geltype product was converted into Na⁺ from (60%) by neutralizing it with a 3% solution of Na₂CO₃. The resulting hydrogel was cut into approximately equal discs and placed in the excess distilled water. The water was changed seven times every 5 h (or 12 h during the night) in order to remove the unreacted monomers and the sol fraction of the polymer. The obtained products were stored in exicator before use.

2.3 Determination of Water Content in Hydrogel

Determination of the water content in analyzed hydrogel (m_{H_2O}) was done by gravimetric analysis. Precise amount of the hydrogel ($m_0 = 1.000$ g) was thermally activated at the temperature $T=110^\circ\text{C}$ until its mass became constant (m_{TN}). Water content was calculated by using equation (1)

$$m_{H_2O} = \frac{m_0 - m_{TN}}{m_0} (g/g) \quad (1)$$

2.4 Kinetics of Exchange of Absorbed Water with Ethanol

Kinetics of exchange of absorbed water with ethanol in hydrogel was investigated by batch method. The reaction mixture was prepared by mixing $m_0 = 1.000$ g of the hydrogel with 250 ml of the absolute ethanol and then homogenized by stirring at the rate of 200 rpm and constant temperature. Samples were taken from the mixture at the predefined time intervals, and they were centrifuged at 2000 rpm for 5 min in order

to achieve phase separation. The supernatant solution was analyzed in order to determine water concentration.

2.5 Determination of Water Concentration Ethanol Solution

Water concentration (c_{H_2O}) in the analyzed sample was determined with Karl-Fischer coulometric titration. For this purpose Metrohm 831 Karl-Fischer coulometer was used. The amount of water exchanged with ethanol was determined as:

$$q_{H_2O} = c_{H_2O} \cdot V_M \quad (2)$$

where c_{H_2O} is mass concentration of water in ethanol solution at reaction time t while V_M is the volume of reaction system at reaction time t . The degree of conversion α of exchanged water with ethanol was calculated as

$$\alpha = \frac{q_{H_2O}}{m_{H_2O}} \quad (3)$$

where m_{H_2O} is the mass of water in hydrogel.

2.6 Determination of Swelling Degree of Hydrogel in Ethanol

The swelling degree of hydrogel (SB) in ethanol at different temperatures was determined by common gravimetric procedure [20].

2.7 Isoconversional Friedman's Method

Isoconversional Friedman's method [21] is based on the following rate equation:

$$\left(\frac{d\alpha}{dt} \right)_{\alpha=const} = Af(\alpha) e^{-\frac{E_{a,\alpha}}{RT}} \quad (4)$$

where T is the temperature, A is the pre-exponential factor, $E_{a,\alpha}$ is the apparent activation energy, $f(\alpha)$ is general expression of the kinetics model and R is the gas constant. The logarithm form of equation (4) leads to:

$$\ln \left(\frac{d\alpha}{dt} \right)_{\alpha=const} = \ln A + \ln f(\alpha) - \frac{E_{a,\alpha}}{RT} \quad (5)$$

For $\alpha = const$, the plot $\ln (d\alpha/dt)_{\alpha=const}$ vs. $(1/T)$, obtained from the conversional curve should be a straight line whose slope allows the evaluation of the apparent activation energy.

2.8 Determining the Kinetic Model of Exchange

Considering the fact that the exchange of absorbed water with ethanol is carried out in solid phase, kinetic model of exchange was determined with model-fitting method. According to the model-fitting method [22], kinetic reaction models of solid state are classified into five groups, depending on the reaction mechanism: (1) power law reaction, (2) phase-boundary controlled reaction, (3) reaction order, (4) reaction explained with the Avrami equation and (5) diffusion controlled reactions. The model-fitting method is based on the following. The experimentally determined conversion curve $\alpha_{\text{exp}} = f(t)$ must be transformed into the experimentally normalized conversion curve $\alpha_{\text{exp}} = f(t_N)$, where t_N is the normalized time, which was defined in the equation:

$$t_N = \frac{t}{t_{0.9}} \quad (6)$$

where $t_{0.9}$ is the moment in time in which $\alpha_{\text{exp}} = 0.9$. The kinetic model of the investigated process was determined by analytically comparing the normalized experimental conversion curves with the normalized conversion curves of the model.

As a criterion of deviation between the normalized experimental conversion curves and the normalized conversion curves of the model, residual sum of squares (rss) was used. Kinetic model of the exchange was determined as the one for which residual sum of squares has minimal value. For comparing the normalized experimental conversion curves and the normalized conversion curves of the model as well as for calculation of residual sum of squares programs in MATLAB programming package were written.

3. RESULTS AND DISCUSSION

Fig. 1 shows isothermal conversion curves of exchange of absorbed water in PAA hydrogel with ethanol (dependence of α on the time) measured at different temperatures.

Conversion curves measured at different temperatures show similar dependence α on t . In all conversion curves are observed three distinct shape of α changes with t , i.e. linear, convex and plateau region. In the beginning of the exchange

process, α increases almost linearly with the t . Then, increase of α with t decelerates and then process ends. With increasing temperature the slope of the linear region of the conversion curves also increase while the time required to reach the plateau region shortens, which indicate that the exchange of absorbed water with ethanol is thermally activated process whose rate increase with temperature.

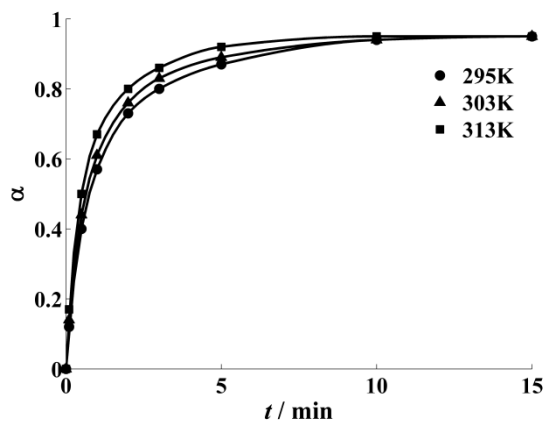


Fig. 1. Isothermal conversion curves of exchange of absorbed water with ethanol measured at different temperatures

Fig. 2 shows the dependence of the changes in swelling degree of hydrogel in ethanol on the exchange time.

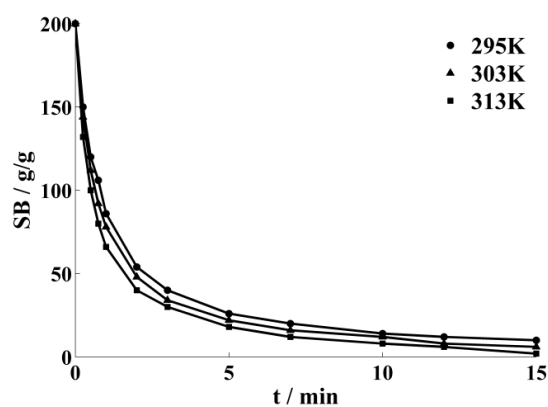


Fig. 2. Change of swelling degree during exchange process

The increase in duration of exchange, at all of the investigated temperatures, leads to concavely decrease in the swelling degree of hydrogel, which indicate that during the exchange hydrogel shrinks i.e. volume phase

transition occurs. At the beginning of the exchange process, actually for $t < 0.5$ min, swelling degree abruptly, almost linearly decrease from 200 g/g to 100 g/g. Subsequently, decrease in the swelling degree with the increase in the duration of exchange slows down until fully shrinking of hydrogel. The increase in temperature of exchange leads to the higher rate of hydrogel shrinking. Based on the results presented in Figs. 1 and 2 it is obvious that swelling degree linearly decrease with the degree of exchange of absorbed water with ethanol. If we propose that within the absorbed water exists different types of water, i.e. bound, interfacial and free water, based on the presented curves of deswelling we can conclude that ethanol interact with all the types of water, but the most intensive and fastest shrinking is at the beginning of the process due to the interaction with the free water.

With the aim to determine the degree kinetic complexity of processes of exchange, by using Friedman's method dependence $E_{a,\alpha}$ on α was determined. The dependence of $E_{a,\alpha}$ on α is shown in Fig. 3.

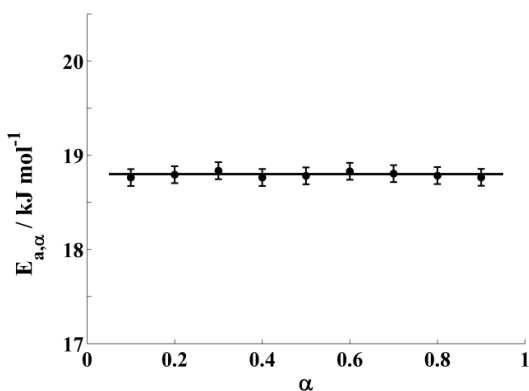


Fig. 3. The dependence of activation energy $E_{a,\alpha}$ on α for exchange of absorbed water with ethanol

As can be seen from Fig. 3, the value of $E_{a,\alpha}$ is independent on α . Therefore, according to the Vyazovkin principle [23] we can conclude that the process of exchange of absorbed water with ethanol is carried out in a single step.

Bearing this in mind, kinetic model of exchange of absorbed water with ethanol was determined by using the model-fitting method. Fig. 4 shows the normalized experimental isothermal curves (dependence of α on t_N) of exchange.

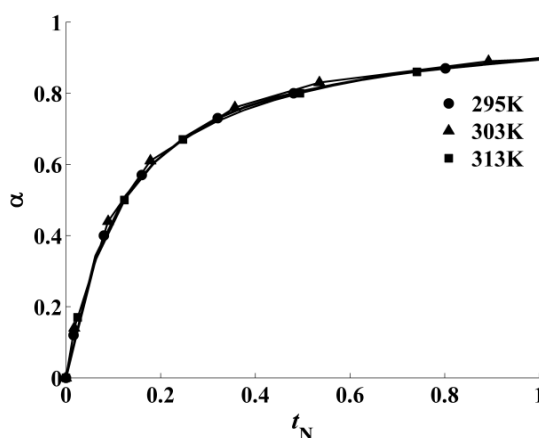


Fig. 4. Dependence of α on normalized time t_N

Normalized isothermal kinetic curves of exchange of absorbed water with ethanol obtained at different temperatures ($T = 295$ K, 303 K, 313 K) are identical which indicates that kinetic model is unique and temperature independent. By applying the model-fitting method it was concluded that kinetics of investigated process can be modeled with kinetic model of Jander three-dimensional (3D) diffusion.

Now, if kinetics of exchange of absorbed water with ethanol can be described with Jander 3D diffusion model, dependence between $[1-(1-\alpha)^{1/3}]^2$ and t should be linear.

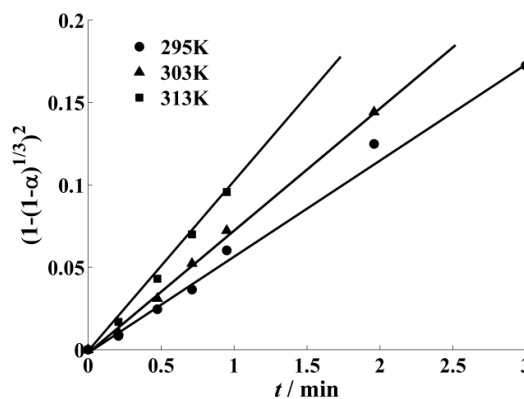


Fig. 5. Dependence of $[1-(1-\alpha)^{1/3}]^2$ on t

Since, isothermal dependence of the relation $[1-(1-\alpha)^{1/3}]^2$ on t is linear for α experimentally measured at three different temperatures, we can conclude that the determined kinetic model (3D diffusion) realistically depicts kinetics of exchange of absorbed water with ethanol.

Table 1. Temperature dependence of k_M

T / K	k_M / min^{-1}	$E_a / \text{kJ mol}^{-1}$	$\ln[A / \text{min}^{-1}]$
295	0.069±0.002	18.8±0.2	4.93±0.07
303	0.086±0.002		
313	0.109±0.003		

In Table 1 above impact of the temperature on the value of the exchange rate constant (k_M) is presented.

Value of the k_M increases with the increase of T which is in accordance with Arrhenius equation. Bearing this in mind, by applying Arrhenius equation we calculated kinetic parameters: activation energy E_a and pre-exponential factor $\ln[A / \text{min}^{-1}]$ (Table 1; columns 3 and 4). Calculated value for E_a is in good agreement with the value obtained using the isoconversional method.

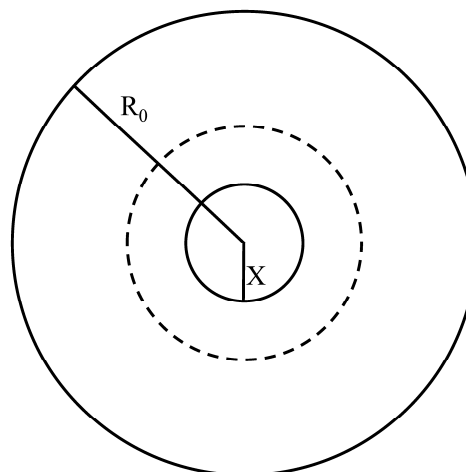
Determined kinetic model and calculated values of kinetic parameters allows us to presume the mechanism of exchange of absorbed water with ethanol in PAA hydrogel. Assumptions on which the presumed mechanism is based are presented below:

- 1) Absorbed water in hydrogel exists in a form of N interconnected spherical pores whose radius R_0 is defined by radius of mesh size of xerogel.
- 2) The rate of diffusion of ethanol to the hydrogel is high.
- 3) The rate of exchange of absorbed water with ethanol is high due to miscibility between water and ethanol.
- 4) Rate of diffusion of exchanged water into ethanol solution is high.
- 5) Exchanged ethanol molecules at time t form the cluster with radius X inside water spherical clusters.
- 6) Growth rate of ethanol spherical clusters is directly proportional to the coefficient of the rate of ethanol diffusion through absorbed water k^* and inversely proportional to its own radius X .

$$\frac{dX}{dt} = \frac{k^*}{X} \quad (7)$$

- 7) Inside each spherical pore, the volume of unexchanged water (V_n) is defined with expression

$$V_n = \frac{4\pi}{3} (R_0 - X)^3 \quad (8)$$

**Fig. 6. Proposed model for the mechanism of exchange of absorbed water with ethanol**

- 8) If we assume that at time t degree of exchange is α , then the following relation for V_n applies

$$V_n = \frac{4\pi}{3} R_0^3 (1 - \alpha)^3 \quad (9)$$

Combination of equations (8) and (9) gives expression (10)

$$X = R_0 \left(1 - (1 - \alpha)^{\frac{1}{3}} \right) \quad (10)$$

- 9) Since,

$$X^2 = 2k^*t \quad (11)$$

the expression which gives a mathematical description of kinetics of exchange of absorbed water with ethanol is obtained in the following way

$$\left(1 - (1 - \alpha)^{\frac{1}{3}} \right)^2 = \frac{2k^*t}{R_0^2} = k_M t \quad (12)$$

In equation (12) k_M is defined as

$$k_M = \frac{2k^*}{R_0^2} \quad (13)$$

Thus, kinetics of exchange of absorbed water with ethanol in PAA hydrogel is limited by the value of the coefficient rate of ethanol diffusion through absorbed water layer [24].

In order to better understand mechanism and kinetics of exchange of absorbed water with ethanol, the thermodynamic parameters of activated complex formation: change of enthalpy (ΔH^*), change of entropy (ΔS^*) and change of free energy (ΔG^*) were calculated from transition-state theory using Eyring equation [25]. Eyring equation in its thermodynamic version becomes:

$$k_M = \frac{k_B T}{h} e^{\frac{\Delta S^*}{R}} e^{-\frac{\Delta H^*}{RT}} \quad (14)$$

where k_M is rate constant, k_B represents Boltzmann constant and h represents Planck constant.

On taking a logarithm from both side of equation (14) one obtains

$$\ln\left(\frac{k_M}{T}\right) = \ln\left(\frac{k_B}{h}\right) + \frac{\Delta S^*}{R} - \frac{\Delta H^*}{RT} \quad (15)$$

By plotting $\ln(k_M/T)$ vs. $1/T$, a linear relationship is obtained and one can determine ΔH^* from the slope which is equal to the value of $(\Delta H^*/R)$ and ΔS^* is determined from the y-intercept $(\ln(k_B/h) + \Delta S^*/R)$.

The change of Gibbs free energy of activation can be calculated by

$$\Delta G^* = \Delta H^* - T\Delta S^* \quad (16)$$

The positive ΔH^* value indicate that process of exchange of absorbed water with ethanol was endothermic in nature, which is in agreement with the experimentally data that the rate of exchange increase with temperature. Positive ΔG^* value confirms the non-spontaneous nature of the exchange process and the need of thermally activation. The negative value of ΔS^* implies that the entropy of the reactant (S^0) is higher than the entropy of the activated complex (S). Therefore, it can be suggested that the degree of arrangement of activated complex is

higher than the degree of arrangement of the initial reagents, which is experimentally approved by the shrinking of hydrogel during exchange. The significantly higher value of the $T\Delta S^*$ than the ΔH^* clearly point out on the dominant effect of the entropic factor on the kinetics of exchange.

Suetoh et al. [26], Ebara et al. [27] and Otake et al. [28] assumed that changing of the structure of water in absorbed phase is the result of interaction between water absorbed on hydrophobic groups of polymer chains and ethanol molecules. The change in the structure of the absorbed water is result of the stronger water-ethanol interaction then the interaction between water and hydrophilic groups of polymer chains. Grinberg et al. [29] considered three different types of interaction between hydrogel and ethanol: (1) polar dehydration (2) apolar dehydration (3) strong interaction between polymer chains. Grinberg [29], Hvidt [30] and Southall [31] calculated the values of enthalpy for rearrangements per PNiPAM monomer unit 1) of the water cages around the hydrophobic parts of polymer chains into the bulk water ($\Delta H_c = 39.9 \text{ kJ mol}^{-1}$) 2) of the bound water around the hydrophilic group into the bulk water ($\Delta H_{hg} = 12-22 \text{ kJ mol}^{-1}$) 3) for the hydrophobic association of the PNiPAM chains or the intermolecular interactions between the PNiPAM residues ($\Delta H_{as} = 49.8 - 22.6 \text{ kJ mol}^{-1}$).

The value of enthalpy of activation obtained in our research ($\Delta H^* = 16.5 \text{ kJ mol}^{-1}$) is in good agreement with the value of the enthalpy of rearrangements of bound water around hydrophilic groups into the bulk water. This indicates that formation of active complex for the exchange process goes through the rearrangements of bound water around polymers hydrophilic groups into the bulk water. Thus, process of exchange of absorbed water with ethanol starts with ethanol diffusion into absorbed water phase. Diffusion leads to increase of ethanol concentration in absorbed water phase. Since the energy of interaction between ethanol and water is higher than the energy of interaction between absorbed water and polymer chains of hydrogel rearrangement of absorbed water phase (transition of the absorbed water into ethanol solutions) occurs. Exchange of water with ethanol facilitates interaction between polymer chains and leads to hydrogel shrinking. Calculated values of the ΔH^* , ΔS^* and ΔG^* are given in Table 2.

Table 2. Isothermal values of the ΔH^* , ΔS^* and ΔG^*

T / K	$\Delta H^* / \text{kJ mol}^{-1}$	$\Delta S^* / \text{J K}^{-1}\text{mol}^{-1}$	$\Delta G^* / \text{kJ mol}^{-1}$
295	16.5	-177	68.73
303			70.15
313			71.92

4. CONCLUSION

The exchange of absorbed water in PAA hydrogel with ethanol is kinetically elementary process. The rate determining step of the exchange process is 3D diffusion of ethanol through the absorbed water in hydrogel. Kinetics of exchange of absorbed water with ethanol can be mathematically described with the kinetic model of 3D Jander. The values of the kinetic parameters and thermodynamics parameters of active complex formation for the exchange process were calculated. A novel model mechanism of the kinetics of exchange of absorbed water with ethanol in hydrogel was suggested. It was found that the value of ΔH^* corresponds to the energy of rearrangements of bound water around hydrophilic groups of polymeric network.

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COMPETING INTERESTS

Authors have declared that no competing interests exist.

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