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Process of adsorption–desorption for a series of chemically similar solvents trough ethylene vinyl acetate polymer. Modelling and experiment

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Abstract

The process of absorption and desorption of some alcohols through polymers materials are studied here in order to evaluate the capacity for absorption for these liquids, and to determine the effect of vinyl acetate incorporated in the polymer. The polymer exhibits low capacity and high diffusivity depending on two parameters: size of sorbed penetrant, and vinyl acetate percent. A mathematical model, based on a numerical method with finite differences, is built in order to describe the process. The model can lead to the kinetic of transfer of alcohols, in good agreement with experiments for either absorption or desorption of alcohols. The profiles of concentration as well as the kinetics are evaluated.

Keywords: Diffusion; Polymer; VAc content

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1. Introduction

The incompatibility of polymers is an awards property for some industrial applications more often than not. As shown in various applications [1,2], the process of matter transfer may be sometimes very complex. For instance when a packaging made of ethylene vinyl acetate EVAc is in contact with a liquid, e.g. food, blood, physiological serum, or solvent like alcohol, some matter transfer may take place leading to the disadvantage of both materials. The liquid may enter the polymer, and additives may leave the polymer with the following drawbacks: a pollution of the liquid, and change in properties of the polymers. Both these transfers are controlled by diffusion [1,3]. These EVAc copolymers are available with compositions ranging from 14 to 40 wt% of vinyl acetate (VAc%). The various usage's of these materials are reported in earlier studies [4,5].

The mathematical treatment of diffusion leading to second Fick's law was made by keeping the dimensions of the solid constant [1,6,7] whatever may be the amount of substance transferred into or out of the solid. With a change in dimension, the second Fick's law is not valid, a general theory taking into account this effect, e.g. subsequent change in dimensions of the solid was established [8]. A numerical model capable of resolving the problem of substance transferred for the following stage of absorption and desorption in succession and with the profiles of concentration of the diffusing substance developed through the sphere [9] was established. The particular case of an infinite coefficient of surface matter transfer, with a constant concentration of the substance on the surface, is studied here.

The main purpose of the present paper was to study the behavior of ethylene-vinyl acetate (EVAc) copolymers chosen as polymers towards alcohol, and especially to precisely determine the various parameters that intervene in the process: the capacity for absorption of the alcohols by EVAc materials towards alcohols, the role of VAc content in the absorption (or desorption), and the diffusivity of alcohols by considering the kinetics of absorption and the profiles of concentration of these liquids developed through the polymer. The selected liquids are a series of chemically similar penetrants, they are alcohols: methanol, ethanol, propanol-1, and butanol-1.

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2. Mathematical treatment

The general expression of the radial diffusion through a sphere with a change in dimension is represented by Eqs. (1) and (2) as noted in the previous paper [8]:

$$\frac{\partial r}{\partial u} = \frac{u^2}{r^2}\left[1 - \frac{C(u,t)}{d}\right]^{-1} \tag{1}$$

$$\frac{\partial}{\partial t}\left[C\left(1-\frac{C}{d}\right)^{-1}\right] = \frac{1}{u^2}\frac{\partial}{\partial u}\left[\frac{u^4}{u^2}D\left(1-\frac{C}{d}\right)\frac{\partial C}{\partial u}\right]. \tag{2}$$

When the volume of liquid transferred is so small that it can be neglected, the radial abscissa and Eq. (2) reduces to the following equation, which is the second Fick's equation for radial diffusion in a sphere [8]

$$\frac{\partial C}{\partial t} = \frac{1}{r^2}\frac{\partial}{\partial r}\left[Dr^2\frac{\partial C}{\partial r}\right], \tag{3}$$

where D is the diffusivity, C the concentration of the liquid and R the radius of the spherical surface considered.

A solution of Eq. (3) is obtained when the diffusivity is constant [1,6,7] and when the surface concentration of the material reaches its final value as soon as the bead is immersed in the liquid

$$\frac{M_t}{M_\infty} = 1 - \frac{6}{\pi^2}\sum_{n=1}^{\infty}\frac{1}{n^2}\exp\left(-\frac{n^2\pi^2}{R^2}Dt\right), \tag{4a}$$

where M_t and M_∞ are the amount of matter transferred at time t and at equilibrium, n is an integer, and R is the radius of the spherical bead.

Another solution is obtained in terms of error functions [1,6,7]:

$$\frac{M_t}{M_\infty} = \frac{6\sqrt{Dt}}{R}\left[\frac{1}{\sqrt{\pi}} + 2\sum_{n=1}^{\infty}\mathrm{i\,erfc}\frac{nR}{2\sqrt{Dt}}\right] - \frac{3Dt}{R^2}. \tag{4b}$$

For short times, Eq. (4b) can be reduced to the following relation

$$\frac{M_t}{M_\infty} = \frac{6}{R}\left[\frac{Dt}{\pi}\right]^{0.5} \quad \text{when } \frac{M_t}{M_\infty} < 0.2\text{–}0.3 \tag{5}$$

and then the diffusivity is calculated from the slope of the straight line (Fig. 4) obtained by plotting the amount of liquid absorbed as a function of the square root of time [5].

The volume expansion as defined in the same paper [8] is:

$$\frac{V(u,t)}{V(u,0)} = \frac{\Delta(r^3)}{\Delta(u^3)} = \left[1-\frac{C(u,t)}{d}\right]^{-1}. \tag{6}$$

3. Numerical treatment

A numerical model has been built and tested for the problem with radial diffusion of substance and constant concentration on the surface, as well as change in dimension [8]. Only main results with equations are thus given.

The sphere free of liquid is divided into N spherical membranes of constant thickness Δu, and the radial abscissa of each spherical surface u is associated with the integer j

$$u = j\frac{R}{N} \text{ with } 0 \le j \le N,$$

within the sphere, with $1 \le j \le N-1$.

The new amount of liquid evaluated in a spherical membrane during the elapse of time Δt, is drawn from Eq. (7)

$$MN_j = V_j C_{j+4\pi}(G_{j+0.5} - G_{j-0.5})\Delta t, \tag{7}$$

upon putting the function G

$$G_{j+0.5} = r_{j+0.5}^2 D_{j+0.5}\frac{C_{j+1}-C_j}{r_{j+1}-r_j}, \tag{8}$$

and the new concentration at time $t+\Delta t$ is:

$$CN_j = MN_j\left[4\pi\left(\frac{R}{N}\right)^3 + \left(j^2+\frac{1}{12}\right)\frac{MN_j}{d}\right]^{-1}. \tag{9}$$

Center of the sphere, with $j = 0$. The new amount of liquid after elapse of time Δt is

$$MN_0 = V_0 C_{0+4\pi} G_0 \Delta t, \tag{10}$$

and the new concentration is:

$$CN_0 = MN_0\left[\frac{4\pi}{3}\left(\frac{R}{2N}\right)^3 + \frac{MN_0}{d}\right]^{-1}. \tag{11}$$

Surface of the sphere with $j = N$. The constant concentration of diffusing substance is:

$$C_{\mathrm{eq}} = C_N \quad \text{stage of absorption} \tag{12a}$$

$$C_N = 0 \quad \text{stage of desorption.} \tag{12b}$$

Amount of liquid located in the sphere. The amount of diffusing substance located in the sphere at time t is expressed in the terms of the concentration of the substance at this time

$$\frac{M_t'}{4\pi}\left(\frac{N}{R}\right)^3 = \frac{C_0}{24}\left(1-\frac{C_0}{d}\right)^{-1} + \sum_{j=1}^{N-1}\times\left(j^2+\frac{1}{12}\right)C_j\left(1-\frac{C_j}{d}\right)^{-1} + \frac{N^3-(N-0.5)^3}{3}\times C_N'\left(1-\frac{C_N'}{d}\right)^{-1}, \tag{13}$$

where the concentration C_N' at position $N-0.25$ can be given by:

$$C'_N = \frac{1}{4}(3C_N + C_{N-1}). \tag{14}$$

4. Experimental

4.1. Apparatuses

Spherical beads of the copolymer ethylene vinyl acetate (EVAc), free from liquid are weighed on a balance with a precision of 10^{-4} g. The radius of the bead is determined by a lens.

4.2. Method used in the absorption–desorption stage of liquid

Two kinds of EVAc beads containing, respectively, low VAc content 14% and high VAc content 28 wt%, were soaked in a series of alcohol in flask at 25 °C with gentle stirring up to saturation. Alcohols are: methanol, ethanol, propanol-1, and butanol-1. The beads were weighed at intervals for determining the kinetics of absorption and desorption. The saturated beads were immersed in a strongly stirred medium of infinite volume with a very high value of the coefficient of mass transfer at the surface corresponding to concentration equal to zero.

5. Results and discussion

Four points are of interest:

1. Study of the process of matter transfer for EVAc beads with composition in VAc.
2. The kinetics of matter transferred along the two stage of absorption and desorption for EVAc beads containing 14% in VAc, and the role of the size sorbed (molecular weight of alcohols) on the rate of matter transfer especially on the diffusivity.
3. Effect of the viscosity on the alcohol's diffusivity.
4. The profiles of concentration of liquid penetrant within EVAc bead.

5.1. Processes of matter transfer for EVAc beads with composition

Beads made of EVAc with various compositions are tested (Table 1) for absorption and desorption. Alcohol enters the polymer regularly, causing a subsequent swelling of the bead depending on the VAc incorporated in the EVAc.

Remarks. No solubility for EVAc bead is observed.

Table 1
Characteristics of pure beads of EVAc at 25 °C

Vac%	14	28
D (cm^2/s) absorption (× 10^7)	1.0	3.0
D (cm^2/s) desorption (× 10^7)	1.05	3.075
Expansion volumic factor	1.01	1.08
M_∞ (%) absorption	4	24.4
M_∞ (%) desorption	4	24.4

1. The amount of alcohol absorbed at equilibrium depends largely on the VAc content of the polymer as shown in Fig. 1 and Table 1.
2. Moreover in the same Fig. 1, straight lines are obtained by plotting the amount of alcohol absorbed as a function of (time)$^{1/2}$, the process of absorption–desorption can then be described by transient diffusion.
3. The diffusivity obtained from the slope of the line in Fig. 1 and from the amount of alcohol absorbed at equilibrium by using Eq. (5) depends on the VAc content in the polymer.
4. Equilibrium is quickly reached in the case of methanol which presents a smaller size Fig. 2.
5. A subsequent swelling is observed with bead containing 28% in VAc. The values of volume expansion are reported in Table 1.

As EVAc bead with a lower VAc 14% content does not present any change in dimension, it was selected for the following study.

5.2. Process of mass transfer during the two stage of absorption and desorption

The kinetics of absorption and desorption of methanol, ethanol, propanol-1, and butanol-1 by EVAc bead with 14% content are determined experimentally and by calculation using the same model, the curves obtained are shown in Fig. 3, and the data summarized in Table 2.

The following conclusions can be drawn

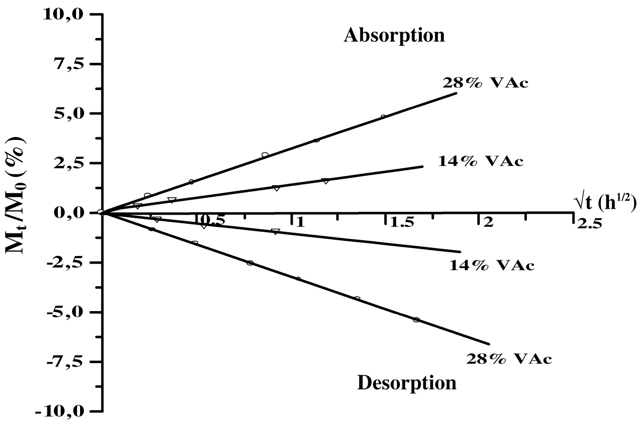

Fig. 1. Variation of the amount of alcohol transferred in absorption and desorption stages by two EVAc bead 28 and 14% versus square root of time (M_0 is the weight of the empty bead).

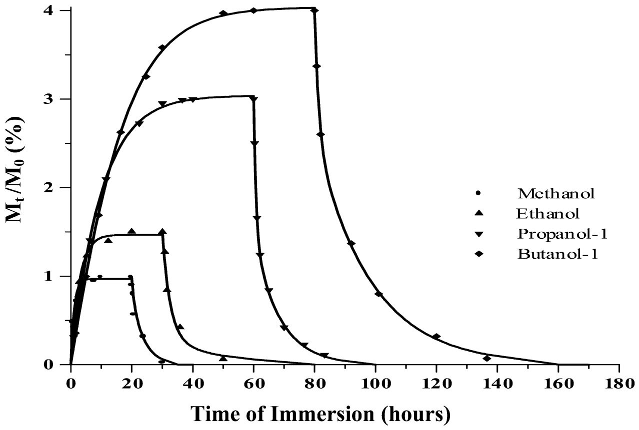

Fig. 2. Kinetics of absorption and desorption of methanol, ethanol, propanol-1, and butanol-1 by EVAc bead 14% (M_0 is the weight of the empty bead).

1. The process of absorption and desorption can be described by transient diffusion, as proved by the linear relationship between the amount of matter transferred and (time)$^{1/2}$ Fig. 4.
2. The values obtained for the diffusivity for absorption and desorption are successfully tested by comparing the experimental results with the theoretical kinetics calculated using the series known in Eq. (4a) obtained by integrating Eq. (3). From this result, the process of matter transfer is shown to be controlled by transient diffusion, and the accuracy of the diffusivities can be appreciated.
3. It is necessary to plot the same experimental results versus the square root of time in order to evaluate the alcohols diffusivities. Fig. 4 shows clearly the different degrees of diffusivities because an oblique tangent at the origin obtained mainly at the beginning of the process, this fact is associated with the vertical tangent at the beginning of the process when the abscissa is time (see Fig. 3). As shown in Fig. 4 the diffusivities of alcohols, deduced from the slope of the line, increases while the size of sorbent penetrant decreases.

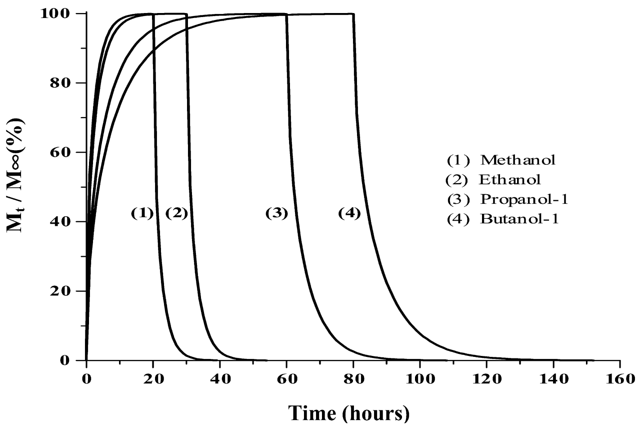

Fig. 3. Kinetics of absorption–desorption of methanol, ethanol, propanol-1, and butanol-1 by EVAC bead 14% (M_∞ is the amount of alcohols tranferred at equilibrium).

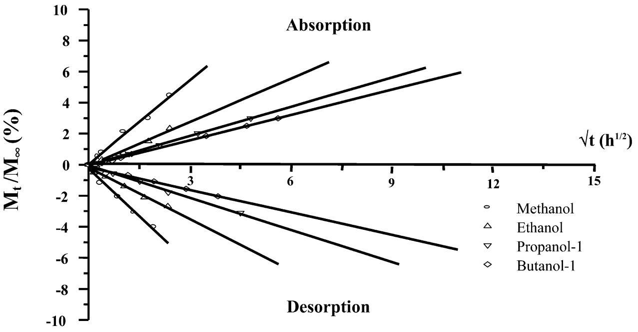

Fig. 4. Determination of diffusivity of alcohols during absorption and desorption stages.

4. For all cases equilibrium is reached, the value of relative volume expansion close to 1 meaning that the volume of liquid absorbed is very low then the swelling is not significant especially for twice alcohols: methanol and ethanol. In this case the kinetics calculated either with the numerical model or the well known solution of the Fick's law for radial diffusion are the same (cf. Eqs. (4a) and (4b), the mathematical treatment is then feasible as the change in dimensions is lower, so the analytical solution and numerical model lead to the same results as described in previous papers [10], however, the value of β found for butanol-1 is near the theoretical limit (1.01) so, it is necessary to use the numerical model elaborated by the Professor Bouzon.
5. The results obtained in point 4 (immediate above) hold either for absorption and desorption. In the case of low absorbed diffusing substance and if the initial concentration of desorption is also uniform, the kinetics of absorption and desorption are the same.
6. The kinetics for absorption decreases with the increasing of the size of alcohols, i.e. the molecular weight, the higher the weight of alcohol (butanol-1), the slower is the kinetic of substance absorbed (Fig. 3). It seems that the successive addition of methylene group $-CH_2-$ on the backbone of methanol CH_3OH does not cause the same effect on the capacity for absorption for the molecule resultant (ethanol, or propanol-1, or butanol-1). The ratio between the absorption capacities of alcohols and methanol are: 1.5 for ethanol/methanol, 3 for propanol-1/methanol, and 4 for butanol-1/methanol. This effect may be correlated to the geometry of the molecules, the butanol-1 is the longest molecule, so it has a tendency to curve giving more free volume in it in the beads.

5.3. Effect of the viscosity on the alcohol's diffusivity

A plot of log D versus viscosity shown in Fig. 5 display a very systematic trend in order of magnitude in coefficient diffusion values so that smaller molecules diffuse more than larger. We note a decrease in the same series of alcohols from butanol-1 to methanol.

Table 2
Characteristic parameters of the diffusional phenomenon

Solvents	Methanol	Ethanol	Propanol	Butanol-1
D (cm^2/s) absorption ($\times 10^7$)	3.5	3.0	1.5	1.0
D (cm^2/s) desorption ($\times 10^7$)	3.45	3.05	1.35	1.0
M_∞ (%) absorption	0.13	0.22	0.36	0.48
M_∞ (%) desorption	0.13	0.22	0.36	0.48
h (cm/s)	Very high	Very high	Very high	Very high
Expansion volumic factor	1.005	1.006	1.007	1.01
Viscosity (P)	0.544	1.074	1.945	2.544

M_∞ is expressed in percent of the initial weight of the empty bead.

5.4. Profiles of concentration of the substance absorbed

The concentration at time t, C_t, is expressed as a fraction of the maximum value of this concentration attained when the solid is saturated with the liquid C_∞. Various profiles are drawn for various values of time of immersion of each alcohol in Fig. 6 for absorption, and in Fig. 7 for desorption. Theses figures allow to evaluate and compare the rate of penetration for the liquids through the EVAc bead at the same moment and at the same position.

The following facts deserve a mention:

1. The profiles did not show an increase in the radius of the bead, the relative volume expansion is in fact close to 1.
2. Because of the very high value of the coefficient of mass transfer on the surface (h), the concentration of the diffusing substance on the solid surface reaches the value at equilibrium as soon as the process starts. In all cases we have found a very high value of coefficient mass transfer (the ratio $hR/D > 100$) as noted in Ref. [11]. This value may be due to the following parameters: experimental conditions where the polymers beads are submitted under an infinite stirred medium of infinite volume of air, and the choice of alcohols which are volatiles liquids (in vapor phase).
3. With the time selected for the stage of absorption rather low 10 h, only the methanol reaches equilibrium, the other alcohols diffuse successively respecting their diffusivities: ethanol, then propanol-1, then butanol-1. This sequence is confirmed at the beginning of the stage of absorption. The same phenomenon is observed for desorption. This effect appears clearly if we choose a long time for the stage of absorption, for instance after 20 h, the beads are completely saturated with methanol and ethanol, e.g. equilibrium is entirely reached, when for propanol-1 and butanol-1 the rate of absorption is, respectively, around 70 and 90% as shown in the kinetics Fig. 3 and in the profile of concentration Fig. 6.

5.5. Interpretation of the phenomenon

The curves obtained represent a preference for sorbed penetrant with a large molecule butanol-1 or propanol-1 than a smaller molecule ethanol or methanol such that magnitude of sorption increases continuously while diffusivity decreases. Then radical R of alcohols play an important role on the capacity for absorption with the following statement: higher is radical R of alcohol, higher is amount of substance transferred through EVAc beads, and smaller is the diffusivity of the corresponding alcohol. In fact, the sorption and diffusion process in the nonporous compounds likes EVAc materials, generally show a greater dependence on the size and shape on the penetrant molecule. The magnitude of sorption increases with

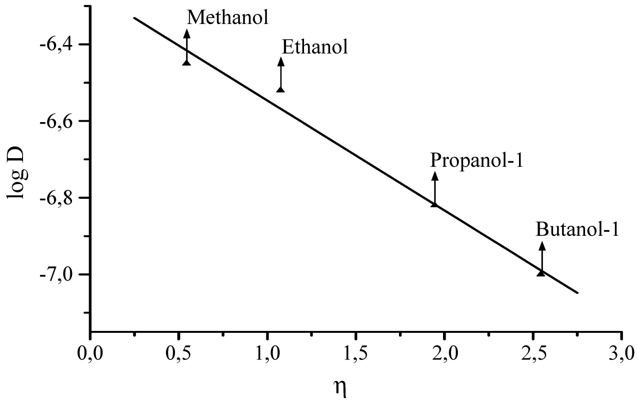

Fig. 5. Diffusivities of alcohols in EVAc beads 14% as a function of their viscosities.

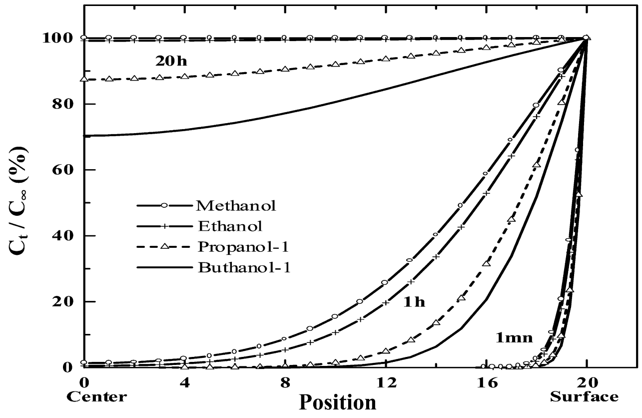

Fig. 6. Profiles of concentration of methanol, ethanol, propanol-1, and butanol-1 through the EVAc bead 14% during absorption at various times.

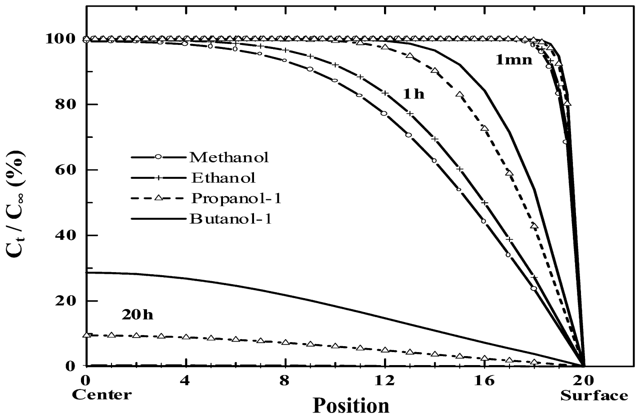

Fig. 7. Profiles of concentration of methanol, ethanol, propanol-1, and butanol-1 through the EVAc bead 14% during desorption at various times.

increasing penetrant size as expected from various polymer solutions, the larger molecules being sorbed more than the smaller [12]. The authors attribute that to the distribution of excess volume which provides fewer sorption sites for small molecules than for large. This interpretation is based on the physicochemical nature of the components, especially on the penetrant size and shape, an increase in the size (e.g. average diameter, molar volume) of a penetrant in a series of a chemically similar penetrants generally leads to an increase in sorption and a decrease in diffusion coefficient [12].

Another factor intervene: the viscosity of liquids: as the viscosity is proportional to the molecular weight, the sorbent penetrant with a larger molecule, respectively, high viscosity must diffuse more slowly than smaller molecule (low viscosity); the sequence found in the diffusivities values is then well justified.

6. Conclusion

It is often necessary to know the behavior of a material, with respect to organic solvents, its compatibility in order to adapt it for a given use. Then it becomes obviously to control the transfer of liquid in many fields: pharmacy, medicine, or environmental. As shown in this paper, some parameters are determining for the process of mass transfer of alcohols within EVAc polymer beads: VAc content, molecular weight of sorbed penetrant, and viscosity of alcohols. The VAc content has been shown to play an important role in the absorption (or desorption) of the liquid: the diffusivity and precisely the capacity for absorption of the liquid varies with the Vac content, and with viscosity of liquids.

The characteristic of nonsolubility and nonswelling of the material EVAc with low VAc content 14% towards the alcohols gives to this material a choice place in various applications.

A mathematical model based on a numerical method with finite differences is successfully tested for describing the process for absorption and desorption. This model led to kinetics of matter transfer in good agreement with experimental.

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