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Modeling of cation diffusion in bifunctional polymers based on *cis*-tetraphenylcalix[4]resorcinarene

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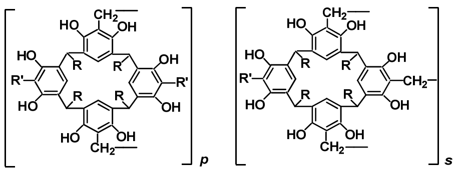
ABSTRACT

In this study, we report that interaction of the network functional polymers based on *cis*-tetraphenylcalix[4]resorcinarene with aqueous solutions of electrolytes is controlled by diffusion of ions in a polymeric phase. The nanoreactor effect consisting in sufficiently high rate increase of a cation diffusion flux in bifunctional polymers containing sulfonic acid and phenol ionogenic groups has been found. For steady and non-steady states the solutions of the fundamental differential equation of cation diffusion in bifunctional polymers by means of the spherical layer model are obtained for a variety of initial and boundary conditions with constant diffusion coefficient. The proposed mathematical model explains the nanoreactor effect in bifunctional polymers.

1. Introduction

The synthesis of *cis*-tetraphenylcalix[4]resorcinarene [1] is of great importance for chemistry of novel functional materials [2]. Due to it's molecular structure (great hydrophobic cavity and the upper hydrophilic rim including eight hydroxylic groups) *cis*-tetraphenylcalix[4]resorcinarene accounts for unique physical and chemical properties. For realizing its properties *cis*-tetraphenylcalix[4]resorcinarene was immobilized into the phase of network polymers. New network functional polymers were synthesized by immobilization of calix[4]arenes on cross-linked polystyrene [3] and by catalytic resol polycondensation of *cis*-tetraphenylcalix[4]resorcinarene derivatives with formaldehyde [4-7]. It was shown that immobilized *cis*-tetraphenylcalix[4]resorcinarenes are nanoreactors for catalytic hydrogenation processes [8], solid polyelectrolytes [9], cation exchangers [4,10,11] and biomemetics, the latter making it possible to consider the processes occurring in biological polymer systems [12,13] at the molecular level. The structure of an elementary unit (Figure 1) of network polymers received by polycondensation of *cis*-tetraphenylcalix[4]resorcinarene with formaldehyde is given in [6].



Polymer 1: R=Ph, R'=H;
Polymer 2: R=Ph-SO_3H, R'=H.

Figure 1. An elementary unit of network polymers based on immobilized *cis*-tetraphenylcalix[4]resorcinarene.

As was previously reported in [5], monofunctional polymer **1**, includes only weakly acidic phenol -OH groups. Bifunctional polymer **2** contains strongly acidic -SO_3H groups which dissociate with the formation of free protons over a wide pH range (0-14), and weakly acidic phenol OH groups. The thermodynamics of ion exchange in polymers **1** and **2** based on *cis*-tetraphenylcalix[4]resorcinarene was investigated in [14,15]. The purpose of the present work is to determine the limiting stage of ion exchange kinetics and to give a mathematical description of cation flux in network polymers **1** and **2** based on *cis*-tetraphenylcalix[4]resorcinarene.

2. Experimental

2.1. Synthesis

Polymer **1** was produced by resol polycondensation of *cis*-tetraphenylcalix[4]resorcinarene with formaldehyde as spherical granules of an adjustable size [4,5]. Polymer **2** was produced by sulfonatation of polymer **1** according to the procedure [7]. The total dynamic ion-exchange capacities (in equiv. per 1 kg of the polymer in the H form dried at 105 °C of the polymers) were 3.90 and 5.65, respectively. The content of acidic -SO_3H groups in polymer **2** was 2.25 equiv. per 1 kg of the dry H form.

2.2. Kinetic studies

For kinetic studies, the selection of spherical granules and the determination of their sizes were performed using the IMTs 100×50, A microscope. Polymer granule size distribution corresponded to a normal (Gaussian) distribution. The particle radius calculated as an arithmetic average of the size of 1000

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spherical granules was $(0.96\pm0.50)\cdot10^{-4}$ m for polymer **1** and $(1.02\pm0.53)\cdot10^{-4}$ m for polymer **2**.

The kinetics of ion exchange was studied by the dynamic thin-layer method [16] at 298 K by sorption from an infinite volume of electrolyte solutions with concentrations of 0.01, 0.03, 0.05, and 0.1 mol/dm^3.

2.3. Calculation details

Molecular structure of the repeating unit of polymer **2** was optimized in terms of enthalpy of formation by the semiempirical PM6 method within the MOPAC 2009 program on Intel (R) Core(TM)2 Duo T7300 processor.

3. Results and discussion

3.1. Kinetics of ion exchange in polymers 1 and 2 based on cis–tetraphenylcalix[4]resorcinarene

The ion exchange process (I) takes place in monofunctional polymer **1**:

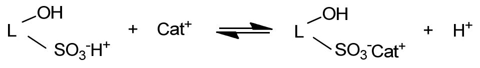
$$\text{L-OH} + \text{Cat}^+ + \text{OH}^- \rightleftharpoons \text{L-O}^-\,\text{Cat}^+ + \text{H}_2\text{O} \qquad \text{(I)}$$

where L - a fragment of elementary unit of polymer based on *cis*-tetraphenylcalix[4]resorcinarene; Cat$^+$–Li$^+$, Na$^+$, Ag$^+$, N(CH$_3$)$_4^+$.

The following ion exchange processes take place in bifunctional polymer **2**: with participation of phenol OH groups

$$\text{L-OH} + \text{Cat}^+ + \text{OH}^- \rightleftharpoons \text{L-O}^-\,\text{Cat}^+ + \text{H}_2\text{O} \qquad \text{(I)}$$

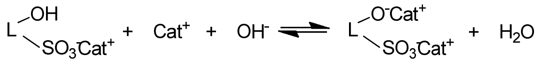
with participation of sulfonic acid groups



$$\text{L}\!\begin{smallmatrix}\text{OH}\\ \text{SO}_3^-\text{H}^+\end{smallmatrix} + \text{Cat}^+ \rightleftharpoons \text{L}\!\begin{smallmatrix}\text{OH}\\ \text{SO}_3^-\text{Cat}^+\end{smallmatrix} + \text{H}^+$$

(II)

with participation both sulfonic acid and phenol OH groups



$$\text{L}\!\begin{smallmatrix}\text{OH}\\ \text{SO}_3^-\text{Cat}^+\end{smallmatrix} + \text{Cat}^+ + \text{OH}^- \rightleftharpoons \text{L}\!\begin{smallmatrix}\text{O}^-\text{Cat}^+\\ \text{SO}_3^-\text{Cat}^+\end{smallmatrix} + \text{H}_2\text{O}$$

(III)

In bifunctional polymer **2** it is possible to obtain phenolate L–O$^-$Cat$^+$ as a result of process (I) and as a sum of processes (II) and (III). To choose the optimal method it is necessary to compare the rates and mechanisms of processes (I)-(III).

The experimental kinetic dependences of the transformation degree (F) on time ($t^{1/2}$) for processes (I)-(III) are resulted in Figure 2. The transformation degree was calculated as $F=M_t/M_\infty$, where M_t - the amount of cations sorbed at time t; M_∞ - equilibrium ion exchange capacity. As seen from Figure 2, ion exchange H$^+$–Cat$^+$ with participation of sulonic acid groups of polymer **2** has the highest rate (Figure 2, (II)), a sorption process of cations Cat$^+$ from alkaline solutions with participation phenol -OH groups of polymer **1** has the lowest rate (Figure 2, (I)).

Rectilinearity of dependences of the transformation degree from $t^{1/2}$ at $F \leq 0.5$ (factors of linear correlation exceed 0.99) and passage of lines through the origin (Figure 2) according to the criteria [19] testify the fact that the interaction of polymers based on *cis*-tetraphenylcalix[4]resorcinarene with aqueous solutions of electrolytes is controlled by diffusion of ions in the polymers. Thus, a “particle-diffusion control” [20] of ion exchange kinetics takes place.

The “particle-diffusion control” of ion exchange kinetics is described [19] by fundamental diffusion equation (1) in the case of constant diffusion coefficient and spherical symmetry [21]

$$\frac{\partial C}{\partial t} = D\left(\frac{\partial^2 C}{\partial r^2} + \frac{2}{r}\frac{\partial C}{\partial r}\right) \qquad (1)$$

Where D – diffusion coefficient of the species; C – current concentration of the species in a polymer; r – radius-vector. Let us consider the solution of equation (1) for processes (I)-(III).

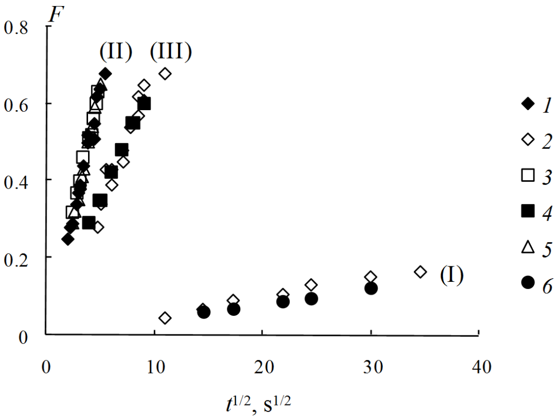


Figure 2. Experimental kinetic dependences of processes (I), (II), (III) of sorption of metal cations by polymers based on *cis*-tetraphenylcalix-[4]resorcinarene from aqueous solutions: *1*–NaCl, *2*–NaOH, *3*–LiCl, *4*–LiOH, *5*–AgNO$_3$, *6*–(CH$_3$)$_4$NOH. (I)– Cat$^+$ sorption from alkaline solutions with participation of phenol OH groups of polymer **1**; (II)– H$^+$–Cat$^+$ ion exchange with participation of sulfonic acid groups of bifunctional polymer 2 in terms of the data [17]; (III)– H$^+$–Cat$^+$ ion exchange with participation both sulfonic acid and phenol OH groups of bifunctional polymer **2** in terms of [18].

3.2. Solution of the diffusion equation for cation exchange process (I) in polymer 1 with participation of phenol OH groups

As was shown [20] the rates of ion exchange processes with participation of weakly acidic ion exchangers are controlled either by interdiffusion of H$^+$ ions and sorbed Cat$^+$ cations or by diffusion of OH$^-$ anions in a polymer. In this case the rate of the process (I) is controlled by diffusion of OH$^-$ anions in a polymer **1**. Equation (2) presented in [20]

$$F = 1 - \left\{\sin\left[\frac{1}{3}\arcsin\left(1 - 12\frac{D_{OH}C_{OH}^0\,t}{C_r\,r_0^2}\right)\right] + \frac{1}{2}\right\}^3 \qquad (2)$$

describes our experimental data on ion-exchange rates in polymer **1** (Figure 2, (I)) in the studied range of concentrations. Here D_{OH} - diffusion coefficient of OH$^-$ anions in polymers, C_{OH}^0 - concentration of OH$^-$ anions on the surface of a spherical particle of a polymer, C_r - total concentration of fixed ionogenic groups (ionized and not ionized hydroxylic groups) in a polymer.

3.3. Solution of the diffusion equation for a cation exchange process (II) in polymer 2 with participation of sulfonic acid groups

The expression [22]

$$\frac{M_t}{M_\infty} = 1 - \frac{6}{\pi^2}\sum_{n=1}^{\infty}\frac{1}{n^2}\exp\left(-D_w\,n^2\pi^2\,t/r_0^2\right) \qquad (3)$$

for the transformation degree of ion exchanger describes the experimental data in all the studied ranges of concentrations for exchange of protons from SO_3H - groups of network polymer **2** by metal cations from solution (Figure 2, (II)). Here, D_w - effective diffusion coefficient in polymer, r_0- average radius of spherical particle of polymer. Values of effective diffusion coefficient of cations in sulfonated polymer based on *cis*-tetraphenylcalix[4]resorcinarene, calculated with probability 0.9 by equation (3), are in the $(1.9 \div 2.1)\cdot 10^{-11}$ m²/s interval.

3.4. Solution of the diffusion equation for a cation exchange process (III) in polymer 2 with participation both sulfonic acid and phenol OH groups

Before the beginning of process (III) bifunctional polymer **2** already contains Cat^+ whose concentration is equal to that of SO_3^- - groups. In process (III) the ion exchange of protons of phenol OH groups by Cat^+ takes place. The rate of process (III) with participation of polymer **2** is controlled by H^+ and Cat^+ interdiffusion in a spherical particle of a polymer.

3.4.1. Effective diffusion coefficient

According to diffusion mechanism of process (III) for constant diffusion coefficient D_H of free protons, the flux equation

$$J_{Cat} = -D_w \, grad \, C_{Cat} \tag{4}$$

is obtained [20]. Here,

$$D_w = \frac{K_a}{C_r + K_a} D_H, \tag{5}$$

at $C_{Cat} \to C_r$ (K_a - dissociation constant of phenol OH groups in a polymer).

Since swelling and hydration values of studied polymer **2** upon conversion (III) remain constant (30 mol H_2O per 1 equiv. of total capacity of polymer), it can be to assumed that the effective diffusion coefficient in polymer D_w in equation (4) is constant. Let us calculate its value. Potentiometric titration of sulfonated calixarenecontaining polymers [6] gives the value $K_a \approx 10^{-5}$ mol/m³. Thus, at $D_H = 10^{-9}$ m²/s [22], $C_r = 1\cdot 10^3$ mol/m³, the effective diffusion coefficient D_w, calculated by equation (5), is equal to 10^{-17} m²/s.

3.4.2. Spherical layer model for a particle of polymer 2

We assume that the spherical particle of polymer **2** should consist of a set of spherical layers. $SO_3^- Cat^+$ groups are located on the outer surface of each spherical layer while phenol OH groups nearest to them are on its inner surface (Figure 3). The surface $r = a$ is maintained at C_1, and $r = b$ at C_2, and the region $a \le r \le b$ is initially at C_0. The diffusion flux of Cat^+ through a spherical layer passes the distance between $SO_3^- Cat^+$ and phenol OH groups (Figure 3).

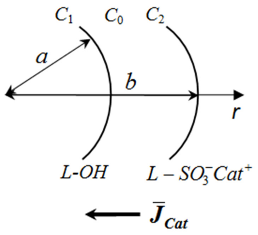


Figure 3. The diffusion flux of Cat^+ through a spherical layer in bifunctional polymer **2**.

3.4.3. Solution of equation (1) for steady state

For steady state equation (1) is transformed into (6)

$$\frac{d}{dr}\left(r^2 \frac{dC}{dr}\right) = 0, \tag{6}$$

in which the general solution is

$$C = B + A/r, \tag{7}$$

where A and B are constants to be determined from the boundary conditions. The surface $r = a$ is kept at a constant concentration C_1, and $r = b$ at a constant concentration C_2, then,

$$C = \frac{aC_1(b-r) + bC_2(r-a)}{r(b-a)}. \tag{8}$$

The total quantity of species which passes through the unit of surface, is

$$q = -\int_0^t D_w \left(\frac{\partial C}{\partial r}\right)_{r=r_0} dt = D_w \frac{ab(C_2 - C_1)t}{(b-a)r_0^2}. \tag{9}$$

The quantity of diffusing species Q_t, which passes through the spherical wall within time t, is given by

$$Q_t = 4\pi r_0^2 q = 4\pi D_w t \frac{ab}{(b-a)}(C_2 - C_1). \tag{10}$$

3.4.4. Solution of equation (1) for non-steady state

For non-steady state the solution of diffusion equation (1) can be obtained by Laplace transforms or a method of separation of variables [21] in case diffusion coefficient is constant. It results in function $C(r, t)$, after its integration [21] the total amount of Cat^+, which accumulates in the spherical layer after time t, is $M_t^{'}$

$$M_t^{'} = \frac{4\pi}{3}(b-a)\left[\left(a^2 + \frac{ab}{2}\right)C_1 + \left(b^2 + \frac{ab}{2}\right)C_2 - (a^2 + ab + b^2)C_0 - \right.$$
$$- \frac{6}{\pi^2}\sum_{n=1}^{\infty}\left\{a^2C_1 - (a^2+b^2)C_0 + b^2C_2 - 2ab\cos n\pi\left(\frac{C_1 + C_2}{2} - C_0\right)\right\}\times$$
$$\left. \times \frac{\exp\{-D_w n^2\pi^2 t/(b-a)^2\}}{n^2}\right]. \tag{11}$$

When $C_0 = 0$, $C_1 = 0$, $C_2 = C_r$

$$M_t^{'} = \frac{4\pi}{3}(b-a)\left[\left(b^2 + \frac{ab}{2}\right)C_r - \frac{6}{\pi^2}\sum_{n=1}^{\infty}\left\{b^2C_r - 2ab\cos n\pi\left(\frac{C_r}{2}\right)\right\}\times \right.$$
$$\left. \times \frac{\exp\{-D_w n^2\pi^2 t/(b-a)^2\}}{n^2}\right], \tag{12}$$

$$M_{\infty}^{'} = C_r \frac{4\pi}{3}\left(b^3 - a^3\right). \tag{13}$$

The transformation degree in time t is

$$F = \frac{M_t^{'}}{M_{\infty}^{'}} = \frac{\left[\left(b^2 + \frac{ab}{2}\right) - \frac{6}{\pi^2}\sum_{n=1}^{\infty}\left\{b^2 - ab\cos n\pi\right\}\frac{\exp\{-D_w n^2\pi^2 t/(b-a)^2\}}{n^2}\right]}{a^2 + ab + b^2}. \tag{14}$$

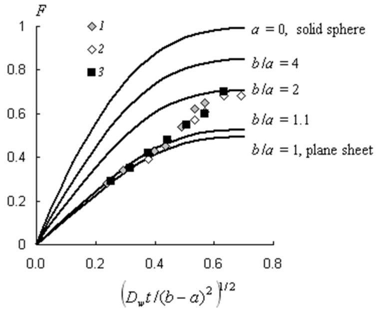


Figure 4. F vs $\left(D_w t/(b-a)^2\right)^{1/2}$. Curves – calculations by equation (14); dots– experimental data: *1* - cation sorption on 0.1 mol/dm³ NaOH solutions; *2* - cation sorption from 0.03 mol/dm³ NaOH solutions; *3* -cation sorption from 0.05 mol/dm³ LiOH solutions by bifunctional polymer **2** (process (III)).

Equation (14) is transformed into equation (2) if $a = 0$; $b = r_0$.

The dependences of the transformation degree from $\left(D_w t/(b-a)^2\right)^{1/2}$ are shown in Figure 4 for different values of b/a. The top curve corresponds to solid sphere ($a = 0$), bottom - to plane sheet ($r >> (b - a)$). In the $0 \leq F \leq 0.5$ range the experimental values correspond to the chosen model at small values of $b - a$. According to equation (14), the rates of process (III) do not depend on the concentration of a solution, and concentration of polymer (at $C_r \neq 0$), probably, neither on the form nor of the size of a spherical particle of polymer. Actually, experimental values $F(t^{1/2})$ for $H^+ - Li^+$ and $H^+ - Na^+$ exchange at various solution concentrations are described by the same functional dependence (Figure 2, (III)).

3.5. Nanoreactor effect

According to equation (4), at constant diffusion coefficient, the diffusion flux depends only on concentration gradient. In monofunctional polymer **1** the value of the concentration gradient is determined by the change in the concentration of a diffusing component at a macroscopic distance from the outer surface of the ion exchanger particle to its center. In bifunctional polymer **2** the cation diffusion flux passes the distance between $SO_3^-Cat^+$ and phenol OH groups (Figure 5), it being equal to, approximately, the size of *cis*-tetraphenyl calix[4]resorcinarene molecule and considerably less than the dimension of the ion exhanger particle. In the repeating unit of polymer **2** the calculated distance is several nanometers. This results in considerable increase in process (III) rate. At the same time the rate of process (III) should be less than that of process (II), which provides for the delivery of cations from a solution to sulfonic acid groups of polymer **2**. Half-transformation periods of time (t at $F = 0.5$), calculated from the experimental data (Figure 2), are equal to ≈16 s for process (II), ≈ 9500 s for process (I), ≈ 50 s for process (III) respectively. Comparing the rates of ion exchange processes with participation of weakly dissociating ionogenic groups for mono- and bifunctional polymers, we find out the nanoreactor effect that consists in hundredfold increase in ion exchange rate. The cup of bifunctional *cis*-tetraphenylcalix[4]resorcin arene, which contains as strongly acidic SO_3H groups and weakly acidic phenol OH groups (Figure 5), immobilized in the network polymer phase acts as nanoreactor.

4. Conclusion

Modeling of cation diffusion in bifunctional polymers based on *cis*–tetraphenylcalix[4]resorcinarene gives the solution for the fundamental differential equation of cation diffusion in bifunctional ion exchangers. The proposed mathematical model explains the nanoreactor effect in bifunctional polymers based on *cis*-tetraphenylcalix[4]resorcinarene. It predicts considerable improvement of the kinetic characteristics of cation exchangers containing weakly dissociating ionogenic groups when strong acidic functional groups are introduced into these cation exchangers. This effect holds good for both bifunctional polymers based on *cis*-tetraphenylcalix[4]resorcinarene and other bifunctional cation exchangers (for example Amberlite IRA-100 type) for producing ion-exchange membranes and selective sorbents. High mobility of protons in the investigated systems substantially affects the activity of catalyst in redox processes with participation of hydrogen.

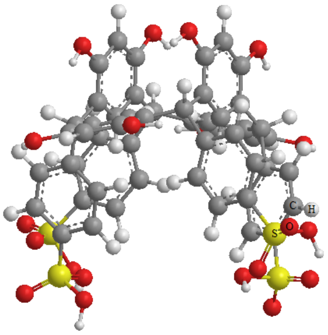


Figure 5. The repeating unit of polymer **2** molecular structure minimized by the semiempirical PM6 method within the MOPAC 2009 program.

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References

[1]. Hogberg, A. G. S. *J. Am. Chem. Soc.* **1980**, *102*, 6046-6050.
[2]. Buchachenko, A. L. *Usp. Khim.* **1999**, *2*, 99-118.
[3]. Alexandratos, S. D.; Natesan, S. *Macromolecules* **2001,** *34*, 206-210.
[4]. Altshuler, H.; Ostapova, E.; Fedyaeva, O.; Sapozhnikova, L.; Altshuler, O. *Macromol. Symp.* **2002,** *181*, 1-5.
[5]. Altshuler, H.; Sapozhnikova, L.; Ostapova, E.; Fedyaeva, O.; Altshuler, O. *Solvent Extr. Ion Exch.* **2002**, *20*, 263-271.
[6]. Altshuler, O.; Sapozhnikova, L.; Altshuler, H. *Polymer Science. Ser. A* **2007,** *49*, 1198-1206.
[7]. Altshuler, H.; Abramova, L.; Altshuler, O. Russian Federation patent, Pat No: 2291171, January 2007.
[8]. Sapozhnikova, L.; Altshuler, O.; Malyshenko, N.; Shkurenko, G.; Ostapova, E.; Tryasunov, B.; Altshuler, H. *Int. J. Hydrogen Energ.* **2011**, *36*, 1259-1263.
[9]. Altshuler, H. N.; Ostapova, E. V.; Evdoshenko, A. A. *Russ. J. Appl. Chem.* **2006**, *79*, 82-84.
[10]. Altshuler, H. N.; Fedyaeva, O. N.; Sapozhnikova, L. A.; Ostapova, E. V. *Vysokomol. Soedin. Ser. B* **2001,** *43*, 755-759.
[11]. Ostapova, E. V.; Altshuler, O. H.; Sapozhnikova, L. A.; Altshuler, H. N. *Russ. J. Phys. Chem. A* **2003**, *77*, 909-913.
[12]. Altshuler, G. N.; Sapozhnikova, L. A.; Abramova, L. P. *Russ. Chem. Bull.* **1998**, *47*, 2146-2148.
[13]. Altshuler, H. N.; Fedyaeva, O. N.; Ostapova, E. V. *Russ. Chem. Bull.* **2000**, *49*, 1468-1470.
[14]. Altshuler, H.; Sapozhnikova, L.; Ostapova, E.; Altshuler, O. *Russ. J. Phys. Chem. A* **2007**, *81*, 1159-1164.
[15]. Altshuler, H. N; Ostapova, E. V.; Sapoznikova, L. A.; Altshuler, O. H. *J. Therm. Anal. Calorim.* **2008**, *92*, 665-669.
[16]. Fedoseeva, O. N.; Cherneva, E. P.; Tunitskii, N. N. *Zh. Fiz Khim.* **1959**, *33*, 936-938.
[17]. Altshuler, H.; Malyshenko, N.; Shkurenko, G. *Russ. J. Appl. Chem.* **2007,** *80*, 1737-1740.
[18]. Altshuler, O. H.; Malyshenko, N. V.; Shkurenko, G. J.; Altshuler, H. N. *Theor. Found. Chem. Eng.* **2009**, *43*, 43-49.
[19]. Helfferich F., Ionenaustauscher, Verlag Chemie, 1959.
[20]. Helfferich, F. *J. Phys. Chem.* **1965,** *69*, 1178-1187.
[21]. Crank J. The Matematics of Diffusion, 2nd edition, Clarendon Press, 1975.
[22]. Boyd, G.; Adamson, A.; Myers, L. *J. Am. Chem. Soc.* **1947,** *69*, 2836-2848.