The concept of gel diffusion in the kinetics of swelling and shrinking of a polystyrene sulfonic acid ion exchanger in the K⁺ form

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The kinetics of swelling and shrinking of polystyrene resins of the sulfonic acid type was investigated. The ion-exchange bead in the K^+ form, equilibrated with a 0.1 M, 0.5 M, 1.0 M or 2 M KCl solution was placed into water and its diameter was measured continuously. In the reverse experiments, the bead, which came into equilibrium with water, was transferred into KCl solutions and the kinetics of grain shrinking was studied analogously. The experimental data were processed by using the theory of "gel diffusion", the parameter of which is the so-called gel diffusion coefficient, similar to the molecular diffusion coefficient. In contrast to previously published works, in which only the first term of the series in the corresponding equation was taken into account, in our work the first ten members of the series were taken into account. It turned out that it is necessary to take into account not only the first member of the series (as was done in previously published works), but also the second member of the series. It also turned out that the values of the obtained gel diffusion coefficient, obtained by this method, quite logically increased somewhat during the process of swelling (for example, in experiments with 1 M KCl from 2.1×10^{-6} to 3.0×10^{-6} cm²/s) and decreased somewhat during the process of shrinking. It was shown that the average values of the diffusion coefficients of the gel make it possible to adequately describe the main part of the kinetic curve. The concept of gel diffusion allows comparing the swelling kinetics of various polyelectrolyte gels in terms of diffusion coefficients, regardless of the particle shape, systematize data for various materials, and comparing their properties with the molecular diffusion of other substances.

It also turned out that in the very final parts (5-10%) of the kinetic curves a sharp decrease in the diffusion coefficient value was observed both in experiments with the swelling and shrinking of grains. It indicates that during the final stages there was a sharp deceleration of the process due to a change in its mechanism.

Keywords: ion exchanger, swelling, swelling kinetics, gel diffusion, diffusion coefficient.

Introduction

One of the key properties of cross-linked polyelectrolytes (including the so-called polyelectrolyte gels, usually weakly cross-linked) and ion exchange resins is the ability to sorb water or other solvent from the external environment (vapor or liquid). The degree of swelling of ion exchangers varies depending on the chemical nature, phase state (liquid or vapor) and the composition of the external environment, its pH value, temperature, etc.

Ion exchange resins occupy a special place among cross-linked polyelectrolytes, as they are produced in the world in hundreds of thousands of tons per year and are widely used in energetics, chemical industry, chemical analysis, sciences, etc. The apparatuses in which ion-exchange processes are carried out vary in volume from miniature analytical columns to multi-ton industrial equipment. Therefore, when creating ion-exchange processes and designing the corresponding apparatus, one must take into ac-

count the fact that ion exchangers can significantly change their volumes. Reference books and monographs on the properties of ion exchange resins and ion exchange processes mainly provide information on the degrees of swelling at equilibrium. The kinetics of swelling and compression of ion exchangers has been studied much less. At the same time, some quite interesting phenomena are observed here. The swelling and shrinking of the same material can proceed at different rates, which results in obtaining not only "traditional" time dependences with a gradual monotonic achievement of equilibrium values, but also of dependences with extrema [1–5]. We also showed [6] that in some cases, different stationary degrees of swelling can be established under the same conditions, depending on the initial state of the ion exchanger from which they are achieved.

The kinetics of swelling of hydrophilic gels based on cross-linked polyelectrolytes and nonionic polymers [7] has been studied much more extensively. A typical and the most studied representative of such gels is polyacrylamide gel cross-linked with N, N-methylenebisacrylamide [8].

When describing the kinetics of swelling (or shrinking) of hydrophilic gels, a formal kinetic equation of the form [9, 10] is used:

$$\frac{M_t}{M_\infty} = kt^n \tag{1}$$

where M_t and M_∞ are the masses of the absorbed (released) substance at time t and after reaching the equilibrium, k and n are coefficients. The swelling mechanism is interpreted as diffusion when the exponent n is close to 0.5, meaning that the relaxation of polymer chains proceeds faster than the diffusion of the substance. When n approaches 1, the mechanism is interpreted as relaxation, meaning the opposite situation.

In order to take both mechanisms into account, the following equation was proposed

$$\frac{M_t}{M_\infty} = k_1 t + k_2 t^{1/2} \tag{2}$$

and other similar kinetic equations [7, 11].

A certain justification for this interpretation can be the solution to the problem of diffusion in a semi-infinite medium with the initial absence of matter in it and constant concentration at the boundary:

$$\frac{C}{C_0} = \text{erfc}\,\frac{z}{2\sqrt{Dt}} \tag{3}$$

where C and C_0 are the concentrations of the substance at time t in the z coordinate measured from the boundary and at the boundary, D is the diffusion coefficient [12, P. 21, 37]. It follows that the distance z from the boundary at which the concentration of the substance reaches the value C and the amount of the substance penetrating into the medium through a unit area on its surface are proportional to $t^{0.5}$. However, this interpretation does not take into account the shape of the swelling particle. In real particles, the semi-infinity condition which implies the absence of sorbate far from the boundary at any moment in time, is only satisfied during the very initial period.

Solutions to the problems of diffusion in particles having the shape of a plane sheet, a cylinder, or a sphere give more complex time dependences [12]. So, for diffusion in a spherical particle of a constant size at a constant concentration on the outer boundary, the total amount of matter that has penetrated into the bead from the outside or, conversely, left it, is described by the equation

$$\frac{Q(t)}{Q_\infty} = 1 - \frac{6}{\pi^2} \cdot \sum_{n=1}^{\infty} \frac{e^{-n^2 \cdot \pi^2 \cdot \frac{D}{R_0^2} \cdot t}}{n^2} \tag{4}$$

where D is the diffusion coefficient, $Q(t)$ and Q_∞ are the amounts of absorbed (released) substance (usually in moles or gram equivalents) at time t and after equilibrium with the external phase is reached, R_0 is the radius of the bead. It was shown in [13] that in the initial period for small values of the parameter $\frac{D}{R_0^2} \cdot t$, when $Q(t)/Q_\infty < 0.05$, an approximation $\frac{Q(t)}{Q_\infty} \approx \frac{6}{R_0} \cdot \sqrt{\frac{D}{\pi} \cdot t}$ can be used. Thus, equation (4) also shows the proportionality to $t^{0.5}$ at the very beginning of the diffusion

process, when the sorbed substance has not yet penetrated to the center of the bead.

Due to the fact that the coefficient k in equation (1) depends on the exponent n, and both parameters depend on the shape of the sample, it is difficult to compare the swelling rates of different materials and to systematize the data on the kinetic properties of different materials. It seems more attractive to characterize the penetration of a solvent consisting of only one component into a bead of a certain shape by a single parameter, the diffusion coefficient.

Equation (4) was obtained for constant sizes of spherical particles. It is widely used in the study of the kinetics of ion exchange on a swollen polymer ion exchanger, since during the exchange of ions, the bead of the ion exchanger usually does not change its size very significantly. However, in many cases, the beads of ion-exchange resins (especially weakly cross-linked ones) change their volumes more significantly. Therefore, strictly speaking, it is necessary to use the solution to the problem of solvent diffusion in a particle with changing dimensions. This circumstance is pointed out in some works, for example [14] (however, when treating their experimental data, the authors nevertheless used the solution for flat disks with constant dimensions).

The diffusion problem for a spherical particle with a variable diameter was considered in [15]. Using this approach, the kinetics of changes of the bead volume of polystyrene sulfonic cation exchanger with 4% divinylbenzene as a result of changes in the composition of the external water-alcohol solution was studied in [1, 2]. The diffusion of the two components occurred simultaneously in the bead, and as a result kinetic dependences of the bead size on time with extrema were observed. For this case the authors presented the balance equations and simulation results, which agreed very well with the experimental kinetic curves. However, the solution to the problem itself was presented very sparingly and, most importantly, the significance of taking the

movement of the outer boundary of the bead into account was not discussed.

Less well known in ion exchange is the theory of polymer gel swelling by Tanaka and Fillmore [16-19]. They assumed that the change in the volume (swelling or shrinking) of a gel bead after its immersion in the liquid phase is controlled by the dynamics of the movement of polymeric chains in the liquid phase.

It is assumed that in the beginning, in the polymer network in a bead immersed in a liquid, there are tensions that cause the polymer chains to move in the liquid until the stress is relieved and the final equilibrium state is reached. The dynamics of the polymer network movement is determined by: (1) stresses in the volume of the gel and (2) retarding pressure as a result of friction of the moving polymer against the liquid. The role of stresses was taken into account according to the theory of elasticity of Landau and Lifshitz [20], and the retarding pressure was taken to be proportional to the speed of polymer motion by analogy with the Stokes formula for a viscous fluid flow around a sphere. As a result of solving the mathematical problem in the case of a spherical bead, the equation of motion of the polymer in a liquid was derived in the form

$$\frac{\partial u}{\partial t} = \frac{K + \frac{4}{3}\mu}{f} \cdot \frac{\partial}{\partial r}\left\{\frac{1}{r^2}\left[\frac{\partial}{\partial r}(r^2 \cdot u)\right]\right\} \tag{5}$$

where f is the friction coefficient between the polymer network and the liquid, K is the bulk modulus, r is the radial coordinate of a certain point of the polymer particle, u is the linear coordinate determining the displacement of this point from its final equilibrium position, and μ is the shear modulus. The coefficient before the derivative on the right side of expression (5) has the same dimension as the molecular diffusion coefficient. Therefore, the authors of the theory [16-19] called it the diffusion coefficient of the gel $D_g = (K + 4\mu/3)/f$.

In the case of a spherical particle, the shear modulus can be neglected. When solving the problem, the authors of [17, 18] assumed that in the initial (stressed) state, the

deviation of a certain point of the gel with coordinate r from its final equilibrium position (after removing the stress) is

$$u(r, t = 0) = (R_0 - R_\infty)\frac{r}{R_0} \quad (6)$$

where R_0 and R_∞ are the particle radii in the initial and final equilibrium state.

The solution to the problem, which determines the kinetics of the change in the radius of a spherical gel particle, was obtained in [17, 18] and can be written in the form

$$\frac{R(t) - R_0}{R_\infty - R_0} = 1 - \frac{6}{\pi^2} \cdot \sum_{n=1}^{\infty} \frac{e^{-n^2 \cdot \pi^2 \cdot \frac{D_g \cdot t}{R_0^2}}}{n^2} \quad (7)$$

Also, in [17, 18], solutions were obtained for particles in the form of cylinders and flat disks, analogous to (7).

Thus, it turned out that the right-hand sides of equations (4) and (7) contain functions of the same form. Consequently, the D_g value in equation (7) is similar to the molecular diffusion coefficient D in equation (4), although it should characterize the "collective" movement of polymer chains of the gel into the external solution.

The authors of [21] considered some assumptions of the theory of Tanaka and Fillmore to be controversial, first of all, the assumption that the polymer network is in a stressed state before immersion in a liquid. They offered a somewhat different problem statement. The solvent penetrates into the grain (or migrates out of it) due to the difference in chemical potential in the grain and outside it. As a result, stresses gradually increase in the grain, affecting the chemical potential in it, and an equilibrium state is established. The analytical solution obtained in [21] remained the same in form as in [17, 18], but the coefficient D_g in equation (7) is interpreted as the diffusion coefficient of the solvent in the grain.

When the degree of swelling of the gel changes, simultaneous movement of polymer chains ("diffusion" of the gel) and diffusion of the solvent in the granule take place. These processes are interdependent, therefore the coefficient D_g in equation (4) is ap-

parently a characteristic of both. In what follows, we will adhere to the previously introduced term "gel diffusion coefficient", which has already been used in many works.

As noted in [14], the theory of Tanaka and Fillmore makes it possible to compare the swelling kinetics of various polyelectrolyte gels in terms of D_g values, regardless of the particle shape, to systematize data for various materials, and to compare their properties with the molecular diffusion of other substances. This approach was used to study the swelling of various weakly cross-linked polyelectrolyte gels [14, 16, 17, 19], but was practically not used in the field of ion exchange resins. We know of only one work [22], in which this theory was used to study the swelling kinetics of sulfonated styrene and divinylbenzene copolymers with the content of the latter being from 2 to 16 wt% when dry granules were immersed in NaCl solutions with different pH values. However, it should be borne in mind that the test samples were subjected to a freeze-drying process. The authors supposed that this procedure led to the porosity of the granules (as a result, the studied samples may differ from industrial ion-exchange resins), which they took into account by introducing some additional coefficients into equation (7).

In our work [23], the kinetics of swelling of spherical grains of an industrial polymethacrylic gel ion exchanger KB-4P2 with 2.5 wt% DVB in the Ca-form (1 mol of DVB per 60 mol of methacrylic acid) in a 1 N CaCl$_2$ solution. The swelling occurred as a result of the fact that the temperature was lowered sharply from 363 K to 298 K.

In the above-mentioned works [14, 16, 17, 19, 23], when determining D_g, only the first term of the series in equation (7) was used, thus reducing it to the form

$$\ln\left(1 - \frac{R(t) - R_0}{R_\infty - R_0}\right) = \ln\frac{6}{\pi^2} - \pi^2 \cdot \frac{D_g}{R_0^2} \cdot t \quad (8)$$

The values of D_g were found from the slope of the experimental linear dependence of the left-hand side of (8) on time for the values of $\ln(R(t)-R_0)/(R_\infty-R_0) > 0.6$.

Thus, it seems relevant to expand the study of the swelling of ion-exchange resins

using the theory of Tanaka and Fillmore. In this work, the following tasks were posed: (a) to estimate the values of D_g in different parts of the kinetic curves of swelling (shrinking) of polystyrene sulfonic cation exchanger, (b) to estimate the need to take into account a larger number of terms of the series in equation (7), (c) to assess the possibility of describing the kinetics of swelling (shrinking) of the <u>grains</u> of the ion exchanger with the concept of "diffusion" of the gel, (d) to compare the D_g values for the polystyrene sulfonic cation exchanger with the data known from the literature for polyacrylamide and polyacrylate gels, as well as for some polymer substances in solutions.

Experimental

We used a commercial sample of a gel sulfonic acid cation exchanger based on styrene and divinylbenzene KU-2x8 (1 mol of the crosslinking agent divinylbenzene per 14 mol of styrene).

To measure the radius of the ion exchanger bead, we used an optical microscope combined with a digital video camera and a personal computer, which made it possible to photograph the images of the bead at short time intervals of the order of 1 second.

In order to study the kinetics of swelling of the ion-exchanger granule, a cuvette with distilled water (optical path length 1 cm) was placed on the microscope stage. At the initial moment of time, the granule, which had previously reached equilibrium with a solution of potassium chloride of a certain concentration, was transferred with tweezers into the cuvette so that the granule fell into the field of video camera. At the same time, the camera was turned on. In time, the size of the granule changed and its images were stored in the computer until its equilibrium size with water was established.

When studying the process of contraction (shrinking) of the granules, a cuvette with a solution of potassium chloride of a certain concentration was placed on the microscope stage, and the ion-exchanger granule, which had previously been equilibrated with distilled water, was transferred into the cuvette with tweezers.

In order to obtain the values of the radius of the granules, the recorded images were processed using a computer program based on the Canny edge detector [24]. To determine the conversion factor for the radius of the granule from the number of pixels to millimeters, we used the results of preliminary photographing of the granule and a ruler with a scale division of 0.01 mm. After processing, the radii of the granules and their changes in time were stored in numerical format.

Some kinetic curves of the processes of swelling and shrinking of the ion exchanger in the coordinates R/R_0 versus time are shown in Figure 1.
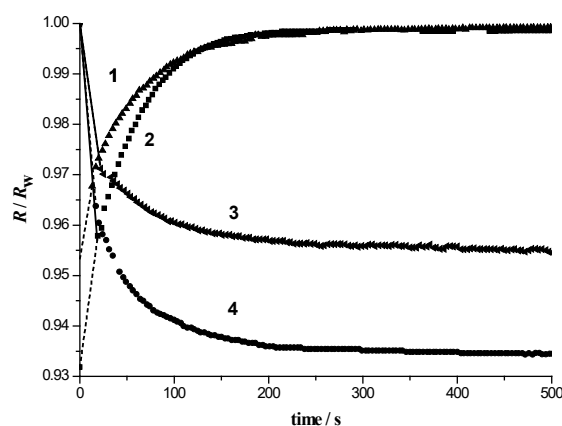

Fig. 1. Changes of the ratio of the radius of a KU-2x8 granule to its equilibrium radius in water R_W with time upon the transfer of the granule: (1) from 1M KCl solution to water, (2) from 2M KCl solution to water, (3) from water to 1M KCl solution, (4) from water to a 2M KCl solution. Points are experimental data, dashed lines are the initial sections of the kinetic curves, when the values of the radius were not recorded in the experiment.

Calculation of the diffusion coefficient from experimental data. In contrast to previously published works, in which only one term of the series in equation (7) was taken into account, in our calculations the first ten terms of the series (n=1-10) were explicitly taken into account. From the experimental values of $R(t)$, R_0, and R_∞ for each $R(t)$ the D_g value was calculated by varying it as a fitting parameter and minimizing the difference between the experimental value of $(R(t)-R_0)/(R_\infty-R_0)$ and the one calculated by Eq. (7). The deviation was minimized by the iteration method by using the Solver add-in in Microsoft Excel.

As in [14, 16, 17, 19], the data was not collected and the calculations were not performed for the initial parts of the kinetic curves (the first 20-40 s), where the most abrupt changes in the size of the granules occur. This is due to the fact that the operation of placing the granule under the microscope eyepiece and positioning it in the field of view of the video camera takes some time.

Discussion of the results

Fig. 2 shows the contributions of the first three terms of the series in equation (7) to the total sum obtained by processing the results of two experiments on the swelling of a granule upon its transfer into water from a KCl solution. Similar dependences were obtained in other experiments. It can be seen that the contribution of the second term of the series remains quite significant up to $(R(t)-R_0)/(R_\infty-R_0) \approx 0.8$ (such values were reached within $\sim$ 2 min) and it is inappropriate to neglect it. At the same time, the third term of the series is insignificant.

For all experiments on the swelling and shrinking of ion exchangers, the dependences of D_g on $(R(t)-R_0)/(R_\infty-R_0)$ were obtained (Figs. 3 and 4).

It turned out that in the range of $(R(t)-R_0)/(R_\infty-R_0)$ from 0.4 to 0.9, the gel diffusion coefficient D_g is not constant and depends on the current degree of swelling. When a grain is transferred from a KCl solution to water, a slight, almost linear increase in D_g is observed, which correlates with the fact that, in this case, the gel swells and becomes less dense. In the case of grain transfer from water to a KCl solution, when the grain is compressed, the D_g values somewhat decrease. However, in the final portions of the kinetic curves (at $(R(t)-R_0)/(R_\infty-R_0)$ more than 0.9-0.95), a very sharp decrease in the D_g value is observed both in experiments with swelling and compression of grains.

For all experiments with sulfonic cation exchanger, the range of variation of the D_g coefficients and their average values (in parentheses) in the range of $(R(t)-R_0)/(R_\infty-R_0)$
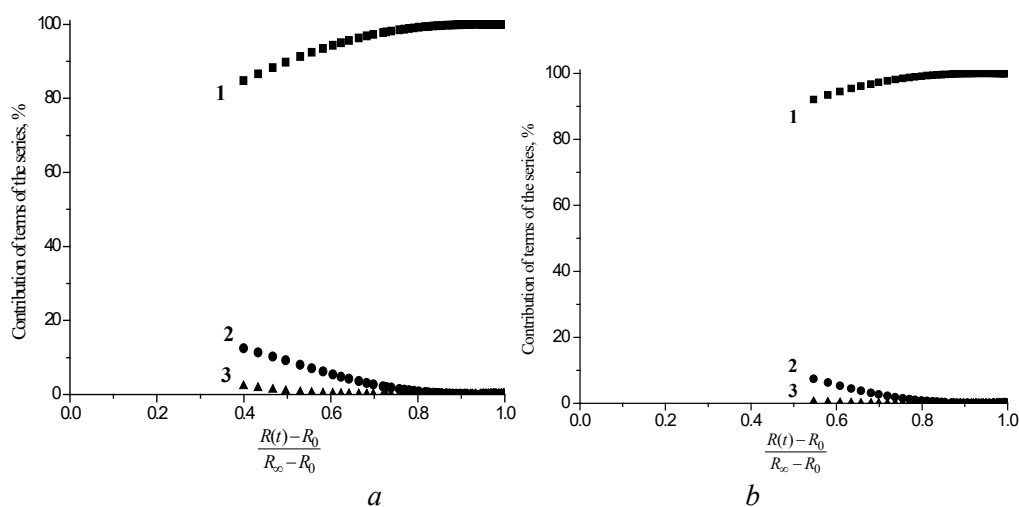

Fig. 2. Contributions of the first (1), second (2), and third (3) members of the series to the total sum in equation (7) as a function of $(R(t)-R_0)/(R_\infty-R_0)$ for the swelling of the granule KU-2x8 (transfer of the granule into water from 1 M KCl (a) and from 2 M KCl (b)).
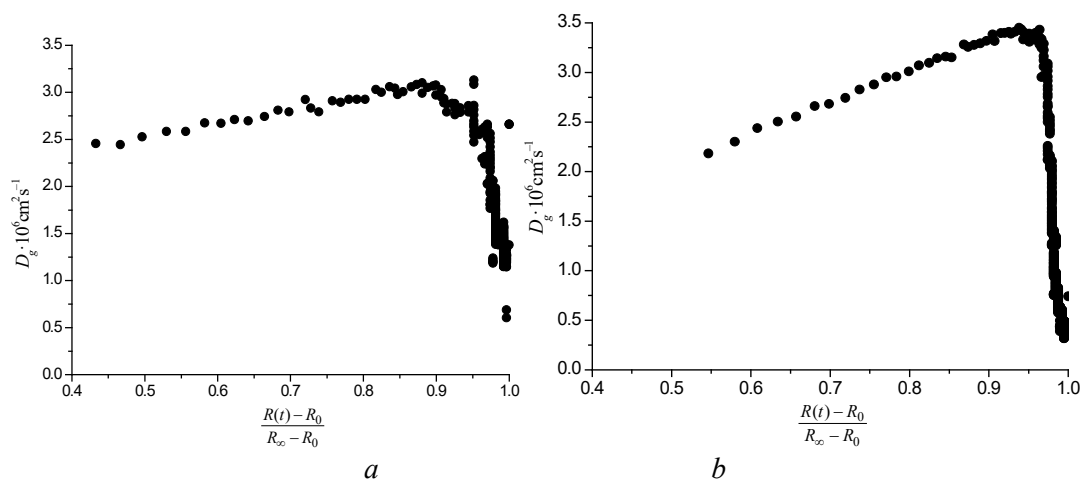
Fig. 3. Dependences of D_g on $(R(t)-R_0)/(R_\infty-R_0)$ when the granule swells
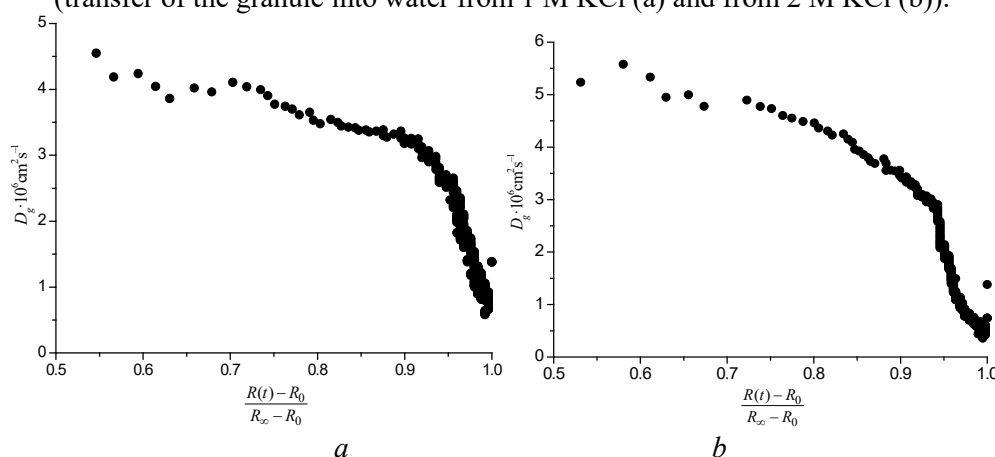(transfer of the granule into water from 1 M KCl (a) and from 2 M KCl (b)).

Fig. 4. Dependences of D_g on $(R(t)-R_0)/(R_\infty-R_0)$ when the granule shrinks
(transfer of the granule from water into 1 M KCl (a) and into 2 M KCl (b)).

from 0.4 to 0.9 are presented in Table 1. Also presented are the values obtained in [14, 16-19] for polyacrylamide gel, as well as the values obtained in [23] for the polymethacrylic type cation exchanger. For comparison, the table also shows the values of the diffusion coefficients of water in organic solvents, glucose and some polymer globular proteins and ribosomal RNA in water.

It can be seen that for sulfonic acid cation exchangers of the polystyrene type, the D_g values are slightly higher than the values found in [23] for polymethacrylic cation exchangers, and higher than those obtained in [16, 17, 19] for polyacrylamide gels in the form of spherical granules. They are also higher than the value found in [14] for swelling in water of disks made from poly (vinyl methyl ether) cross-linked by irradiation. The relatively slow kinetics of swelling of

these gels could be due to the fact that, in contrast to sulfonic cation exchangers, they do not contain dissociating groups. In addition, in these works the swelling was carried out from the dry states of the gels. The D_g values obtained for sulfonic acid and polymethacrylic cation exchangers seem logical if we compare them with the diffusion coefficients of some other polymeric substances in aqueous solutions, which are also presented in the table. The values of the diffusion coefficients of the gels turned out to be 1-2 orders of magnitude lower than the diffusion coefficients of water in organic liquids. No differences in the values of D_g for swelling and shrinking of sulfonic cationite were found.

At the same time, a sharp decrease in D_g at $(R(t)-R_0)/(R_\infty-R_0)$ more than 0.9-0.95 in
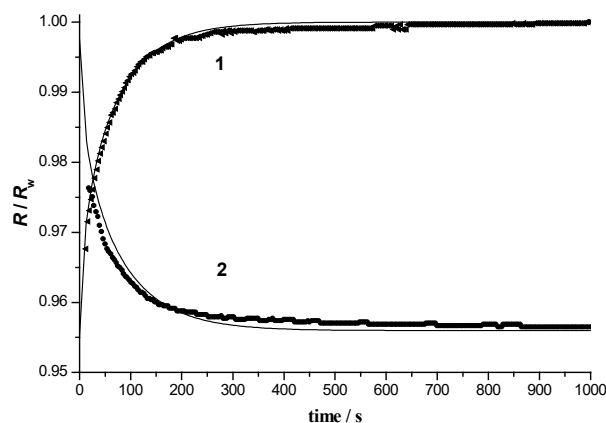
Fig. 5. Changes of the ratio of the radius of a KU-2x8 granule to its equilibrium radius in water R_W with time upon the transfer of the granule: from 1M KCl solution into water (1), from water into 1M KCl solution (2). Points are experimental data, solid lines are calculations with a constant value of $D_g = 3.0 \times 10^{-6}$ cm^2/s.

experiments both with swelling and shrinking of grains (Figs. 4 and 5) indicates that at the final stages there is a sharp deceleration of the process due to a change in its mechanism. This correlates to some extent with the fact that earlier in our work [7], in kinetic experiments with grains of polymethacrylic cation exchanger in the ionic form of doubly charged ions, it was found that in some cases even different stationary degrees of swelling can be established under the same conditions, depending on from which initial state of the ion exchanger they are reached.

Fig. 5 shows the results of direct calculation of the kinetic curves with the average D_g value for the corresponding experiment (see Table 1) in comparison with the experimental kinetic data. It can be seen that on the whole, the experimental dependences are satisfactorily described by the calculated curves with a constant diffusion coefficient.

Table 1. Values of diffusion coefficients of some substances and gels

	Temperature	D, D_g cm^2/s	
Water in acetone	298 K	$4.56 \cdot 10^{-5}$	[25]
Water in ethanol	298 K	$1.24 \cdot 10^{-5}$	[25]
Water in n-butanol	298 K	$0.56 \cdot 10^{-5}$	[25]
Glucose (180 Da) in water		$4.7 \cdot 10^{-6}$	[26]
Ribonuclease ($1.37 \cdot 10^4$ Da) in water	293 K	$1.1 \cdot 10^{-6}$	[27]
Bovine serum albumin ($6.7 \cdot 10^4$ Da) in water	293 K	$6.7 \cdot 10^{-7}$	[27]
Ribosomal RNA ($1.1 \cdot 10^6$ Da) in water		$1.6 \cdot 10^{-7}$	[28]
Polyacrylamide cross-linked by N, N-methylenebisacrylamide (2.6 wt%) in water	~298 K	$3 \cdot 10^{-7}$	[16, 17, 19]
Poly (N-isopropylacrylamide) cross-linked by N, N-methylenebisacrylamide (2.4 wt%) in water	~298 K	$2 \cdot 10^{-7}$	[16, 17, 19]
Poly (vinyl methyl ether) cross-linked by irradiation in water	~297 K	$4.6 \cdot 10^{-7}$	[14]
KB-4P2 in 0.1 N CaCl$_2$	298 K	$2.85 \cdot 10^{-7}$ $3.74 \cdot 10^{-7}$ $2.78 \cdot 10^{-7}$	[23]

	Temperature	D, D_g cm^2/s	
KU-2x8 (from 0.5 M KCl into water)	298 K	$1.0\cdot10^{-7}$-$1.2\cdot10^{-6}$ ($0.6\cdot10^{-6}$)	this work
KU-2x8 (from water into 0.5 M KCl)	298 K	$1.0\cdot10^{-7}$-$1.2\cdot10^{-6}$ ($0.6\cdot10^{-6}$)	this work
KU-2x8 (from 1.0 M KCl into water)	298 K	$2.1\cdot10^{-6}$ - $3.6\cdot10^{-6}$ ($2.9\cdot10^{-6}$)	this work
KU-2x8 (from 1.0 M KCl into water)	298 K	$2.5\cdot10^{-6}$-$3.0\cdot10^{-6}$ ($2.8\cdot10^{-6}$)	this work
KU-2x8 (from 1.0 M KCl into water)	298 K	$1.2\cdot10^{-6}$-$2.5\cdot10^{-6}$ ($1.8\cdot10^{-6}$)	this work
KU-2x8 (from water into 1.0 M KCl)	298 K	$3.2\cdot10^{-6}$-$3.0\cdot10^{-6}$ ($3.1\cdot10-6$)	this work
KU-2x8 (from water into 1.0 M KCl)	298 K	$4.2\cdot10^{-6}$-$2.5\cdot10^{-6}$ ($3.4\cdot10^{-6}$)	this work
KU-2x8 (from water into 1.0 M KCl)	298 K	$4.2\cdot10^{-6}$-$3.2\cdot10^{-6}$ ($3.7\cdot10^{-6}$)	this work
KU-2x8 (from 2.0 M KCl into water)	298 K	$2.0\cdot10^{-6}$-$3.6\cdot10^{-6}$ ($2.8\cdot10^{-6}$)	this work
KU-2x8 (from 2.0 M KCl into water)	298 K	$3.3\cdot10^{-6}$-$3.6\cdot10^{-6}$ ($3.5\cdot10^{-6}$)	this work
KU-2x8 (from 2.0 M KCl into water)	298 K	$2.2\cdot10^{-6}$-$3.4\cdot10^{-6}$ ($2.8\cdot10^{-6}$)	this work
KU-2x8 (from water into 2.0 M KCl)	298 K	$3.1\cdot10^{-6}$-$3.5\cdot10^{-6}$ ($3.3\cdot10^{-6}$)	this work
KU-2x8 (from water into 2.0 M KCl)	298 K	$4.8\cdot10^{-6}$-$3.8\cdot10^{-6}$ ($4.3\cdot10^{-6}$)	this work
KU-2x8 (from water into 2.0 M KCl)	298 K	$4.8\cdot10^{-6}$-$3.0\cdot10^{-6}$ ($3.9\cdot10^{-6}$)	this work

Conclusion

The concept of gel diffusion of Tanaka and Fillmore is very fruitful for describing the kinetics of processes of changes in the degree of swelling of the sulfonic ion-exchange material in the K$^+$ form with a change of KCl concentration in external solution. The values of the obtained gel diffusion coefficient quite logically increase somewhat during the main part of the process of swelling and decrease somewhat during the main part of the process of shrinking. The average values of the diffusion coefficients of the gel make it possible to adequately describe the main part of the kinetic curve. The concept of gel diffusion allows one to compare the swelling kinetics of various polyelectrolyte gels in terms of D_g values, regardless of the particle shape, systematize data for various materials, and compare their properties with the molecular diffusion of other substances.

In the very final parts (5-10%) of the kinetic curves a sharp decrease in the diffusion coefficient value is observed both in experiments with the swelling and compression of grains. It indicates that during the final stages there is a sharp deceleration of the process due to a change in its mechanism.

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Концепция диффузии геля в кинетике набухания и сжатия полистирольного сульфокислотного ионообменника в форме K⁺

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Исследована кинетика набухания (сжатия) полистирольных смол сульфокислотного типа. Зерно ионита в форме иона K⁺, равновесное с 0.1; 0.5; 1,0 или 2 М раствором KCl, переносили в воду и

непрерывно измеряли диаметр. В обратных опытах зерно, пришедшее в равновесие с водой, переносили в раствор KCl и изучали кинетику сжатия зерна. Результаты экспериментов обрабатывали с использованием теории «диффузии геля», параметром которой является так называемый коэффициент диффузии геля, аналогичны коэффициенту молекулярной диффузии. В отличие от ранее публиковавшихся работ, в которых в соответствующем математическом выражении учитывали лишь один член ряда, учитывали первые десять членов ряда. Оказалось, что необходимо учитывать не только первый член ряда (как это делалось в ранее публиковавшихся работах), но и второй член ряда. Оказалось также, что в экспериментах с набуханием гранулы значения коэффициента диффузии геля совершенно логично несколько возрастают (например, в экспериментах с 1 M KCl от $2.1 \cdot 10^{-6}$ до $3.2 \cdot 10^{-6}$ см^2/с) и, напротив, несколько снижаются в обратных экспериментах. Показано, что средние значения коэффициентов диффузии геля позволяют достаточно адекватно описать основную часть кинетической кривой.

Концепция диффузии геля позволяет сравнивать кинетику набухания различных полиэлектролитных гелей с точки зрения значений коэффициента диффузии, независимо от формы частиц, систематизировать данные для различных материалов и сравнивать их свойства с молекулярной диффузией других веществ.

Оказалось также, что на самых конечных участках (5-10%) кинетических кривых наблюдается резкое снижение значения коэффициента диффузии как в экспериментах с набуханием, так и при сжатии зерен. Это указывает на то, что на завершающих стадиях происходит резкое замедление процесса из-за изменения его механизма на недиффузионный.

Ключевые слова: ионообменник, набухание, кинетика набухания, диффузия геля, коэффициент диффузии.

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