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The Effects of Polymer Properties and Solution Composition on the Distribution, Properties, and Amount of Water in Swollen Ion Exchangers

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Abstract—The effects of the composition and concentration of an external solution on the swelling degree of polystyrene-based ion exchangers crosslinked with different amounts of divinylbenzene have been analyzed within the heterophase model of polymer gel structure. It has been confirmed experimentally that, upon variations in the composition of the external solution, the swelling degree of polymers is determined by the content of "sorbed" water alone. Therewith, the volume of the external solution incorporated into the swollen polymer remains constant; i.e., it depends neither on an ionic form of an ion exchanger nor the concentration and composition of the external solution, but rather depends linearly on the polymer crosslinking degree. An algorithm has been proposed for calculating the volume of water in a polymer gel and some quantitative estimates have been presented.

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INTRODUCTION

The overwhelming majority of ion-exchange processes involving ion exchangers take place in aqueous solutions. In this case, the swelling degree of the polymers is varied in a wide range, thereby complicating the process equipment. Ion exchanger's swelling in water and in aqueous solutions gives rise to the formation of polymer gels (PGs), i.e., polymer–solvent systems (mainly of the binary type; however, the presence of solutes and/or several solvents is possible) with a three-dimensional network of polymer molecules, with this network being capable of retaining large amounts of a solvent [1]. In air, PGs retain their shape, thereby differing from polymer solutions.

The description of PG swelling encounters some problems relevant to the absence of exact information on PG structure and to changes in PG volume with variations in the composition of an external solution. As has been shown previously [2–4], PGs may be described as two-phase systems consisting of a polymer solution (PS), i.e., a solution which, in the simplest case, consists of a polymer and water sorbed in it, and an external solution (ES), which is located inside the swollen polymer and has the same composition as that of an outer solution, in which the polymer is immersed. The volume fractions of the aforementioned solutions in the PG bulk depend on the polymer properties and are determined by the polymer-network structure. A method for a priori determining the amount of water sorbed by polymer and the volume of the PS phase has been proposed in [5]; however, data on a method for evaluating the volume of the ES phase are unavailable. In [6–8], it has been shown that the PG volume changes as a result of variations in the volume of the PS phase alone, which is determined by water activity in the external solution. At the same time, the volume of the ES phase remains unchanged. This finding requires both an explanation and a more thorough investigation, because it is possible that changes in the sizes of a polymer network, the cells of which contain the ES, may cause corresponding changes in its volume.

In this work, the changes in the swelling degree of ion exchangers in solutions of different compositions and concentrations were measured by the method of optical micrometry (MOM) [9]. The swelling degrees of commercial cation exchangers and anion exchangers based on polystyrene crosslinked with different amounts of divinylbenzene were measured for different ionic forms. Changes in the swelling degrees of such gels in solutions of different compositions were determined and the volumes occupied by the ES phase in these gels were calculated.

Table 1. Characteristics of solutions

Parameter	HCl			KCl		
C, M	2.96	1.48	0.74	2.75	1.38	0.69
a_w	0.85	0.94	0.98	0.904	0.954	0.977

ALGORITHM OF CALCULATION OF ES PHASE VOLUME IN PG

According to the heterophase model [2–4], PG volume V_g consists of the following volumes: dry ion exchanger V_r, “bound” (sorbed) water V_s, and ES phase V_f.

$$V_g = V_r + V_s + V_f, \tag{1}$$

where V_g [milliliters] is the experimental value, which is determined by MOM.

Change ΔV in the PG volume is the difference between the PG volumes in water and in a solution. This value was also found from the MOM data:

$$\Delta V = V_0 - V_{eq}, \tag{2}$$

where V_0 is the PG volume in water and V_{eq} is the equilibrium volume of PG in a solution of a given concentration.

As the change in volume is related to water sorption, the number of polar groups in a granule E [mg-equiv of polar groups] may be calculated with the use of the isotherm of water sorption by the given polymer via the following formula:

$$\Delta V = V_{H_2O} E \left(n_w^0 - n_w^i\right), \tag{3}$$

where $V_{H_2O} = 18$ mL/mol is the molar volume of water; n_w^0 [mol H_2O/mol polar groups] is the specific sorption of water from vapor at $p/p^0 = 1$; and n_w^i [mol H_2O/mol polar groups] is the specific sorption of water from vapor at $p/p^0 = 1 - i$, i.e., in the equilibrium solution.

The volume of sorbed water was also calculated on the basis of the water-sorption isotherm as follows:

$$V_s = V_{H_2O} E n_w^i. \tag{4}$$

Volume V_r was calculated from the values characterizing the specific exchange capacity of the given polymer. This capacity was determined experimentally or taken from the literature. The specific characteristics of ion exchangers were determined by methods described in [10].

$$V_r = \frac{E}{e}, \tag{5}$$

where e [mg-eq/mL] is the specific content of polar groups in a dry ion exchanger.

The ES phase volume was found from the calculation results as follows:

$$V_f = V_g - V_r - V_s. \tag{6}$$

MATERIALS AND REAGENTS

In the experiments, the influence of ion exchanger–solution system parameters, such as the nature of a solute, solution concentration, granule size, crosslinking degree (weight percentage of divinylbenzene (DVB)), and the nature of polar groups in ion exchangers based on polystyrene crosslinked with DVB, on the swelling degree of ion exchangers was studied. Sulfonic cation exchangers in the H and K forms (a crosslinking degree from 4 to 25%) and strongly basic anion exchangers with the quaternary ammonium base in the Cl form (a crosslinking degree from 4 to 12%) were examined. Table 1 lists the main parameters of the solutions used in this work (concentration C [mol/L] and water activity a_w). The brands and main characteristics of the aforementioned ion exchangers are listed in Table 2.

EXPERIMENTAL UNIT AND PROCEDURE

MOM allows one to determine the sizes of a swollen polymer sample directly in a solution at any moment of time. The experimental unit consists of a camera giving images with real (noninterpolated) frame sizes of 1280 × 960 pixels, a microscope, and a computing system incorporating a personal computer.

Since the volumes of spherical particles are most convenient to calculate, spherical granules were selected for the measurements. The diameters of the selected granules swollen in water ranged from 0.3 to 1.1 mm. The resolution of the instrument was 660 pixel/mm. Thus, the minimum measurement error for diameter was equal to 1 pixel, i.e., 0.15–0.5% of a granule diameter; hence, the measurement error for the granule volume was 0.45–1.5%.

The measurements were carried out as follows. A cell containing water and a swollen polymer granule was placed onto the stage and covered with a cover glass; the granule was photographed, and two diameters of the granule were determined using a graphics editor, with the third diameter being calculated as the half-sum of the two measured values; then, granule volume V_0 was calculated.

The time required to reach the equilibrium volume of PG in a new solution was determined by studying the swelling kinetics of a given polymer. For this purpose, a polymer granule was transferred into a cell with a solution of a known concentration and variations in granule volume were recorded with the camera at a frequency of 1 frame/s until the equilibrium was established. Then, the granule was transferred into a cell with distilled water and the kinetics of polymer swelling in water was recorded analogously.

Table 2. Characteristics of ion exchangers

Ion exchanger brand	DVB content, wt %	Polar group	Ionic form	*e*, mg-eq/mL
KU-2×4	4	RSO_3^-	H^+	9.1 ± 0.1
			K^+	7.7 ± 0.1
KU-2×8	8	RSO_3^-	H^+	9.1 ± 0.1
			K^+	7.7 ± 0.1
DW-50×12	12	RSO_3^-	H^+	9.1 ± 0.1
			K^+	7.7 ± 0.1
DW-50×16	16	RSO_3^-	H^+	9.1 ± 0.1
			K^+	7.7 ± 0.1
KU-2×20	20	RSO_3^-	H^+	9.1 ± 0.1
			K^+	7.7 ± 0.1
KU-2×25	25	RSO_3^-	H^+	9.1 ± 0.1
			K^+	7.7 ± 0.1
ARA-4p	4	$R(NH_3)_3^+$	Cl^-	4.83 ± 0.05
AV-17×8	8	$R(NH_3)_3^+$	Cl^-	4.17 ± 0.05
ARA-12p	12	$R(NH_3)_3^+$	Cl^-	2.86 ± 0.03

The obtained photographs were processed with the program, which determined the granule boundaries using the Canny edge detector. After that, an ellipse best in terms of the least square method was drawn through the found boundary points. As a result of the image processing, the program yielded, in the text format, the calculated sizes of the granules including relative volume V_i/V_0 taken as the ratio of the measured granule volume to its volume in water.

Before the experiments, granules of the aforementioned ion exchangers were transformed into a required ionic form in ion-exchange columns and washed with water. Each granule selected for the experiments was placed into its own well of a plate, water added to the wells, and the volume of each granule in water V_0 was measured. Then, water was removed from the wells and solutions of known concentrations were poured using 5 or 6 granules for each concentration. In this case, the ionic form of an ion exchanger was identical to the counterion nature in a solution. The well plate was covered and kept for 1.5–2.0 h to reach the polymer–solution equilibrium (time necessary for the equilibrium establishment was determined before the main experiments when studying the swelling kinetics of the ion exchangers under investigation). After equilibrium was reached, the granule sizes in solutions of known concentrations V_{eq} were measured, and the granules were transferred into wells with water. It was shown that they restored their initial volumes (in water) V_0.

RESULTS AND DISCUSSION

The data obtained were used in the calculations carried out by Eqs. (1)–(6). As an example, the results of processing one of the experiments involving simultaneously 6 granules of different sizes are given in Table 3. Analogous calculations were carried out for all ion exchangers listed in Table 2 and for all solutions presented in Table 1.

It has been found that, for all examined ion exchangers, the fraction of the ES phase volume (i.e., V_f/V_0) in the PG granules is, within the experimental error, dependent on neither the granule size nor the polar groups nature and ionic form of an ion exchanger, but is determined by the crosslinking

Table 3. Parameters calculated for PG of KU-2×4 ion exchanger swollen in 2.96 N HCl solution

Sample number	V_0, mL	$\frac{V_{eq}}{V_0}$	*E*, mg-eq	$\frac{V_r}{V_0}$, %	$\frac{V_s^0}{V_0}$, %	$\frac{V_f}{V_0}$, %
1	0.710	0.69	0.72	11.2	46.2	42.6
2	0.325	0.68	0.34	11.5	47.5	41.0
3	0.651	0.68	0.69	11.6	48.1	40.3
4	0.621	0.68	0.64	11.4	47.2	41.4
5	0.599	0.68	0.62	11.3	46.8	41.9
6	0.447	0.68	0.46	11.4	47.4	41.2
Average values				11.4	47.2	41.4 ± 1.2

Table 4. Effect of crosslinking on the distribution of volume fractions V_r, V_s, and V_f in granules of ion exchangers swollen in water

Polymer	Form	DVB content, wt %	$\frac{V_r}{V_0}$, %	$\frac{V_s^0}{V_0}$, %	$\frac{V_f}{V_0}$, %
KU-2	H^+	4	11.4	47.2	41.4 ± 1.2
		8	17.2	43.6	39.2 ± 1.2
DW-50×12		12	22.5	39.7	37.8 ± 1.2
DW-50×16		16	26.4	37.6	36 ± 1.2
		20	31.2	34.6	34.2 ± 1.2
		25	37.2	31.1	31.7 ± 1.2
KU-2	K^+	4	13.5	46.6	39.9 ± 1.2
		8	27.1	35.1	37.7 ± 1.2
DW-50×12		12	36.6	27.1	36.1 ± 1.2
DW-50×16		16	43.2	22.1	34.7 ± 1.2
		20	50.0	17.3	32.7 ± 1.2
		25	56.1	13.5	30.4 ± 1.2
ARA-4p	Cl^-	4	25.2	33.5	41.3 ± 1.2
AV17 × 8		8	33.6	27.2	39.2 ± 1.2
ARA-12p		12	44.1	18.6	37.3 ± 1.2

degree alone. The calculated volume fractions of polymers, "bound" water, and ES phase as depending on the crosslinking degree, polar group nature, and ionic form of ion exchanger samples swollen in water are given in Table 4.

The study of the effect of solution concentration has shown that the changes in the granule volumes are related to the V_s value alone, whereas V_r and V_f remain unchanged. This is partly illustrated in Fig. 1, which shows the effect of not only crosslinking degree, but also solution concentration on the ES phase volume.

Figure 2 shows the volume fractions of the ES phase (V_f/V_0) in the granules calculated for sulfonic cation exchangers with different crosslinking degrees in the H and K forms in HCl and KCl solutions with different concentrations, as well as for strongly basic anion exchangers in the Cl form with different crosslinking degrees in KCl solutions of different concentrations. These data indicate that PGs based on polystyrene crosslinked with DVB have a common property: the volume fraction of the ES phase in these PGs is a function of only the content of crosslinking agent. This finding is in good agreement with the results of the measurement of PG swelling kinetics, which show that the coefficient characterizing the effect of the polymer matrix on the kinetics of polymer swelling depends on the amount of the crosslinking agent alone [11].

According to the data presented in Fig. 2, the change in the volume fraction of the ES phase in PG as depending on the crosslinking degree is described by the following linear relation:

$$100\% \frac{V_f}{V_0} = 43\% - 0.45P, \qquad (7)$$

where P is the crosslinking degree (DVB content in wt %).

The form of the obtained equation leads us to suppose that a crosslinking agent (in this case, DVB) occupies part of ES phase volume V_f and its amount affects this volume. On the other hand, an approximation of the obtained results to zero crosslinking degree yields the volume fraction occupied by the ES phase in the Gaussian coil of a hydrated polystyrene molecule

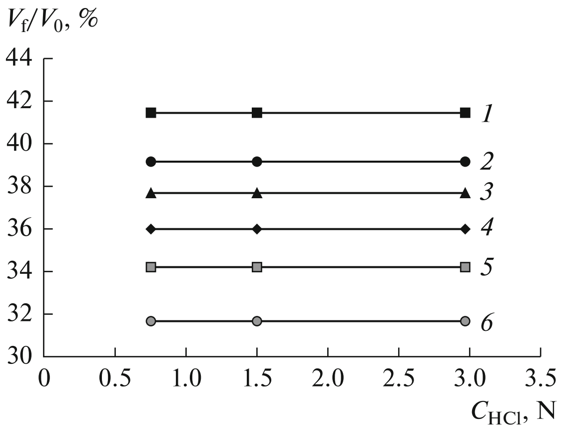

Fig. 1. The effect of the external solution concentration on ES phase volume V_f in sulfonic cation exchangers in H form with different crosslinking degrees: (*1*) KU-2×4, (*2*) KU-2×8, (*3*) DW-50×12, (*4*) DW-50×6, (*5*) KU-2×20, and (*6*) KU-2×25.

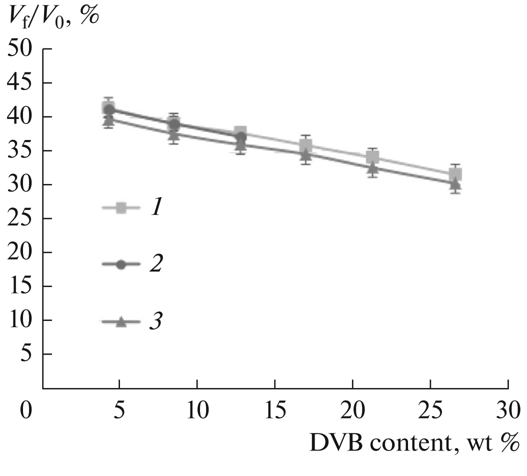

Fig. 2. ES volume V_f as depending on ion exchanger brand, ionic form, and content of crosslinking agent: (*1*) KU-2 (H form), (*2*) AV-17 (Cl form), and (*3*) KU-2 (K form).

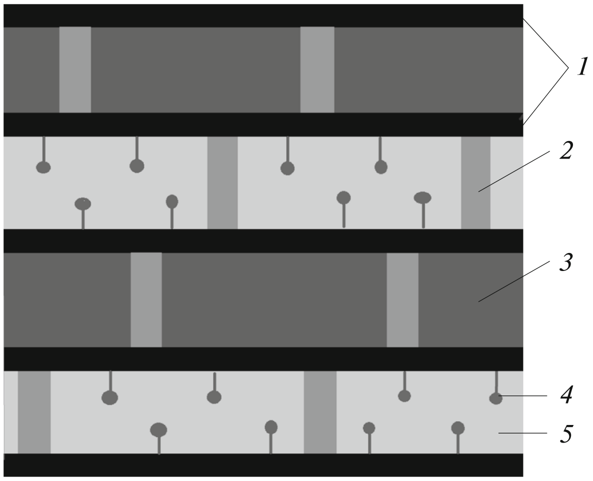

Fig. 3. Model of polymer gel structure: (*1*) polymer chains, (*2*) cross links, (*3*) "free" water (ES phase), (*4*) polar groups, and (*5*) "bound" water (PS phase).

with grafted polar groups. Formula (7) shows that this value is equal to 43 ± 1.2%.

The amount of the crosslinking agent affects the PS phase volume as well. The crosslinking degree affects the sorption properties of the polymers in this phase. The average distance between polymer chains and polar groups depends on this parameter, thereby influencing water sorption by the polymer. As a result, unlike the ES phase, in the PS phase, water content varies not only with the crosslinking degree, but with the activity of the outer water. In PS, the specific amount of water "sorbed" by polymer is described by the water sorption isotherm [5]. As is known [12], water sorption isotherms for samples of the same polymer with different crosslinking degrees must be dissimilar.

CONCLUSIONS

The results obtained in this work have been used to propose a model of the structure of the PGs based of polystyrene crosslinked with DVB. As was shown previously [8], PGs must have a layered structure composed of layers of ES and PS. The scheme of the proposed model PG structure is presented in Fig. 3.

The formation of the layered PG structure may be related to the conditions of synthesis of crosslinked gel ion exchangers, which provide the closest arrangement of polymer chains in the polymer bulk [13]. For this reason, water sorption by polar groups both in water vapor and at the first stage of the dissolution in a liquid is accompanied by the integration of the hydrate shells of polar groups into a common volume [14]. This energetically justified process is associated with the minimization of the surface of sorbed water layers and the formation of the PS phase. Under the action of surface tension forces, the mutual arrangement of both polar groups and, partially, polymer chains is transformed to yield regions with "bound" and "unbound" water.

The mutual orientation of polar groups caused by water sorption remains preserved at the second stage of the polymer dissolution [15]. The presence of sorbed water results in the association of polymer chains into groups, which are separated at a distance permitted by crosslinks, and the liquid located outside of a granule penetrates into the space formed between the chains. This results in formation of a PG consisting of fragments of hydrated polymer chains (PS phase) and a liquid located between them (ES phase). Thus, the following statement is confirmed: the crosslinked hydrophilic polymers in water and in aqueous solutions form two-phase elastic bound-disperse systems, in which each phase has the properties of a solution, with water playing the role of a solvent. According to the proposed model, some properties of PGs must be identical to the properties of emulsions.

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