

Interaction of cross-linked polyelectrolytes with solutions of low-molecular-weight electrolytes

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Abstract

We offer a method for calculation of the composition and the amount in solution of cross-linked polyelectrolyte. Methods to determine amounts and properties of the components in a solution of cross-linked polyelectrolyte are formulated from the viewpoint of a two-phase model and the law of interphase equilibria. An algorithm to calculate the composition of a solution of cross-linked polyelectrolyte was developed. We present the results of comparison of theoretical and experimental values and show that the heterophase model of the swollen gel can serve as a tool for description of such systems. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Two-phase model; Swollen cross-linked polyelectrolyte; Properties of the components; Theory of solutions

1. Introduction

Equilibrium between cross-linked polyelectrolytes and water vapor was studied considerably in the 1950s to 1970s. The so-called isopiestic method of studying the sorption of water by ionites is given along with the experimental data, which is traditionally presented as isotherms of sorption of water, in Refs. [1–4]. In these studies the influence of different parameters (such as the nature of polarity of exchange groups, the counter-ion, and the number of cross-links) on the amount of water sorbed from the vapor, was analyzed.

A somewhat different situation is observed when the cross-linked polyelectrolyte comes into contact with the liquid phase. If the gel, in equilibrium with the water vapor, is placed into a solution with the same activity of water, the mass of the gel increases. This occurs because the inside volume that cannot be filled by absorbing water vapor becomes filled due to the swelling of the cross-linked polyelectrolyte in water or solution. This illustrates the difference in the condition of water in the gel and, therefore, allows us to consider phase heterogeneity.

Further development of the heterophase model occurs in Refs. [5–7], where the definition of a solution of cross-linked polyelectrolyte, as consisting of cross-linked polyelectrolyte, water, and low-molecular-weight elec-

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trolyte, was fully developed. This solution forms a new phase that is in equilibrium with that of the solution of low-molecular-weight electrolyte, which exists on both the inside and the outside of the gel. It is important to note that not only 'isopiestic water' can get into the solution of cross-linked polyelectrolyte, but the solution of low-molecular-weight electrolyte as well. In this case, the solution of cross-linked polyelectrolyte must be in contact with the solution of low-molecular-weight electrolyte, rather than with water vapor. It is evident that mixtures which, in the general case, consist of water, electrolyte and cross-linked polyelectrolyte, exhibit phase heterogeneity. At the same time, the position of the border between the phases, and, therefore, the composition of the phase of a solution of cross-linked polyelectrolyte are still a topic of great discussion. Without describing other approaches, we concentrate on the heterophase model of a swollen cross-linked polyelectrolyte [5]. This model allows for the presence of a volume, inside the swollen gel, where there is water or a solution of the same composition as that on the outside of the gel. Davies and Yeoman first suggested this possibility in 1953 [8]. The next step in that direction was made by Arhangelskiy [9,10]. In his studies with the example of sulfopolystyrene cationites he showed that the specific amounts of water for a given polyelectrolyte (moles of H_2O /equivalent of exchange groups) depend on the activity of water in the outside phase and not from its physical phase (vapor or liquid). Arhangelskiy observed that the amount of water sorbed by one group changes depending on the activity of water in the outside solution, in accordance with the isotherm sorption of water for this ionite, as obtained by the isopiestic method. He explained the presence of electrolyte in the gel by the existence of pores, which are filled by the solution of low-molecular-weight electrolyte that comes from the outside.

At a first glance, the entrance of low-molecular-weight electrolyte into the solution of cross-

linked polyelectrolyte seems unlikely because of the high concentration of the latter, but upon a more detailed consideration of the matter, the reason that this event is possible becomes clear. At equilibrium, there are two solutions in water, and the boundary between the phases does not prevent the low-molecular-weight electrolyte from crossing over it. If the low-molecular-weight electrolyte can interact with the polar group, it can cross the phase boundary and remain in the solution of cross-linked polyelectrolyte. There are several kinds of interactions that can take place: hydrogen bonds, Van der Waals interactions, coordination interactions, and others. Such equilibrium will be described in detail further on in this work.

2. Theory

2.1. Behavior of water in solutions of cross-linked polyelectrolytes

Traditionally, the main characteristic in the description of the properties of a solution is its concentration. This applies to solutions of cross-linked polyelectrolytes as well. The easiest way to determine the concentration of exchange groups in a solution of cross-linked polyelectrolyte is by using isopiestic. They give sufficiently accurate information about the amount of water per gram equivalent of polar groups for a given activity of water on the outside. As Ref. [7] points out, the properties of polar groups in a solution of cross-linked polyelectrolytes and its monomer are different only because in the cross-linked polymer there is a certain starting concentration of these polar groups due to the presence of cross-links. Without changing the properties of the polar groups, cross-links fix the distance between groups (i.e. concentration), and thus change the structure of the system, making a phase of the solution of cross-linked polyelectrolyte.

At interphase equilibrium, the chemical potentials of components that are present at the

same time in both phases are equal, and, therefore, the influence of the number of cross-links on properties of water can be accounted for by introducing the constant of water distribution, K_{distr}^w , which characterizes the interdependence of the activities of water in phases in contact:

$$K_{\text{distr}}^w = \frac{\bar{a}_w}{a_w} \quad (1)$$

where \bar{a}_w is the activity of water in solution of cross-linked polyelectrolyte and a_w is the activity of water in solution of low-molecular-weight electrolyte.

The value of K_{distr}^w for a given solution of cross-linked polyelectrolyte can be calculated if \bar{a}_w is known. The difference of this water activity from one determines K_{distr}^w and describes the influence of the cross-links on the concentration of the solution of cross-linked polyelectrolyte. The value \bar{a}_w is obtained from the isopiestic data and the dependence $n_w = f(a_w)$ for the corresponding monomer. For the desired degree of cross-linkage, one finds the activity of water, to which the value of n_w^0 (amount of water sorbed by this ion exchange resin at equilibrium with water) in the expression for a monomer, $n_w = f(a_w)$, corresponds (see Fig. 1). This activity of water is the value of \bar{a}_w . The amount of cross-links in the polyelectrolyte is denoted by Ψ , a parameter that has units of number of cross-links/amount of monomer. In polyelectrolytes that are not cross-linked $\Psi=1$, while in cross-linked polyelectrolytes this value is in the range of $1.00 < \Psi < 1.25$. The values of \bar{a}_w and n_w^0 for sulfopolystyrene cationite in hydrogen form with 2, 4, 8, 10, and 13% of divinylbenzene are presented in Fig. 1, and the corresponding values of Ψ are $\Psi=1.02$, 1.04, 1.08, 1.10, and 1.13, respectively. Knowing the value of K_{distr}^w and the dependency $n_w = f(a_w)$, it is possible to determine \bar{a}_w and n_w for a given polyelectrolyte and any activity of water.

The data concerning the activity of water in solutions of monomers of different concentra-

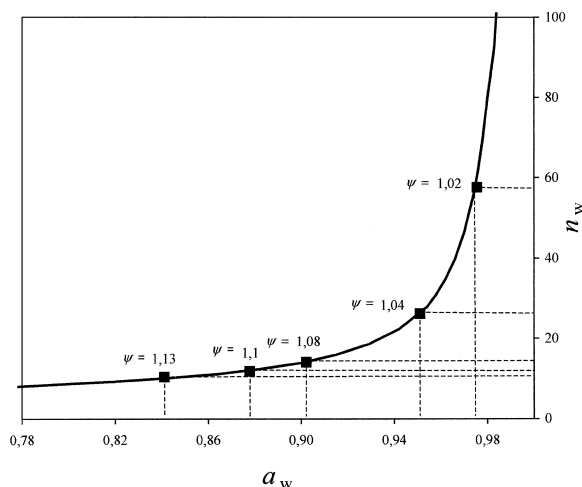


Fig. 1. Dependence of n_w (mole H_2O /mole electrolyte) on the activity of water for a solution of benzene sulfoacid (monomer).

tions, that correspond to many of the commonly used ionites, can be found in the literature. Using these data, the dependencies $n_w = f(a_w)$ can be determined in order to use them in calculations of the parameters of components in the solutions of cross-linked polyelectrolytes. Knowing the amount of water and its activity in the solution of cross-linked polyelectrolyte, it is possible to determine the activities of ion-exchange groups.

2.2. Determination of the activity of an ion exchange group in the absence of sorption of low-molecular-weight electrolytes

The Gibbs–Duhem equation for solutions of cross-linked polyelectrolytes is:

$$n_w d\bar{\mu}_w + n_{\text{AR}} d\bar{\mu}_{\text{AR}} = 0 \quad (2)$$

where n_w and n_{AR} are the number of moles of the components of the solution of cross-linked polyelectrolyte, and $\bar{\mu}_w$ and $\bar{\mu}_{\text{AR}}$ are their chemical potentials. AR is the ionic form A of cross-linked polyelectrolyte R.

As a reference system for the solution of cross-linked polyelectrolyte, we choose an infinitely dilute solution of the monomer of the corresponding type. Where

$$\bar{a}_w = 1, \quad \bar{a}_{AR} = 0, \quad \bar{\gamma}_{\pm AR} = 1.$$

Integrating Eq. (2), the following is obtained:

$$\ln \bar{a}_{AR} = - \int_{\bar{a}_w(m \rightarrow 0)}^{\bar{a}_w(m)} \frac{n_w}{n_{AR}} d \ln \bar{a}_w \quad (3)$$

where m is the molality of the solution of polyelectrolyte.

At equilibrium with water, the solution of cross-linked polyelectrolyte has its minimal concentration, $m_{\min}(\psi)$. Thus, it is reasonable to divide the interval of integration (from $\bar{a}_w = 1$, as $m \rightarrow 0$ to \bar{a}_w at m) in this fashion:

I – from $\bar{a}_w (m \rightarrow 0)$ to $\bar{a}_w (m = m_{\min})$

and

II – from $\bar{a}_w (m = m_{\min})$ to $\bar{a}_w (m)$.

This way Eq. (3) becomes

$$\ln \bar{a}_{AR} = - \left(\int_{\bar{a}_w = 1(m \rightarrow 0)}^{\bar{a}_w(m = m_{\min})} \frac{n_w}{n_{AR}} d \ln \bar{a}_w + \int_{\bar{a}_w(m = m_{\min})}^{\bar{a}_w(m)} \frac{n_w}{n_{AR}} d \ln \bar{a}_w \right). \quad (4)$$

As the limits of integration, the literature values of the dependency $n_w = f(a_w)$ for the monomer (Fig. 1) are used.

Since the number of cross-links in a given polyelectrolyte is a constant value, $\psi = \text{const}$, the first member of Eq. (4) for this case is also a constant. This constant is called $S_0(\psi)$. Thus, Eq. (4) becomes:

$$\ln \bar{a}_{AR} = - S_0(\psi) - \int_{\bar{a}_w(m = m_{\min})}^{\bar{a}_w(m)} \frac{n_w}{n_{AR}} d \ln \bar{a}_w. \quad (5)$$

It follows from the above that in order to calculate the activity of an ion-exchange group, the dependency $n_w = f(a_w)$ must be known for

the solution of the monomer of the corresponding kind, K_{distr}^w , as well as the activity of water in the outside equilibrium solution.

2.3. Equilibrium between electrolytes and the solution of cross-linked polyelectrolyte

2.3.1. Distribution of electrolytes between phases

As in the case of equilibrium of the solution of cross-linked polyelectrolyte with water, we assume that the distribution of electrolyte between the solution of cross-linked polyelectrolyte (\bar{a}_{el}) and the solution of low-molecular-weight electrolyte (a_{el}) can be described by the constant of electrolyte distribution:

$$K_{\text{distr}}^{\text{el}} = \frac{\bar{a}_{el}}{a_{el}}. \quad (6)$$

To find $K_{\text{distr}}^{\text{el}}$ value the activity of the low-molecular-weight electrolyte in the solution of cross-linked polyelectrolyte \bar{a}_{el} must be determined. For that, the composition of the equilibrium solution of the low-molecular-weight electrolyte and its properties, as well as K_{distr}^w for investigating the polyelectrolyte must be known. In addition n_{el} (the determination of n_{el} is shown below) is found from experiment. The value n_{el} is the amount (in moles) of the low-molecular-weight electrolyte in the solution of cross-linked polyelectrolyte containing 1 mole of the polar groups.

Calculation of the electrolyte activity \bar{a}_{el} in the solution of cross-linked polyelectrolyte is the same as in a ternary solution of low-molecular-weight electrolytes. For convenience we use the method of calculation for parameters of ternary mixtures (Zdanovskiy's method [11] or Pitzer's method [12]). To do so we must know concentrations of both the low-molecular-weight electrolyte and the polyelectrolyte in the mixture being investigated. In other words we must know the amount of water in the solution of cross-linked polyelectrolyte.

It is helpful to look at how the solution of cross-linked polyelectrolyte absorbs the elec-

trolyte, according to our model. The composition of a swollen grain of cross-linked polyelectrolyte is shown schematically in Fig. 2. Here the volume of the solution of cross-linked polyelectrolyte $\equiv V_{123}$ is divided conditionally into three volumes, V_{12} , V_3^w , and V_3^{el} .

As mentioned earlier, in a solution of cross-linked polyelectrolyte at equilibrium with a solution of low-molecular-weight electrolyte, the activity of water differs from the activity of water in the surrounding solution. The ‘isopiestic’ amount of water ensures this equilibrium. The low-molecular-weight electrolyte that penetrates the solution of cross-linked polyelectrolyte should not change the value of \bar{a}_w . It is obvious that this is only possible when the low-molecular-weight electrolyte enters the solution of cross-linked polyelectrolyte together with a certain amount of water that compensates its contribution to the activity of water in the

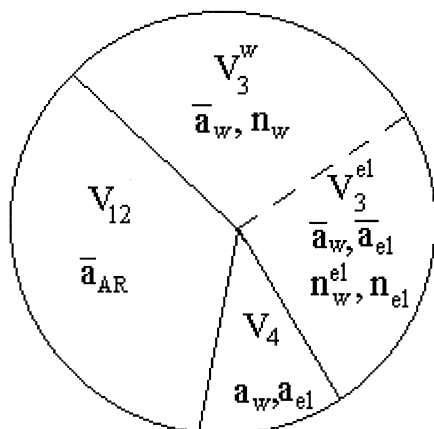


Fig. 2. Structure of a swollen grain of cross-linked polyelectrolyte (scheme drawing). V_{12} is the volume of polymer matrix with counter-ions; V_3^w is the volume of water associated with the polar group of polyelectrolyte (isopiestic water); V_3^{el} is the volume of solution of electrolyte inside the solution of cross-linked polyelectrolyte; and V_4 is the solution of low-molecular-weight electrolyte inside the grain; \bar{a}_w is the activity of water in solution of cross-linked polyelectrolyte and a_w is the activity of water in solution of low-molecular-weight electrolyte; n_w and n_{el} are the number of moles of the components of the solution of cross-linked polyelectrolyte; n_w^{el} is the number of moles of water that is in V_3^{el} ; \bar{a}_{el} is the activity of electrolyte in solution of cross-linked polyelectrolyte and a_{el} is the activity of electrolyte in the solution of low-molecular-weight electrolyte; \bar{a}_{AR} is the activity of the polar groups of the polyelectrolyte.

solution of cross-linked polyelectrolyte. The amount of water necessary for this can be easily determined, since it is known [11] that the mixture of two binary solutions with equivalent activities of water results in a ternary solution with the same activity of water as the original two solutions. The proportion in which the original solutions are taken does not matter, therefore, the low-molecular-weight electrolyte enters the solution of cross-linked polyelectrolyte as a solution, in which the activity of water is the same as that of the solution of cross-linked polyelectrolyte.

Since the activity of water is known, the concentration (in this case, molality) \bar{m}_{3_i} in V_3^{el} can be determined. The amount of water in this volume is determined according to the formula:

$$n_w^{el} = \frac{55.55}{\bar{m}_3} n_{el}. \tag{7}$$

Then we determine the total amount of water in the solution of cross-linked polyelectrolyte:

$$n_\Sigma = n_w + n_w^{el}$$

and calculate molal concentration of exchanging groups and low-molecular-weight electrolyte:

$$\begin{cases} \bar{m}_{AR} = \frac{55.55}{n_\Sigma} \\ m_3 = \frac{55.55}{n_w^{el} + n_w} n_{el} \end{cases} \tag{8}$$

Taking into account that the average molal coefficients of activity is the function of activity of water, we write:

$$K_{distr}^{el} = \frac{\bar{a}_{el}}{a_{el}} = \frac{m_3^2 \bar{\gamma}_\pm^2}{m^2 \gamma_\pm^2}. \tag{9}$$

Here all values besides K_{distr}^{el} are known.

Thus, if K_{distr}^{el} is known we can calculate the amount and the composition of the solution of cross-linked polyelectrolyte when it contains the low-molecular-weight electrolyte.

The amount of electrolyte in solution of the cross-linked polyelectrolyte, Q , is determined by using the results of analyses, in the column

at equilibrium with the solution of sorbed electrolyte BX and label AX. The last is an electrolyte that has no ability to penetrate into the solution of cross-linked polyelectrolyte. Only the solution of low-molecular-weight electrolyte contains this label AX. Then the contents of the column are washed out with water, collecting all the filtrate into the flask with volume V_f and the amounts of electrolyte in the filtrate are determined (with normal concentrations C'_{AX} and C'_{BX} , respectively):

$$\begin{aligned} Q_{AX} &= V_f C'_{AX} \\ Q_{BX} &= V_f C'_{BX} \end{aligned} \quad (10)$$

We can calculate the volume of the solution of low-molecular-weight electrolyte in the column (V_s) because the value of Q_{AX} is known:

$$V_s = \frac{Q_{AX}}{C_{AX}} \quad (11)$$

where C_{AX} is the concentration of electrolyte AX in the initial solution. Then, the amount of sorbed electrolyte BX in the solution of cross-linked polyelectrolyte is calculated:

$$q_{BX} = Q_{BX} - V_s C_{BX} \quad (12)$$

where C_{BX} is the concentration of electrolyte BX in the initial solution. Knowing the ion exchange capacity of the ion exchange resin we can calculate the n_{el} (the amount of the low-molecular-weight electrolyte in the solution of cross-linked polyelectrolyte containing 1 mole of the polar groups):

$$n_{el} = \frac{q_{BX}}{E}. \quad (13)$$

2.3.2. Activities of ion-exchange groups in the solution of cross-linked polyelectrolyte containing low-molecular-weight electrolyte

The Gibbs–Duhem equation for a solution of cross-linked polyelectrolyte containing low-molecular-weight electrolyte is as follows:

$$n_w^\Sigma d\bar{\mu}_w + n_{AR} d\bar{\mu}_{AR} + n_{el} d\bar{\mu}_{el} = 0. \quad (14)$$

Here n_i and $\bar{\mu}_i$ are the number of moles and the

chemical potential of components of the solution of cross-linked polyelectrolyte, respectively.

As a reference system, as in Section 2.2, we choose an infinitely dilute solution of monomer of the corresponding kind. Integrating Eq. (14), we get:

$$\ln \bar{a}_{AR} = - \left(\int_{\bar{a}_w=1}^{\bar{a}_w} \frac{n_w^\Sigma}{n_{AR}} d \ln \bar{a}_w + \int_{\bar{a}_{el}=0}^{\bar{a}_{el}} \frac{n_{el}}{n_{AR}} d \ln \bar{a}_{el} \right). \quad (15)$$

Changing the first integral as in Section 2.2 and taking into account that for interval I, $n_w^\Sigma = n_w$ and for interval II, $n_w^\Sigma = n_w + n_w^{el}$, we get

$$\ln \bar{a}_{AR} = -S_0(\psi) - \left(\int_{\bar{a}_w(m=m_{\min})}^{\bar{a}_w(m)} \frac{n_w^\Sigma}{n_{AR}} d \ln \bar{a}_w + \int_{\bar{a}_{el}=0}^{\bar{a}_{el}} \frac{n_{el}}{n_{AR}} d \ln \bar{a}_{el} \right). \quad (16)$$

Determination of the variables included in Eq. (16) is described in Sections 2.2 (\bar{a}_w) and 2.3 (n_w^Σ , n_{el} , \bar{a}_{el}). The desired activities of ion-exchange groups in solution of cross-linked polyelectrolyte are obtained from Eq. (16) using these variables.

3. Results and discussion

3.1. The effect of number of cross-links on K_{distr}^w

The results of this work allowed us to compose an algorithm to calculate composition and properties of solution of cross-linked polyelectrolyte, mainly applying the literature values with minimal use of experiment.

Since the value of K_{distr}^w for this polyelectrolyte is determined exclusively by the value Ψ [$K_{distr}^w = f(\Psi)$], this dependency was studied in detail. The analysis of the data obtained for the solution of cross-linked polyelectrolyte with different Ψ showed that the values of K_{distr}^w depend practically linearly on the number of cross-links for $\Psi \geq 1$. The results that show this dependency are given in Fig. 3. Here, it is clear that straight lines with different slopes characterize different polyelectrolytes. If the tangents are known, then K_{distr}^w can be determined with a good degree of accuracy for a desired cross-linked polyelectrolyte even if there are no isopiestic data about its cross-linkage:

$$K_{distr}^w = 1 - (\Psi - 1)\tan \alpha \quad (17)$$

where $\tan \alpha$ is the tangent of the angle. Therefore, in order to determine the amount of water in a solution of cross-linked polyelectrolyte, it is sufficient to know the dependency $n_w = f(a_w)$ for the corresponding monomer and the dependency $K_{distr}^w = f(\Psi)$, which can be calculated if at least one value of K_{distr}^w is known.

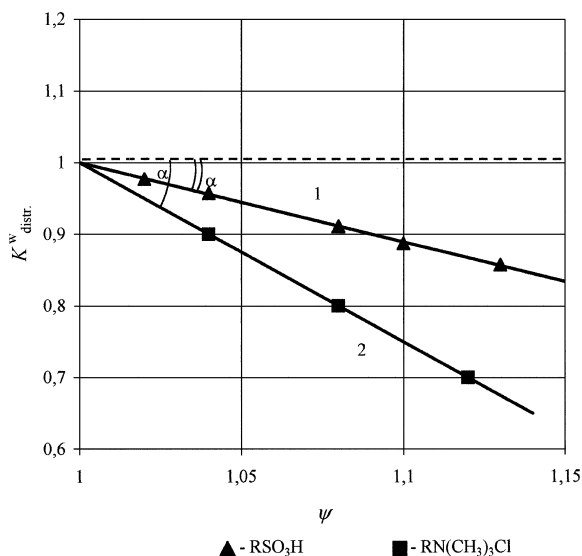


Fig. 3. Dependence of K_{distr}^w on the nature of polyelectrolyte and the number of cross-links: (1) strongly acidic polyelectrolytes (of the type DW-50), and (2) strongly basic polyelectrolytes (of the type DW-1).

Use of these dependencies in order to create isotherms of sorption of water by ionites gave data that correlates well with the experimental isotherms, which were determined by the isopiestic method (Fig. 4).

3.2. Calculation of the parameters of a solution of cross-linked polyelectrolyte

If the properties of an equilibrium solution of low-molecular-weight electrolyte are known, in order to obtain full information about the solution of cross-linked polyelectrolyte the following need to be known:

- dependency $n_w = f(a_w)$ for the monomer from which the cross-linked polyelectrolyte is synthesized;
- the amount of cross-linking agent or Ψ ;
- one isopiestic curve for the given cross-linked polyelectrolyte with any degree of cross-linkage;
- the constant of distribution of electrolyte.

The calculations of parameters of a solution

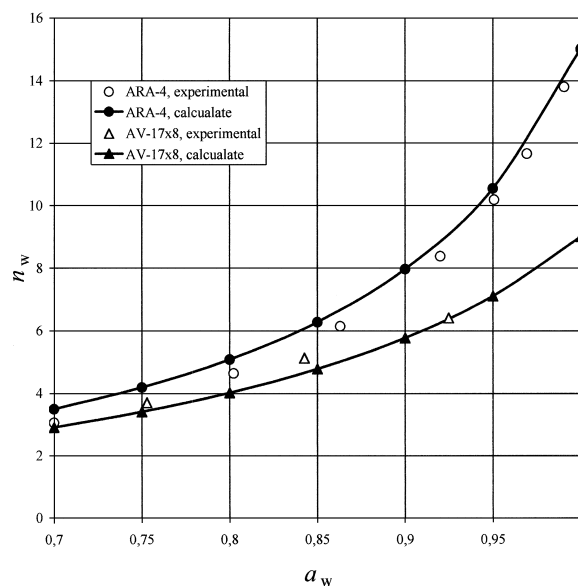


Fig. 4. Comparison of calculated isotherms (lines with solid dots) and isopiestic isotherms (open circle dots) of water sorption.

of cross-linked polyelectrolyte are carried out in the following order.

1. Using the value of n_w^o when $a_w = 1.00$ and $n_w = f(a_w)$, the corresponding values of \bar{a}_w are found, and then K_{distr}^w is determined for the given degree of cross-linking (Fig. 1).
2. As shown in Section 3.1 and in Fig. 3, the function $K_{\text{distr}}^w = f(\Psi)$ is linear; thus, having

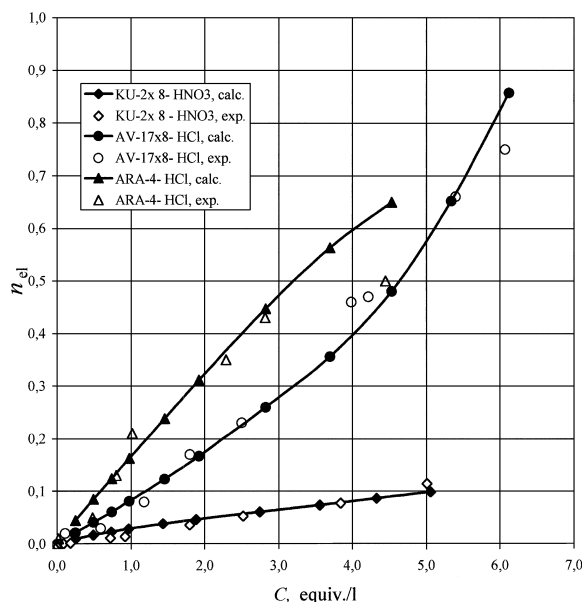


Fig. 5. Comparison of experimental and calculated isotherms of electrolyte distribution in a solution of cross-linked polyelectrolyte.

3. With a known K_{distr}^w the activity of water, \bar{a}_w , and its amount n_w in the solution of cross-linked polyelectrolyte at a given activity of water in the outside solution, a_w , can be determined. If low-molecular-weight electrolyte is absent from the solution of cross-linked polyelectrolyte, then the activity of the polar group can be calculated immediately from Eq. (5).
4. The activity of low-molecular-weight electrolyte when it enters the solution of cross-linked polyelectrolyte can be calculated with Eq. (6).
5. The molal concentration of exchanging groups and low-molecular-weight electrolyte can be determined by using the system of Eqs. (8).
6. The final stage is determination of activity of the polar group in a ternary mixture, which can be done with the help of Eq. (16).

This algorithm was tested for systems with strongly basic anionites: ARA-4 – HCl, LiCl; AV-17x8 – HCl, LiCl, NH_4Cl ; ARA-12 – NH_4Cl and for systems with sulfopolystyrene cationites: KU-2x4 – HNO_3 , KNO_3 ; KU-2x8 – HNO_3 , KNO_3 . Some of the results are shown in Fig. 5 and in Table 1.

Table 1
Parameters of the study systems in accordance with the model

No.	Ion exchange resin	% DVB	Ionic form	Equilibria electrolyte	K_{distr}^w	$K_{\text{distr}}^{\text{el}}$
1	ARA	4	Cl^-	LiCl	0.8861	0.668
2	AV-17	8	Cl^-	LiCl	0.7886	0.3368
3	ARA	4	Cl^-	HCl	0.8861	1.177
4	AV-17	8	Cl^-	HCl	0.7886	2.60
5	AV-17	8	Cl^-	NH_4Cl	0.7886	0.0047
6	ARA	12	Cl^-	NH_4Cl	0.6886	0.0541
7	KU-2	8	K^+	KNO_3	0.92	0.058
8	KU-2	4	K^+	KNO_3	0.96	0.332
9	KU-2	8	H^+	HNO_3	0.912	0.648
10	KU-2	4	H^+	HNO_3	0.956	0.758

4. Conclusion

The effect of the number of cross-links on the properties of the system electrolyte–water was studied in this work. We showed that the peculiarity of systems that include cross-linked polyelectrolyte is that the polar groups are fixed in the polymer carcass and cannot fill the entire volume of the swollen gel. That is, in the swollen granule, there are two solutions with the same solvent, but with different composition, in contact. This results in the system being divided into two phases, one of which has polar groups, and the other one does not. Using the laws that describe interphase equilibria, and in particular, the equality of chemical potentials of the components that exist in both parts of the system, we have found relations that describe water and electrolyte distribution between the phases. These relations allowed us to determine amounts and properties of components in solution of cross-linked polyelectrolyte, mostly utilizing literature values. An algorithm to determine parameters of solution of cross-linked polyelectrolyte was developed and the results of calculations were presented.

Thus, in this work we have shown the usefulness of the heterophase model as an instrument for description of systems consisting of water, electrolyte and cross-linked polyelectrolyte.

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