

Thermodynamics of interphase equilibrium in system ion exchanger-solution of low molecular weight electrolyte

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Abstract

This work deals with thermodynamic description of equilibrium between an ion exchange resin and the solution of low molecular weight electrolyte. The suggested approach allows calculating thermodynamic constant of ion exchange equilibrium.

In order to calculate the activity of ion exchange groups in the resin having monoionic form we used published reference data assuming that the activity of resin exchange sites and that of corresponding monomer are equal in the solutions with equal concentrations. For ion exchange resin in mixed form in equilibrium with the mixed solution of corresponding low molecular weight electrolytes the method of calculating each of ionic forms was also suggested. These activities were used to determine the constant of ion exchange equilibrium.

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1. Introduction

A bead of ion exchange resin represents a three-dimensional polymeric matrix (network) with positively or negatively charged functional groups. The study of water and electrolyte sorption by ion exchange resins was proceeding vigorously as far back as 50–60th of the last century. These studies were reviewed in many books; see for instance [1–5]. The notions of these phenomena currently present in physical chemistry of ion exchange resins are

based on the concept of quasi-homogeneity of swollen resin. Moreover, the notions employed the model of electrolyte Donnan distribution in which the bead surface is likened to semi-permeable membrane [6,7].

In practice, the distribution law followed from the Donnan equation is not always fulfilled. To explain the discrepancies Glueckauf and Watts [8] supposed that both the functional sites and cross linking bridges are distributed non-uniformly throughout the entire volume of resin beads. Certain shortcomings of this approach were reported in [3, p. 31–32].

Davies and Yeoman [9] were the first to suggest the idea of heterogeneous structure of ion exchange

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Nomenclature

$K_{\text{distr}}^{\text{w}}$ is the distribution constant of water between phases of solution of low molecular weight electrolyte and of the solutions of cross-linked polyelectrolyte

$K_{\text{distr}}^{\text{el}}$ is the distribution constant of electrolyte between these phases

K_{B}^{A} is the equilibrium constant of ion exchange

$K_{\text{distr}}^{\text{AX}}, K_{\text{distr}}^{\text{AY}}$ are the distribution constants of individual electrolytes

$a_{\text{w}}, \bar{a}_{\text{w}}$ are the activities of water in the solutions of low molecular weight electrolyte and in the solutions of cross-linked polyelectrolyte

$a_{\text{el}}, \bar{a}_{\text{el}}$ are the activities of electrolytes in the phases of solution of low molecular weight electrolyte and of the solutions of cross-linked polyelectrolyte

$\bar{n}_{\text{w}}^{\Sigma}$ is the amount of water in the solution of cross-linked polyelectrolyte

$\bar{n}_{\text{w}}^{\text{RA}}, \bar{n}_{\text{w}}^{\text{RB}}$ are the specific amounts of water sorbed by two ionic forms

$\bar{n}_{\text{w}}, \bar{n}_{\text{w}}^{\text{el}}$ are the amounts of water around the polar groups and low molecular weight electrolyte

$\bar{n}_{\text{w}}^{\text{R}}$ is the specific sorption of water by polar groups

\bar{n}_{el} is the specific sorption of low molecular weight electrolyte.

$y_{\text{RA}}, y_{\text{RB}}$ are mole fractions of two ionic forms

$m_{\text{el}}^{\text{bin}}$ is the molality of respective ion in the binary solution with the activity of water which is equal to activity of water in investigating mixture

$x_{\text{el}}, y_{\text{el}}$ are their equivalent fractions in corresponding solutions

$\gamma_{\pm\text{el}}^{\text{bin}}$ are the average molal activity coefficients of electrolytes in the binary solution

resins as early as 1953. The next step in this direction was done by Arkhangelsky in 60th [10]. When using sulfonated polystyrene resins as an example, he has demonstrated that specific quantity of water absorbed by the resin is dependent upon the activity of water in outer solution but independent of its physical state (vapor or liquid). He explained the presence of electrolyte inside the resin bead by the availability of pores in which the low molecular weight electrolytes (LMWE) may diffuse from outer solution.

The thermodynamic consideration of ion exchanger phase as well as the process of ion exchange is conveniently to perform on the basis of solution theory. Several researchers suggested to consider an ion exchange group as low molecular weight compound. This brings up the need to reveal a peculiar behavior of resin–water mixture as a solution.

Different compounds modeling AR and BR components have been used namely:

- low molecular weight electrolytes [11–16];
- low molecular weight organic electrolytes (monomers) or their mixtures [17–19];
- slightly cross linked organic polyelectrolytes of the chemical nature identical to that of ion exchange resin under study [20–23].

Chemical potentials of the components of swollen resin bead have usually been calculated taking into consideration (or not) the pressure of swelling. However, in all publications listed above the resin bead was considered to be single-phase system, the concentration of ion exchange groups being calculated per weight or volume of water available in the bead.

To describe the properties of components of cross linked polyelectrolyte (CPE) solution in this study we use suggested early two-phase model of the swollen bead of ion exchange resin [24,25]. This model postulates that ion exchange resin in equilibrium with the solution of low molecular weight electrolyte composed of two phases. One phase represents the solution of cross-linked polyelectrolyte incorporating the cross-linked polyelectrolyte, water and, in general case, low molecular weight electrolyte which may penetrate into this phase from outer solution. The model also assumes that the outer solution may occupy a part of bead interior thus forming another phase. This model helps to determine the composition, quantities and activities of components in the phase of solution of cross-linked polyelectrolyte if the chemical nature of polymer matrix and the composition of outer solution are known.

2. Determination of activities of components in binary solution of cross-linked polyelectrolyte

First of all, let us consider the simplest case when ion exchange resin and solution of low molecular weight electrolyte contain the same ion and low molecular weight electrolyte does not penetrate into the phase of the solution of cross-linked polyelectrolyte. In this case, the phase of solution of cross-linked polyelectrolyte represents the binary solution of cross-linked polyelectrolyte in water. In order to describe this solution the information about physico-chemical properties of the solution of corresponding monomer in water should be used. It is known [26, pp 52–98] that polymerisation changes neither chemical structure nor properties of the polar groups of the monomer and so these properties are believed to be the same in the solutions of equal concentrations.

The concentration of exchange groups in a solution of cross-linked polyelectrolyte can be determined from means of the isotherm of water vapours sorption. The latter can be obtained by successive establishment equilibrium between the ion exchanger and vapour of aqueous solutions with known activities. These solutions support the constant vapour pressure in the system. The concentration of solution of cross-linked polyelectrolyte is

determined by specific amounts of water sorbed by ion exchanger (mole of water per mole of dissolved substances). The activities of water in this solution and in the outer solution are in equilibrium but they are not equal to each other. The amount of the cross-linking agent in polymeric matrix influences both the concentration of the solution of cross-linked polyelectrolyte and the activity of water in this solution. Sorption of water by resin is the greater the smaller the amount of cross-linking agent.

The relation between the activities of water in equilibrium phases is usually described by a constant of distribution as follows:

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

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

The activity of water in the outer solution is known. The activity of water in CPE solution is calculated as a function of the monomer concentration when this concentration corresponds to the amount of absorbed water.

As an example, Fig. 1 shows the isotherm of water sorption into sulfonated polystyrene resin Dowex 50 × 8 in hydrogen form that was obtained

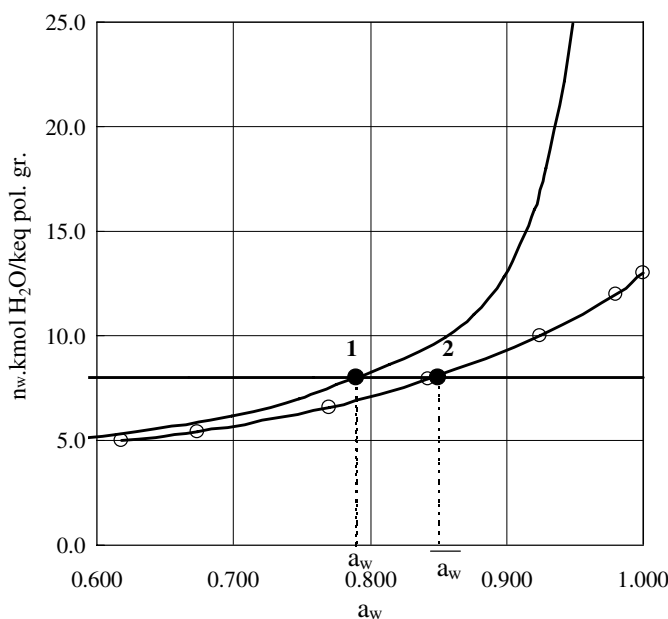


Fig. 1. The influence of the activity of water on the sorption of water by polar groups. Here, (1) is ethyl-benzensulphonic acid and (2) is Dowex 50 × 8 in the H^+ -form.

by isopiestic method as well as the dependence of concentration on the activity of water in the solution of ethyl-benzensulphonic acid, corresponding monomer. The latter data were taken from [18]. As was mentioned above, the properties of polar groups in the cross-linked polyelectrolyte and those of in the low molecular weight electrolyte should be the same. Therefore, both curves in Fig. 1 should coincide. However, it is not the case. Possibly, the existence of cross-links in polymer is responsible for observed discrepancy.

If now one depicts a line parallel to activity axis one may see that at the same concentration the activities of water are different. The point 1 characterizes the activity of water in CPE solution while the point 2 indicates the activity of water in the outer solution. The ratio of these activities gives the value of water distribution constant. That reflects the influence of the amount of cross-linking agent on the degree of CPE swelling.

As for the activity of polar groups in the phase of CPE solution, it is determined as the activity of monomer in a binary solution of the same concentration.

3. Ion exchanger in mixed ionic form. Constant of equilibrium

A mixed ionic form of cross-linked polyelectrolyte can be obtained by exposing cross-linked polyelectrolyte to an excess mixed solution of low molecular weight electrolytes, AX and BX, A and B being the ions identical to the counterions of cross-linked polyelectrolyte. As a result, the equilibrium between phases is the equilibrium between the solution of low molecular weight electrolytes AX and BX and the solution of cross-linked polyelectrolyte in the mixed RA and RB forms.

From the point of view of the two-phase model the swollen mixed ionic form should be considered

as a solution of two polyelectrolytes RA and RB in water. The amount of water in the solution of cross-linked polyelectrolyte can be determined in accordance with Eq. (2):

$$\bar{n}_w^\Sigma = \bar{n}_w^{\text{RA}} y_{\text{RA}} + \bar{n}_w^{\text{RB}} y_{\text{RB}}, \quad (2)$$

where $\bar{n}_w^{\text{RA}}, \bar{n}_w^{\text{RB}}$ are the specific amounts of water sorbed by two ionic forms; $y_{\text{RA}}, y_{\text{RB}}$ are their molar fractions ($y_{\text{RA}} + y_{\text{RB}} = 1$).

The law of acting masses has been usually used to describe the equilibrium of ion exchange. When electrolytes are taken in molar ratio of 1:1 and ion exchange group is univalent the equilibrium constant is determined by the following equation:

$$K_B^A = \frac{a_{\text{AX}} \bar{a}_{\text{RB}}}{a_{\text{BX}} \bar{a}_{\text{RA}}}. \quad (3)$$

After experimental determination of the molar fractions of each ionic form, y_{RA} and y_{RB} , constant of ion exchange equilibrium can be found as follows. First, using the results of [27, 28 (pp 304–329), 29], equations for activities and coefficients of activities for each component of Eq. (3) can be derived:

$$\begin{aligned} a_{\text{el}} &= x_{\text{el}} m_{\text{el}}^{\text{bin}^2} \gamma_{\pm \text{el}}^{\text{bin}^2} \\ \bar{a}_{\text{el}} &= y_{\text{el}} m_{\text{el}}^{\text{bin}^2} \gamma_{\pm \text{el}}^{\text{bin}^2}, \end{aligned} \quad (4)$$

where $m_{\text{el}}^{\text{bin}}$ is the molality of respective ion in the binary solution with the activity of water, which is equal to that of water in mixture under study; $x_{\text{el}}, y_{\text{el}}$ are their equivalent fractions in corresponding solutions; and $\gamma_{\pm \text{el}}^{\text{bin}}$ are the average molal activity coefficients of electrolytes in the binary solution.

In order to find $\bar{\gamma}_{\pm \text{RA}}^{\text{bin}}$ and $\bar{\gamma}_{\pm \text{RB}}^{\text{bin}}$ the activity of water in the phase of the solution of cross-linked polyelectrolyte, \bar{a}_w , has to be determined from Eq. (1). Then the expression (3) transforms to the next one:

Table 1
Thermodynamic constants of ion exchange in KU-2 × 8-HCl–KCl system

No	m_{KCl}	m_{HCl}	x_{KCl}	x_{HCl}	a_w	y_{RK}	y_{RH}	K_H^K
1	0.097	0.227	0.299	0.701	0.985	0.402	0.598	1.1
2	0.188	0.212	0.470	0.530	0.987	0.642	0.358	1.4
3	0.304	0.108	0.738	0.262	0.987	0.818	0.182	1.0
4	0.377	0.046	0.891	0.109	0.986	0.921	0.079	1.0
5	0.290	0.944	0.235	0.765	0.955	0.367	0.633	1.7
6	0.547	0.604	0.475	0.525	0.960	0.637	0.358	1.7
7	0.605	0.626	0.491	0.509	0.957	0.626	0.374	1.5
8	0.919	0.306	0.750	0.250	0.959	0.822	0.182	1.3

Average value: 1.3 ± 0.2

$$K_B^A = \frac{x_{BX}(\gamma_{\pm BX}^{\text{bin}} m_{BX}^{\text{bin}})^2}{x_{AX}(\gamma_{\pm AX}^{\text{bin}} m_{AX}^{\text{bin}})^2} \frac{y_{RA}(\bar{\gamma}_{\pm RA}^{\text{bin}} \bar{m}_{RA}^{\text{bin}})^2}{y_{RB}(\bar{\gamma}_{\pm RB}^{\text{bin}} \bar{m}_{RB}^{\text{bin}})^2}. \quad (5)$$

Thus, it is possible to calculate the equilibrium constant of ion exchange for the cases when the low molecular weight electrolyte is absent in the phase of the solution of cross-linked polyelectrolyte.

An example of such calculation is given in [30]. This study reports the experimental results of determining thermodynamic equilibrium constants for cation exchanger KU-2 × 8 (type Dowex 50 × 8) - HCl-KCl system. The solutions with different ratio of the acid to the salt were taken for separation. The fractions of ionic forms (y_{RH} and y_{RK}) in ion exchange resin were found in experiment. Originating from this data and Eqs. (4) and (5) K_B^A was calculated. The compositions of initial solutions and the results of calculations are given in Table 1. From this Table 1 it follows that K_B^A is considered to be constant studied interval of concentrations and ratios.

4. The low molecular weight electrolyte in the phase of the solution of cross-linked polyelectrolyte

Penetration of the low molecular weight electrolyte into the phase of the solution of cross-linked polyelectrolyte was stimulated by interaction of the hydrated molecule of electrolyte, or, more precisely, the hydrated ionic pair, with a polar group of cross-linked polyelectrolyte. This interaction may incorporate hydrogen bonds, Van der Waals interactions, coordination interactions, etc. As it has been demonstrated in the work [31], the resulting associate has the following properties.

1. The hydrated ionic pair bound to the polar group becomes a component of the phase of the solution of cross-linked polyelectrolyte. Thus, the activity of low molecular weight electrolyte (\bar{a}_{el}) in the phase of the solution of cross-linked polyelectrolyte depends on the activity of water in this phase (\bar{a}_w). That is, the activity of electrolyte in the phase of the solution of cross-linked polyelectrolyte (\bar{a}_{el}) is different from its activity in the phase of the solution of low molecular weight electrolyte (a_{el});
2. The formation of the associate does not change the number of charged particles:



In other words, the polar group acts as an adsorption centre. Because of this, the amount of water that surrounds a given $RA \cdots X^+A^-$ dipole is a function of the nature and concentration of the low molecular weight electrolyte. If the low molecular weight electrolyte penetrates into the phase of solution of cross-linked polyelectrolyte, according to the law of interphase equilibrium the K_{distr}^w value should stay the same. That is, the activity of water (\bar{a}_w) also should not change. This is possible only if the solution of low molecular weight electrolyte of a certain concentration penetrates into the phase of solution of cross-linked polyelectrolyte. This concentration should be corresponding to \bar{a}_w .

Specific sorption of low molecular weight electrolyte \bar{n}_{el} is the only unknown value in equation for the determination of the total amount of water in the phase of the solution of cross-linked polyelectrolyte (7).

$$\bar{n}_w^\Sigma = \bar{n}_w + \bar{n}_w^{\text{el}} = (1 - \bar{n}_{el})\bar{n}_w^R + \frac{\bar{n}_{el}55,55}{\bar{m}_{el}^{\text{bin}}}. \quad (7)$$

where \bar{n}_w and \bar{n}_w^{el} are the amounts of water belonging to the polar groups and low molecular weight electrolyte, respectively; \bar{n}_w^R is the specific sorption of water by polar groups; \bar{n}_{el} is the specific sorption of low molecular weight electrolyte.

The value \bar{n}_{el} can be found from the following expression¹:

$$K_{\text{distr}}^{\text{el}} = \frac{\bar{a}_{el}}{a_{el}} = \frac{\bar{n}_{el}\bar{m}_{el}^{\text{bin}^2} \bar{\gamma}_{\pm el}^{\text{bin}^2}}{m_{el}^2 \gamma_{\pm el}^{\text{bin}^2}}, \quad (8)$$

Thus, the information about the composition of the phase of solution of cross-linked polyelectrolyte can be found from $K_{\text{distr}}^{\text{el}}$. After values \bar{n}_{el} is found for different concentrations of equilibrium solution of a low molecular weight electrolyte, an isotherm of sorption of this electrolyte can be plotted in coordinates $\bar{n}_{el} = f(a_w)$.

5. Two low molecular weight electrolytes in the phase of the solution of cross-linked polyelectrolyte

Let us consider the situation when a solution of cross-linked polyelectrolyte (ion exchanger) in the mixed A, B-ionic form is in equilibrium with the solution of two low molecular weight electrolytes AX and BX which have a common co-ion X. Both low molecular weight electrolytes can be extracted

¹ The expression (8) is written for 1:1 electrolytes.

by the solution of cross-linked polyelectrolyte. As in the previous case, the distribution of electrolytes between the phases can be described by means of the distribution constants of individual electrolytes, $K_{\text{distr}}^{\text{AX}}$, and $K_{\text{distr}}^{\text{AY}}$.

It can be seen from Eq. (8) that the presence or absence of one more low molecular weight electrolyte in the phase of the solution of cross-linked polyelectrolyte already containing low molecular weight electrolyte does not change the value of \bar{n}_{el} . We can arrive at the same conclusion considering the conditions of interface equilibrium. Thus, sorption of low molecular weight electrolytes from their mixture can also be calculated using the individual distribution constants of electrolytes. In this case, it is necessary to take into account the fact that the sorption occurs from multi-component mixed solution rather than from a binary solution but from mixed solution.

Then, the equation for the distribution constant of electrolyte is

$$K_{\text{distr}}^{\text{el}} = \frac{\bar{n}_{\text{el}} \bar{m}_{\text{el}}^{\text{bin}^2} \bar{\gamma}_{\pm \text{el}}^{\text{bin}^2}}{x_{\text{el}} \bar{m}_{\text{el}}^{\text{bin}^2} \gamma_{\pm \text{el}}^{\text{bin}^2}}. \quad (9)$$

This is a general expression for $K_{\text{distr}}^{\text{el}}$ which illustrates the relationship between the fraction of low molecular weight electrolyte in the outer solution and its amount in the phase of the solution of cross-linked polyelectrolyte. If the solution of low molecular weight electrolyte contains two electrolytes, AX and AY, and both of them are absorbed by the cross-linked polyelectrolyte, then due to different values of constants the relation between the amounts of low molecular weight electrolytes in the equilibrium phases is different. This result allows suggesting the method of description of sorption separation of low molecular weight electrolytes [32–35].

6. Equilibrium constant

When the ion exchanger in the mixed ionic form is in equilibrium with the solution of low molecular weight electrolytes AX and BX, the distribution of water between two phases can be also described by distribution constants. It is clear that the non exchange sorption of low molecular weight electrolytes by ion exchanger influences the equilibrium of ion exchange. In other words, there exists a definite relation between the equilibrium constants and distributions constants electrolytes. The equilibrium

constant for phase of the solution of cross-linked polyelectrolyte can be determined as (10):

$$K_{\text{B}}^{\text{A}} = \frac{a_{\text{BX}} \bar{a}_{\text{AR}}}{a_{\text{AX}} \bar{a}_{\text{BR}}} = \frac{K_{\text{distr}}^{\text{AX}} \bar{a}_{\text{BX}} \bar{a}_{\text{AR}}}{K_{\text{distr}}^{\text{BX}} \bar{a}_{\text{AX}} \bar{a}_{\text{BR}}}. \quad (10)$$

The activities can be described as the ionic product:

$$\bar{a}_{\pm} = \bar{a}_{+} \bar{a}_{-},$$

then

$$\frac{\bar{a}_{\text{BX}} \bar{a}_{\text{AR}}}{\bar{a}_{\text{AX}} \bar{a}_{\text{BR}}} = \frac{\bar{a}_{\text{B}^{+}} \bar{a}_{\text{X}^{-}} \bar{a}_{\text{A}^{+}} \bar{a}_{\text{R}^{-}}}{\bar{a}_{\text{A}^{+}} \bar{a}_{\text{X}^{-}} \bar{a}_{\text{B}^{+}} \bar{a}_{\text{R}^{-}}} = 1. \quad (11)$$

Therefore, the ion exchange equilibrium constant is the ratio of distribution constants of electrolyte:

$$K_{\text{B}}^{\text{A}} = \frac{K_{\text{distr}}^{\text{AX}}}{K_{\text{distr}}^{\text{BX}}} \quad (12)$$

This Eq. (12) does not contain values, which obviously determine the properties of ion exchange groups. It is possible to determine the activities of components of the phase of solution of cross-linked polyelectrolyte using the experimental data and then calculate the constants of ion exchange equilibrium. The results of such experimental investigation are described in paper [36]. This publication describes two methods for determining equilibrium constant using AV-17 × 8 (type DW-1)-HCl-HNO₃ system as an example. The first method is based on calculating the constant as the ratio of distribution

Table 2
Experimental equilibrium constants of ion exchange for AV-17 × 8-HCl-HNO₃-H₂O system

No	m_{HCl}	m_{HNO_3}	a_w	$K_{\text{Cl}}^{\text{NO}_3}$
1	2.11	0.97	0.869	1.76
2	2.13	1.04	0.865	1.49
3	1.62	1.82	0.859	1.85
4	1.11	2.08	0.875	1.75
5	0.62	0.51	0.960	1.14
6	0.77	1.51	0.915	1.28
7	0.26	0.76	0.965	0.97
8	1.40	0.72	0.917	1.27
9	0.61	0.36	0.966	1.16
10	1.06	1.01	0.921	1.03
11	0.95	0.97	0.928	1.50
12	0.49	0.67	0.959	0.75
13	0.95	0.95	0.929	1.55
14	0.49	0.67	0.959	0.75
15	0.36	1.82	0.922	1.91
16	0.17	0.90	0.963	1.00
17	0.77	0.22	0.964	1.70

Average value: 1.3 ± 0.3

constants (13). These constants were obtained from sorption isotherms for HCl и HNO₃. The values of obtained constants are

$$K_{\text{distr}}^{\text{HCl}} = 7.9 \pm 0.1 \quad K_{\text{distr}}^{\text{HNO}_3} = 8.9 \pm 0.1$$

In accordance with (13) the equilibrium constant equals $8.9:7.9 = 1.13$.

The second method consists in experimental determination of the fraction of each acid in the phase of solution of cross-linked polyelectrolyte followed by K_B^A calculation. Table 2 shows the list of studied solutions and corresponding K_B^A . They show a good accordance with theoretical and experimental values.

7. Conclusion

To describe the composition of solution of cross-linked polyelectrolyte and to determine the activities of all components in this phase the authors employed suggested earlier two-phase model of resin-swollen bead. Moreover, it has been also suggested the using information about physico-chemical properties of low molecular weight electrolyte solution published in handbooks, in this case the structure of low molecular weight electrolyte molecule and that of polymer repeating unit should be identical. This approach to the description of solution of cross-linked polyelectrolyte allowed combining information about the adsorption isotherms for water onto resin and the dependence of low molecular weight electrolyte solution concentration on water activity. The relation between these two dependencies is shown in Fig. 1. The influence of the amount of cross-linking agent and water activity in outer solution on the activity of water in the phase of solution of cross-linked polyelectrolyte is expressed by means of constant of water distribution.

In order to find the activity of ion exchange groups in monoionic form one uses reference data taking into account the fact that the activity of resin exchange sites and the activity of corresponding monomer are equal in the solutions with equal concentrations. For ion exchange resin in mixed form in equilibrium with the mixed solution of corresponding low molecular weight electrolyte the method of calculating each of ionic forms was suggested. These activities are used for the determination of equilibrium constant.

The cases were also considered when low molecular weight electrolyte penetrates into the phase of solution of cross-linked polyelectrolyte. This penetration changes the quantity and the composition

of solution of cross-linked polyelectrolyte and, therefore, the activities of components. In this work, the equations are derived for calculation of the activities of all components. The activity of low molecular weight electrolyte penetrating into the phase of solution of cross-linked polyelectrolyte as well as the activity of water is determined by means of distribution constants. The difference in the distribution constants of electrolytes is the reason for different distribution of low molecular weight electrolyte between the phases. This result is the basis for a new method of low molecular weight electrolyte separation.

When two low molecular weight electrolytes penetrate into the solution of cross-linked electrolyte the constant of ion exchange equilibrium becomes equal to the ratio of distribution constants for these low molecular weight electrolytes.

This study also shows the results of experimental verification of the suggested model. The equilibrium constant was found to be a constant quantity, within a confidence interval it depends neither on concentration of solution, nor on the ratio of dissolved compounds. Besides, good correlation between the values of equilibrium constants obtained by different ways testifies to adequacy of suggested model.

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