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Calculation of the Ion-Exchange Equilibrium Constant for MK-40 Sulfo Cation-Exchange Membranes from Conductometric Data

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Abstract—A method was proposed for determining the apparent ion-exchange equilibrium constant for MK-40 sulfocationite membranes in alkali metal chloride aqueous solutions containing hydrochloric acid. The method is based on measurements of the ac electrical resistance of the membrane at equilibrium with the corresponding electrolyte solution. The equations derived for this case account for the ionic composition of the membrane and its structure inhomogeneity. Variants of the conductometric method were discussed. It was demonstrated that ion-exchange equilibrium constants determined conductometrically are in agreement with those determined by independent analytical methods.

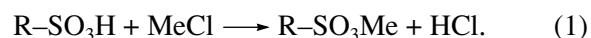
Investigations of ion-exchange equilibria provide information about apparent and true ion-exchange constants, constants of distribution of ions between the ion exchanger and solution phases, and about the influence of the polymer structure and the nature of its functional groups on the ionic composition of the ion exchanger. These data are required for predicting the efficiency of ion separation processes not only under equilibrium conditions but also under conditions when an electric current passes through the system (electrodialysis or membrane electrolysis). The efficiency of electromembrane separation of ions is primarily determined by the conductance and selectivity of the ion-exchange membrane.

The selectivity and sorption capacity are traditionally estimated using laborious chemical analysis. At the same time, there are well-developed methods for measuring the membrane conductance based, as a rule, on the use of simple instruments. Therefore, conductometric methods are used for determining the thermodynamic parameters of the ion exchanger–solution and ion-exchange membrane–solution systems [1, 2]. For example, in [2], the ionic composition of a membrane was estimated from concentration dependences of the conductivity (κ) in individual electrolyte solutions and in their mixtures. The use of high-frequency conductometry offers new prospects for estimating characteristics of ion-exchange equilibria, because, in this case, measurements of the active part of the impedance of a membrane in equilibrium with an electrolyte solution do not disturb the equilibrium in the system.

The aim of this work was to develop a method for determining ion-exchange equilibrium constant from experimental concentration dependences, for an MK-40 membrane in HCl, NaCl, LiCl, and KCl solutions and

their mixtures, as an example. The calculation equations were derived from the known Nikol'skii equation [3] and the equations for the generalized conductivity of structurally inhomogeneous media [4].

For a cation-exchange membrane at equilibrium with a mixture of two binary electrolytes having a common anion (for example, Cl^-), the exchange occurs according the reaction



For a membrane in equilibrium, for example, with a mixture of HCl and MeCl, the relationship between concentrations of the exchanging counterions in the solution and in the ion exchanger gel phase [3] is given by the Nikol'skii equation

$$Q_{\text{Me}}/Q_{\text{H}} = K c_{\text{Me}} \gamma_{\text{Me}} / c_{\text{H}} \gamma_{\text{H}}, \quad (2)$$

where K is the ion-exchange equilibrium constant; c_{H} and c_{Me} are the H^+ and Me^+ concentrations in the solution; Q_{H} and Q_{Me} are the exchange capacities of the membrane, i.e., the ion concentrations in the ion exchanger gel phase; and γ_{Me} and γ_{H} are the activity coefficients of the respective ions in the solution.

Under the assumption that the first approximation of the Debye–Hückel theory [5] holds in the concentration range under investigation, Eq. (2) can be rewritten as

$$Q_{\text{Me}}/Q_{\text{H}} = K c_{\text{Me}} / c_{\text{H}}. \quad (3)$$

We express ion concentrations in the solution and membrane phases in terms of their equivalent fractions:

$$\alpha_{\text{H}} = c_{\text{H}}/c_0; \alpha_{\text{Me}} = c_{\text{Me}}/c_0; \beta_{\text{H}} = Q_{\text{H}}/Q_0; \beta_{\text{Me}} = Q_{\text{Me}}/Q_0, \quad (3a)$$

where c_0 is the total concentration of the equilibrium solution, and Q_0 is the total exchange capacity of the membrane. Taking into account that $\alpha_{\text{Me}} + \alpha_{\text{H}} = 1$ and

$\beta_{\text{Me}} + \beta_{\text{H}} = 1$ (the sorbed electrolyte can be disregarded, because, in a 0.1 N equilibrium solution, it takes up fractions of a percent of the total capacity of an MK-40 membrane and, in an 1.0 N solution, no more than 5% [2]), from (3), we obtain the equilibrium isotherm as

$$\beta_{\text{Me}} = ((1/\alpha_{\text{Me}} - 1)/K + 1)^{-1}. \quad (4)$$

According to the two-phase model of the ion exchanger inhomogeneity [4], the conductivity of a membrane in equilibrium with a mixed electrolyte solution (κ_{Σ}) can be represented as

$$\kappa_{\Sigma} = \bar{\kappa}_{\Sigma} \frac{f_{\Sigma} (1 - f_{\Sigma})}{\kappa_{\text{sln}}}, \quad (5)$$

where κ_{Σ} is the conductivity of the membrane and the solution at the isoconductivity point, κ_{sln} is the conductivity of the equilibrium solution, f_{Σ} is the volume fraction of the gel phase in the membrane, and $(1 - f_{\Sigma})$ is the volume fraction of the solution in the membrane.

Under conditions of isoconductivity, the conductivity of the gel phase depends on the content of each counterion of the phase and on their properties as charge carriers. Under the assumption that the conductivity of each part of the gel phase in the respective counterion form does not depend on the equivalent fraction of the counterion, the conductivity at the isoconductivity point can be represented as

$$\bar{\kappa}_{\Sigma} = \bar{\kappa}_{\text{H}}(1 - \beta_{\text{Me}}) + \bar{\kappa}_{\text{Me}}\beta_{\text{Me}}, \quad (6)$$

where $\bar{\kappa}_{\text{Me}}$ and $\bar{\kappa}_{\text{H}}$ are the conductivities of the membrane at the isoconductivity point in MeCl and HCl solutions, respectively.

Investigations into the structure of ion-exchange membranes [6] showed that the volume fraction of the internal solution in the membrane does not depend on the form of the ion exchanger. Therefore, in our case, the following equality should hold: $f_{\text{H}} = f_{\text{Me}} = f_{\Sigma}$ (f_{H} and f_{Me} are the volume fractions of the gel phase in the membrane for the respective individual electrolyte solutions; in the general case, f). However, this equality often does not hold, probably due to a difference in the swelling ability of different forms of the membrane. In this case, we can use the averaging:

$$f_{\Sigma} = f_{\text{H}}(1 - \beta_{\text{Me}}) + f_{\text{Me}}\beta_{\text{Me}}. \quad (7)$$

The solution conductivity is calculated by the equation

$$\kappa_{\text{sln}} = (\lambda_{\text{H}}(1 - \alpha_{\text{Me}}) + \lambda_{\text{Me}}\alpha_{\text{Me}} + \lambda_{\text{Cl}})c_0, \quad (8)$$

where λ_{H} , λ_{Me} , and λ_{Cl} are the equivalent conductivities of the respective ions in the solution. In this case, the electrolytes are assumed to dissociate completely.

Thus, it is necessary to determine the Nikol'skii constant from Eqs. (4)–(8). Since the fractional number β_{Na} appears in the equations as a multiplier (Eq. (6)) and as a power (Eq. (5)), the system of equations can be solved only numerically. The initial data for the calcu-

lation ($\bar{\kappa}_{\text{H}}$, $\bar{\kappa}_{\text{Me}}$, f_{H} , f_{Me} , λ_{H} , λ_{Me} , λ_{Cl} , c_0 , α_{Me} , and κ_{Σ}) should be taken from reference books or measured. The solution algorithm involves, as the first step, the use of a trial value of the Nikol'skii constant along with the above-listed values. The parameter β_{Me} is calculated by Eq. (4) and then used in calculating $\bar{\kappa}_{\Sigma}$ by formula (6). Then, f_{Σ} and κ_{sln} are calculated by formulas (7) and (8) and are then used to calculate κ_{Σ} by relation (5). The method of successive approximations makes it possible to determine a value of the desired constant that brings in agreement the calculated and experimental values of the membrane conductivity in the electrolyte mixture κ_{Σ} .

Another approach to calculating the Nikol'skii constant is based on measuring the coordinates of isoconductivity points of the membrane in individual electrolyte solutions and also on determining the isoconductivity of the membrane in a heteroionic form (method II). In this case, under all the assumptions made above, the ion-exchange constant can be directly determined from (4) as

$$K = (1/\alpha_{\text{Me}} - 1)/(1/\beta_{\text{Me}} - 1), \quad (9)$$

where β_{Me} is calculated by Eq. (6):

$$\beta_{\text{Me}} = (\bar{\kappa}_{\text{H}} - \bar{\kappa}_{\Sigma})/(\bar{\kappa}_{\text{H}} - \bar{\kappa}_{\text{Me}}). \quad (10)$$

In order to test the suggested approach, we studied the conductivity of an MK-40 sulfo cation-exchange membrane in LiCl, NaCl, KCl, and HCl solutions and equimolar mixtures of Li, Na, and K chlorides with hydrochloric acid over the concentration range from 0.001 to 0.2 M. We also studied the dependence of the conductivity of the MK-40 membrane on the Na⁺ equivalent fraction α_{Na} in NaCl–HCl mixture at a constant total solution concentration of 0.1 M. These systems were chosen for the following reasons. In recent years, the electrogenic transport properties of membranes in acidic electrolyte solutions and also membrane separation processes under conditions beyond the ultimate regime have been intensely studied. Under these conditions, ion-exchange membranes exist in mixed forms, as they do in electrolyte aqueous solutions (in this case, the mobility of hydrogen ions in membranes is higher than that of the other ions). At the present time, the relationship between the electrogenic transport and sorption properties of ion-exchange materials in acid solutions is as yet insufficiently understood. On the other hand, binary electrolytes are frequently used in studies of the physical chemistry of ion-exchange membranes, because the hydration characteristics and mobilities of ions of this series are well known. In addition, the thermodynamic equations contain no stoichiometric coefficients, a circumstance that substantially simplifies the situation.

Prior to experimentation, MK-40 membranes were chemically conditioned as described in [7]; as a result, they were converted into the H⁺ form. The conductivity

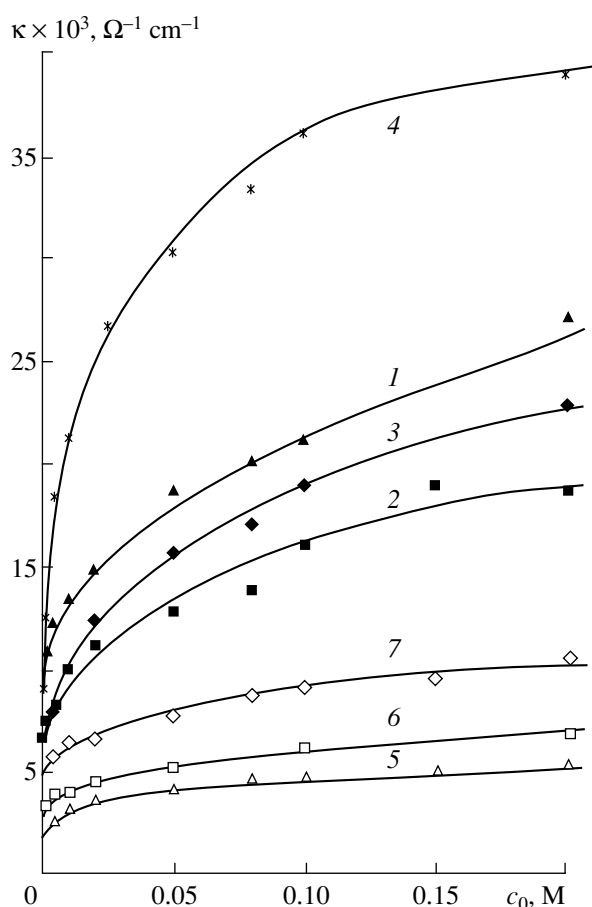


Fig. 1. Concentration dependences of the conductivity of MK-40 membranes in solutions of binary electrolytes and equimolar electrolyte mixtures: (1) HCl–LiCl, (2) HCl–NaCl, (3) HCl–KCl, (4) HCl, (5) LiCl, (6) NaCl, and (7) KCl.

was studied on MK-40 membrane samples arranged in four groups, five samples in each. One of the groups was used for measuring κ in HCl solutions, while the other groups were used for measuring κ in metal chloride solutions and then in equimolar mixtures of the respective salt MeCl with hydrochloric acid. Prior to measurements in MeCl solutions, the samples were treated in a 2 N solution of the respective metal chloride for 48 h. Then the samples were washed out of electrolyte sorbed with distilled water. In order to convert the membrane samples into the heteroionic (Me^+/H^+) form, they were treated in a solution containing 1 mol/l MeCl and 1 mol/l HCl for 48 h. Then the samples were washed with distilled water. The attainment of the equilibrium distribution of the ions between the membrane and the solution was controlled conductometrically. The equilibrium was considered attained when the resistance of the solution over the sample was equal to the resistance of the initial solution.

The static exchange capacity of a membrane Q was determined by the commonly accepted procedure [8]. The ion-exchange constants for the exchange of pro-

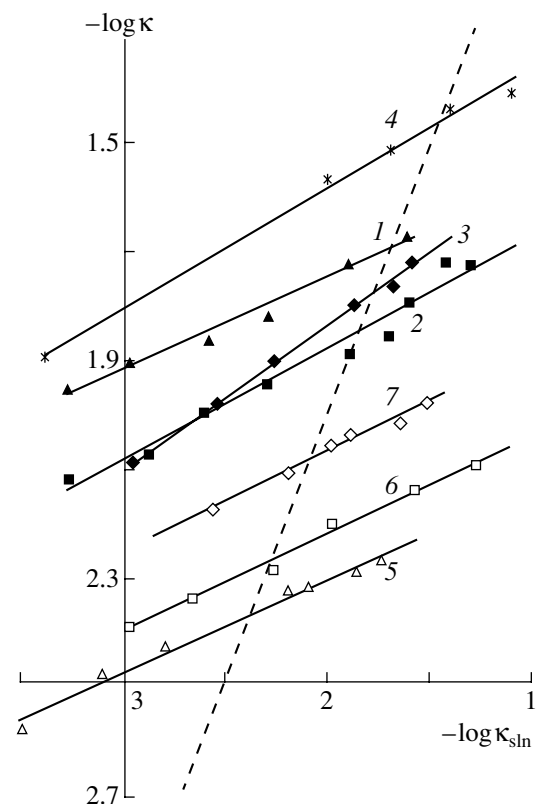


Fig. 2. Log-log dependencies of the conductivity of MK-40 membranes in solutions of binary electrolytes and their equimolar mixtures. The dotted line is defined by the equality $\log \kappa = \log \kappa_{\text{sln}}$. For designations, see Fig. 1 and Table 1.

tons for alkali metal ions were independently measured by the static method. H^+ -form 2–3-g membrane samples were carefully washed with water and placed in a 0.1 M metal chloride solution of a volume of 50 ml. Once the equilibrium was established (after 48 h), the membrane was removed from the solution, where the H^+ ion concentration was determined by titration. The ion-exchange constant was calculated by the formula [9]

$$K = \frac{Vc_{\text{H}}^2}{(gQ - Vc_{\text{H}})(c_0 - c_{\text{H}})}, \quad (11)$$

where g is the mass of the ion exchanger sample, and V is the solution volume.

The transverse resistance R of samples was measured by the mercury-contact method at an ac frequency of about 200 kHz [10]. The membrane conductivity was calculated by the formula

$$\kappa = l/RS, \quad (12)$$

where l is the thickness of the sample, and S is the surface area of the membrane. The maximum error in the membrane conductivity was no higher than 5%.

The concentration dependences of the conductivity of MK-40 membranes in LiCl, NaCl, KCl, and HCl

Table 1. Coordinates of isoconductivity points and the structural parameters of MK-40 membranes

Solution (1 : 1)	$\bar{\kappa} \times 10^3, \Omega^{-1} \text{ cm}^{-1}$	$c_{\text{iso}} \times 10^2, \text{ mol/l}$	f	$(1-f)$
HCl–LiCl (1)	19.95 ± 0.39	8.10 ± 0.16	0.83 ± 0.02	0.17 ± 0.02
HCl–NaCl (2)	14.00 ± 0.28	5.62 ± 0.11	0.79 ± 0.01	0.21 ± 0.01
HCl–KCl (3)	16.56 ± 0.28	6.26 ± 0.09	0.73 ± 0.01	0.27 ± 0.01
HCl (4)	34.02 ± 0.28	8.60 ± 0.08	0.77 ± 0.01	0.23 ± 0.01
LiCl (5)	4.19 ± 0.07	5.20 ± 0.09	0.83 ± 0.01	0.17 ± 0.01
NaCl (6)	5.27 ± 0.09	4.92 ± 0.10	0.82 ± 0.01	0.18 ± 0.01
KCl (7)	8.25 ± 0.20	6.36 ± 0.18	0.82 ± 0.01	0.18 ± 0.01

solutions and equimolar mixtures of Li, Na, and K chlorides with HCl are presented in Fig. 1. As can be seen from these dependences, the conductivities of the MK-40 membranes in different ionic forms differ over the entire concentration range. Of the homoionic forms, the H⁺ form exhibits the highest conductivity throughout the concentration range. This agrees with the previously obtained data for MK-40 membranes.

The mobility of the alkali metal ions in the solution varies in the series $\text{K}^+ > \text{Na}^+ > \text{Li}^+$. The conductivity of the membranes in the respective ionic forms varies in the same order throughout the entire concentration range, which agrees with the data for this type of heterogeneous membranes [11]. For the mixed solutions, the conductivity of the MK-40 membranes varied in a different order: $\text{Li}^+/\text{H}^+ > \text{K}^+/\text{H}^+ > \text{Na}^+/\text{H}^+$. Over the entire concentration range covered, the conductivity of the membranes in the LiCl–HCl mixtures was higher than that in the KCl–HCl and NaCl–HCl mixtures. This effect is due probably to a higher exchange sorption of H⁺ from LiCl–HCl mixtures as compared with KCl–HCl and NaCl–HCl mixtures [12]. Another plausible reason is a more developed hydration shell of the Li⁺ ion, which favors relay proton transport [5].

The coordinates of the isoconductivity points ($\bar{\kappa}$, c_{iso}) (where c_{iso} is the concentration of the equilibrium solution at the isoconductivity point) and values of the structure inhomogeneity parameters f and $(1-f)$ were determined from $\log \kappa$ vs. $\log \kappa_{\text{sln}}$ dependences for the systems under study (Fig. 2). The conductivity of the mixed electrolyte solutions was calculated by formula (8). The coordinates of the isoconductivity points for systems under investigation were determined as points of intersection of the $\log \kappa - \log \kappa_{\text{sln}}$ curves with the straight line $\log \kappa = \log \kappa_{\text{sln}}$ (dotted line). The $\log \kappa - \log \kappa_{\text{sln}}$ dependences for all samples were approximated by individual equations using an EXCEL program built in an IBM PC. The averaged (over five samples) coordinates of the isoconductivity points for the MK-40 membranes in the solutions studied and also the fractions of the gel phase f and the intervening space $(1-f)$ are presented in Table 1.

The ion-exchange equilibrium constants were calculated by formulas (4)–(8) from the data of Table 1 and Fig. 1. The calculations were carried out on an IBM PC using a BASIC software. When calculating the ion-exchange constants by method I, we used the conductivity values measured for five membrane samples at all the concentrations of the equimolar mixtures. The average constants determined by method I are listed in Table 2.

When calculating the constants by method II, we used the conductivity values at the isoconductivity

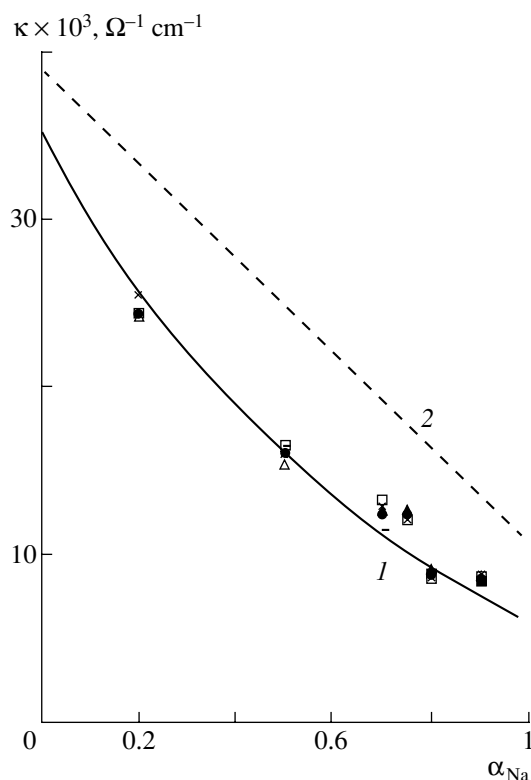


Fig. 3. Dependence of the conductivity of MK-40 membranes in 0.1 N NaCl–HCl mixed solutions on the equivalent fraction of sodium ions in the equilibrium solution: (1) the calculation by Eqs. (4)–(8) (experimental values of the membrane conductivity are represented by points) and (2) the conductivity of the equilibrium solution.

Table 2. Ion-exchange equilibrium constants for MK-40 membranes obtained by different methods

System	K (I)	K (II)	K (analyt.)
Li ⁺ /H ⁺	0.87 ± 0.05	0.89 ± 0.03	0.86 ± 0.05
Na ⁺ /H ⁺	2.03 ± 0.30	2.30 ± 0.08	2.10 ± 0.05
K ⁺ /H ⁺	2.15 ± 0.16	2.01 ± 0.05	2.45 ± 0.12

Notations: I and II are different methods of calculating the exchange constants K .

points of the homo- and heteroionic forms and also the constants determined from the static experiments by using formula (9); the results are presented in Table 2. It is seen that the two methods proposed for estimating equilibrium constants from conductivity measurements yield similar results, which, in addition, are close to those obtained independently by the analytical method. Note that the obtained values of the constant K are in agreement with the average value of the ion-exchange equilibrium constant for the KU-2*8 cationite sample in the HCl–KCl mixture [13].

If the ion-exchange equilibrium constant for two single-charged ions and the isoconductivity of the membrane in the respective homoionic forms are known, the conductivity of the material in mixed solutions at other ratios and concentrations of the electrolytes can be calculated by Eqs. (4)–(8). The dependences of the conductivities of the equilibrium electrolyte solution and the membrane in 0.1 N NaCl–HCl solution on the Na⁺ equivalent fraction in the solution [calculated by formula (3a)] are presented in Fig. 3. The solid line was calculated by Eqs. (4)–(8) using the average value of the obtained ion-exchange equilibrium constants for the Na⁺/H⁺ system. The experimental and calculated values of κ are in good agreement (Fig. 3).

Thus, the selectivity of sorption of ions by an ion exchanger can be determined from the concentration dependences of the conductivity of the ion exchange membrane in the respective homoionic and heteroionic forms. On the other hand, knowing the isoconductivity points of the membrane in its homoionic forms and the ion-exchange constant, we can estimate the membrane conductivity in mixed electrolyte solutions at other compositions of the equilibrium solution.

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