THE DEPENDENCE OF ELECTRICAL CONDUCTIVITY OF ION-EXCHANGE MEMBRANES ON THE CHARGE OF COUNTER IONS

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Abstract. In this work the impedance of cation- and anion-exchange membranes has been measured in electrolyte solutions with ions of different charges in a wide range of concentrations. It is shown that the true value of membrane specific conductivity can be obtained only with the infinite dilution of the equilibrium electrolyte. It has been found that the cation-exchange membrane conductivity decreases with increasing the charge of the counter ions. The specific conductivity of anion-exchange membranes at the infinite dilution is constant due to the fact that multiply charged anions in a neutral medium are transferred to singly charged counter ions.

Keywords: impedance meter, contact-difference method, cation- and anion-exchange membranes, multiply charged ions, specific conductivity.

INTRODUCTION

The idea of Equilibrium in a semi-permeable membrane — solution system was first considered by *D. V. Gibbs* (1876) in his first work "The Equilibrium of Heterogeneous Substances" [1], and it was written rigorously by mathematical language and not readily available for many chemists of the time; hence, many of them were rediscovered again. In particular, the theory of membrane equilibrium was published by *F. G. Donnan* in 1911 [2] which refers to the distribution of ion species between two ionic solutions separated by semi-permeable membrane and was named Gibbs — Donnan equilibrium.

The basic idea of Gibbs — Donnan equilibrium was the equilibration of concentrations of mobile ions in the membrane (the counter ions and co-ions) and in solution regardless of the presence of fixed ions in the membrane. Donnan equilibrium considered a cation-exchange membrane with a 1—1 charges of strong electrolyte solution:

$$\bar{c}_+ \cdot \bar{\bar{c}}_- = c_+ \cdot c_- = c^2, \qquad (1)$$

where $\bar{c}_+$ and $\bar{\bar{c}}_-$ are the concentration of counter ions and co-ions in membrane phase respectively, and c_+ — and c_- are concentrations of counter ions and co-ions in solution phase respectively. The co-ions have the same charge sign as that of the fixed ions. Since the concentration of cations and anions is equal in the solution while maintaining electro-neutrality condition, then they can be written as the product of the square of the concentration of the electrolyte (1). Electro-neutrality condition in phase boundary between solution and ion-exchange membrane of cation-exchanger, which has a high concentration of fixed ion X:

$$X + \bar{\bar{c}}_- = \bar{c}_+, \qquad (2)$$

leads to the inequality of the concentration of mobile ions, since the concentration of counter ions is significantly higher than that of the concentration of co-ions. At low concentrations of the equilibrium electrolyte solution, the concentration of co-ions is close to zero (1), due to the electrostatic repulsion of like-charges of fixed ions (Donnan exclusion effect), so the concentration of counter ions is close to the concentration of the fixed ions (2):

$$X \approx \bar{c}_+. \qquad (3)$$

The ion-exchange membranes find application in diverse processes (electrodialysis, electro-deionization, storage batteries, electro-chemical synthesis, fuel cells etc), which are energy source and environmental saving. The development of high chemical, mechanical and thermal stabilities of ion-exchange membrane,

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which meet the growing demands of the aforementioned processes, is of great importance. In all the above mentioned electrochemical processes, ion exchange membrane works as highly conducting medium of the interior concentration of the inorganic fixed ions in it [3]. The specific conductivity of ions in solution and membrane is proportional to the concentration of mobile ions in the system:

$$k = \sum_i z_i \lambda_i c_i, \qquad (4)$$

where λ_i — molar conductivity of ion, z_i — dimensionless charge number of ion. In strongly diluted solutions, conductivity of membrane is constant due to the fact that the concentration of mobile counter ion is equal to the concentration of fixed ions (3). The increment of concentration into a membrane inter-phase system permeates the Donnan electrolyte sorption which leads to the increment of specific conductivity of the membrane.

In the previous scholarly works done, conductivity measurements of ion-exchange membranes were carried out mainly in solutions of singly charged cations and anions in the high and medium concentration levels. The aim of this work is to study the concentration dependence of the conductivity of ion-exchange membranes in electrolyte solutions containing multiply charged ions with wide ranges of concentrations.

EXPERIMENTAL METHOD

Methods for measuring the electrical conductivity of ion-exchange membranes can be divided into three groups — the difference, contact and contact-difference methods. In difference method, measuring the conductivity of the membrane is done using the sample cell that contains two electrodes connected to the cell in the bottom and the upper part of it. Between the electrodes the solution and membrane can be placed. The electrical resistance of the cell is measured first for that of solution with membrane and then for solution without membrane, and by taking the difference between them the electrical resistance of the membrane is determined [4]. The disadvantage of this method is that the difficulty of measuring the conductivity of membranes in diluted electrolyte solution, mainly in an infinitely diluted solution the conductivity is equal to that of the pure solution, because in this case there is no membrane Donnan sorbed electrolyte. The cause of the fundamental errors of this method is the need to calculate the difference between two electrical resistances of the solution and solution with membrane which is very large.

The second possible method of measuring the conductivity of membrane is the contact method in which a direct measurement of the electrical resistance of the membrane between the electrodes is taken place [5, 6]. Fig. 1 shows a scheme of the contact method, when a single membrane is placed between the electrodes and its electrical resistance is measured. The disadvantage of this method is the presence of a resistivity of the boundary phase between the electrode and the membrane, which constitutes a significant amount. This deficiency has been corrected by measuring the resistivity of two and single membranes in the contact cell (Fig. 1). The difference between the electrical resistances of two and single membranes is taken as a true value of the electrical resistivity of the membrane. This method is called contact — difference method [7].

In this work, the sample cell shown in Fig. 1 is connected to impedance meter TESLA 507, which measures the total complex resistivity (impedance) Z. In the coordinates of the Nyquist plot $\mathrm{Im}(Z), \mathrm{Re}(Z)$ under the phase angle of ϑ, the magnitude of Z is obtained from the total measured value of impedance vector, a line is drown perpendicular to the axis $\mathrm{Re}(Z)$, which gives the value of pure resistance R. To measure the resistance of the membrane in contact-difference method, it is necessary to use the characteristics of vector differences of impedances of two and single membranes, as shown in Fig. 2. From impedance values of the two and single membranes $Z_2 - Z_1$ is obtained by drowing a line perpendicular to the coordi-
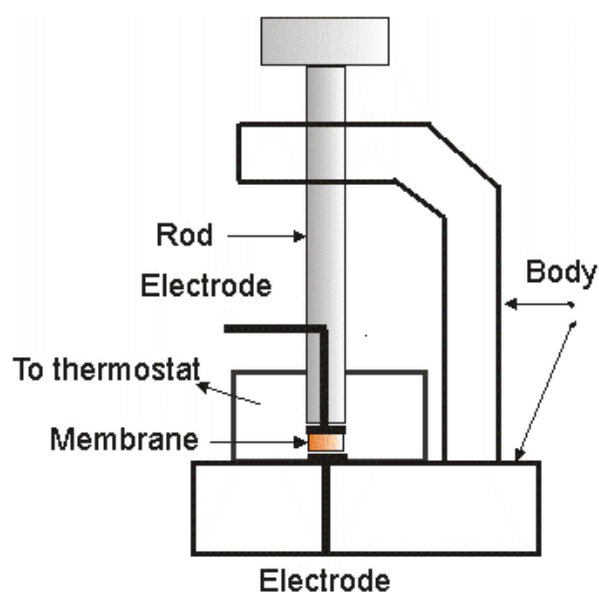

Fig. 1. Scheme of sample cell for measuring the conductivity of membrane using contact and contact-difference methods

nate of the real axis of Nyquist plot that allows to find the true resistivity of the membrane R:

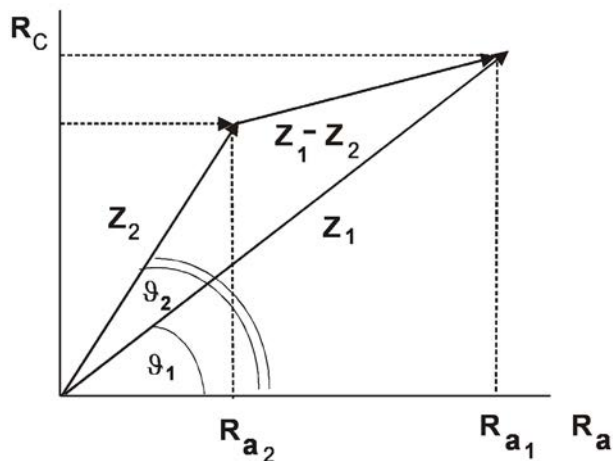$$R = R_{a_1} - R_{a_2} = \frac{d}{\kappa S}, \qquad (5)$$

Fig. 2. Scheme of the vector difference in measuring impedance of membranes

where d — the membrane thickness, measured by a micrometer, κ — electrical conductivity of the membrane, S — the surface area of the electrodes or membranes. Thus, the conductivity of the membrane is determined by the equation:

$$\kappa = \frac{d}{(R_{a_1} - R_{a_2})S}. \qquad (6)$$

For this experimental works, the serial of heterogeneous membranes MC-40 and MA-41 were taken that have been produced by compressing the composites consisting of 2/3 of the ion-exchangers and polyethylene. Cation-exchange membrane MC-40 was prepared from a strong acid cation-exchanger KU-2 and anion-exchange membrane MA-41 from the highly basic anion exchanger AV-17. Prior to the measurements of the conductivity of the membrane MC-40 it was equilibrated with the chloride salt solution of sodium, magnesium and aluminum ions with concentration ranging from 0.1 mol /L to 10^{-5} mol/L, in the same manner anion-exchange membrane MA-41 was equilibrated with the sodium salt solution of chloride, nitrate, sulphate and phosphate ions with concentration ranges from 0.1 mol /L to 10^{-5} mol/L in separate containers for at least 24 hours. After the equilibration of ions between solution and membrane, the electrical resistivity of the membrane was measured using the impedance meter connected with the contact- difference sample cell (Fig. 1). And then the resistivity was converted to the specific conductivity using the equation (6).

RESULTS AND DISCUSSION

Fig. 3 shows the measured values of conductivity of cation-exchange membranes MC-40 as a function of the equilibrium concentration of the electrolyte solutions containing differently charged cations. Commonly to all, the dependencies of the conductivities of the membranes are exponentially decaying upon the dilution of equilibrium concentration of solutions. Conductivities values of membranes MC-40 were measured at the equilibrium concentration of sodium chloride 0.6 mol /L, which is close to the value of its concentration in seawater. This suggests selecting the appropriate concentration of the standard solution in solving the technical problem of demineralization of sea water, but not a scientific problem, since the standard concentration in the membrane phase is the main contributor of the conductivity that comes from the non-exchangeable sorbed sodium chloride in the cation-exchange membrane. The minimum values of the conductivity for all of the cation-exchange membranes were prepared at a maximum dilution where almost no non-exchangeable sorbed electrolyte concentrations in the membrane and the concentration of counter ions is close to the concentration of fixed ions.
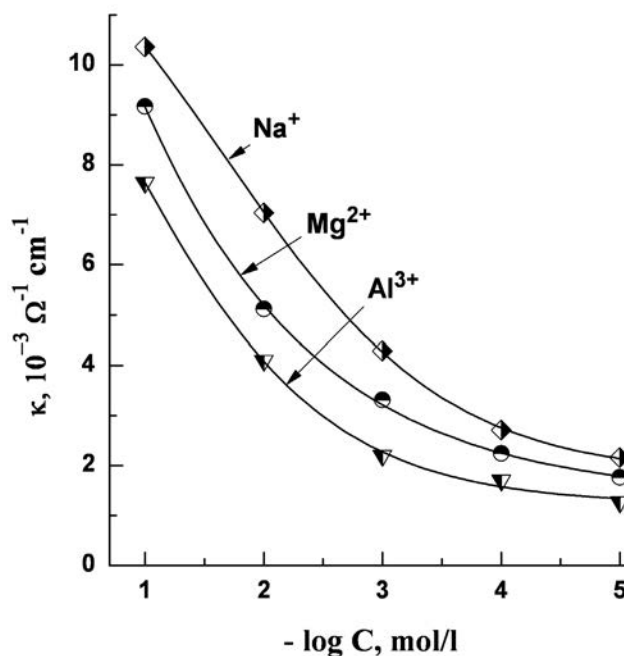

Fig. 3. Dependence of specific conductivity of cation-exchange membrane MC-40 on the concentration of chloride salt solutions of sodium, magnesium and aluminum

In all of the concentrations of equilibrium solutions, the specific conductivity of the membrane in the

form of singly charged sodium counter ion is higher than that of the doubly charged magnesium and triply charged aluminum ions. The cause of the differences in conductivities of membrane MC-40 in different ionic forms is that sulfo-cation exchanger has higher affinity to multiply charged ions as compared to singly charged ions. Previously we have calculated the structure of cation-exchangers in the form of differently charged counter ions using quantum — chemical (ab initio) method and the obtained structures were used to calculate the energy of the electrostatic interaction of a fixed ions with counter ions of different charge numbers [8]. The resulting structures have allowed us to find the distance between fixed ion and the counter ions and their effective charges that have been used to calculate the energy of the electrostatic interaction between the sulfonate groups in the cation-exchanger and counter ions of different charge numbers using the integral form of the equation of Coulomb's law [9]:

$$E = \frac{z_+ z_- e^2}{\varepsilon r}, \qquad (7)$$

where z_+ — the number of charges of the cation, z_- — the number of charges of anion, e_0 — the charge of electron, ε — dielectric permittivity, r — the distance between the oxygen atoms of sulfo-group and counter ion. The result of calculation of the electrostatic interaction energy of a fixed ion with singly charged counter-ion of sodium gave a value of 3.8 kJ/mol, with doubly charged counter ion of magnesium 12.8 kJ/mol, and with triply charged counter ion of aluminum 20.8 kJ/mol. The larger the value of the Columbic interaction energy of a fixed ion with that of counter ions, the lower the electrical mobility of the mobile ions and the lower the value of specific conductivity. These results explain the reason why the conductivity of singly charged counter ion of sodium is larger than that of doubly charged ion of magnesium and triply charged ion of aluminum for the entire range of concentrations of the equilibrium solutions. Fig. 4 shows the dependence of the conductivity of the anion exchange membrane MA-41 on the equilibrium concentration of electrolyte solutions containing multiply charged anions. Comparing Figs. 3 and 4, it is possible to find the common features and differences between them. The Common features of the two are that with the dilution of concentrations of the equilibrium solutions, the specific conductivity of the membrane decreases in both cases, this is due to a decrease in the non-exchangeable sorbed electrolytes.
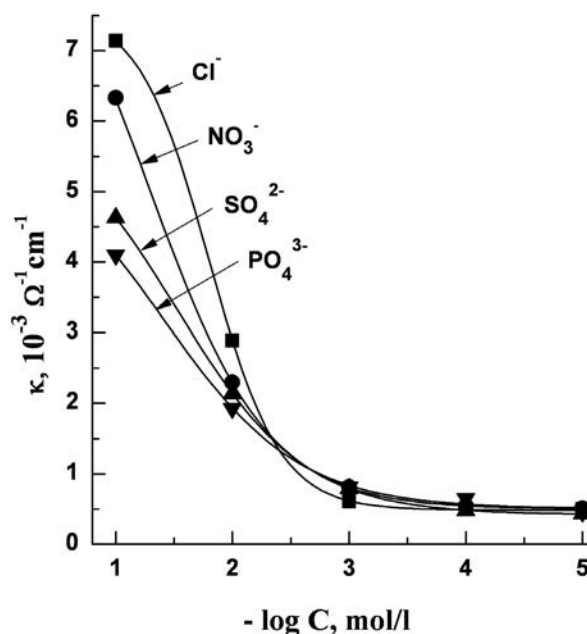

Fig. 4. Dependence of specific conductivity of anion-exchange membrane MA-41 on the concentration of sodium salt solutions of chloride, sulphate and phosphate

The difference between the concentration dependence of anion- and cation-exchange membranes is that at infinite dilution of equilibrium electrolyte solutions, the specific conductivities of anion-exchange membranes are not dependent on the number of charge of anions, where as the conductivities of cation-exchange membranes are highly dependent on the number of charges. The cause of these equal conductivities of anions at infinite dilution is that multiply charged anions are preferably changed to the acids form of multiply charged anions. In particular, sodium phosphate, dissolved in distilled water at pH 5.7, can form a monovalent sodium dihydrogenphosphate, because of this the effect of the charge on conductivity of anion exchange membrane was not observed upon infinite dilution of solution.

CONCLUSIONS

It was shown that the conductivities of ion-exchange membranes in the forms of multiply charged ions decrease exponentially upon dilution of solutions. In this work we have proved that the true resistivity of ion-exchange membranes should be measured by impedance meter with a contact-difference method at infinite dilution of equilibrium solution. In this work we also found that the various values of conductivities of the cation-exchange membranes, in which upon infinite dilution of the solution, their value decreases with increasing charge of the counter ions; however,

in the case of anion-exchange membranes in which multiply charged anions in neutral solutions transfer to singly charged ions, the dependence of the conductivity of membrane on the number of charges was not observed at infinite dilution of the solutions.

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