Self-diffusion coefficient of ions and the types of chemical bonds in the cation exchanger

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Abstract

Using method of direct conductometry and theoretical ab initio quantum-chemical method we obtained the results allowing us to identify the type of chemical bonds exist in the cation exchanger that plays the determining role in the elementary act of transport of ions through cation exchange membrane. There has been found that for singly charged ions of alkali metals hydrogen bond plays the decisive role in their transport, where as for the multi charged cations the contributions of hydrogen and ionic bonds are more or less the same.

Keywords: Self-diffusion coefficient, mobility, ion-exchanger, conductivity, quantum-chemical method

Методом прямой кондуктометрии и теоретически неэмпирическим квантово- химическим методом получены результаты, позволяющие определить тип химической связи в катионообменниках при элементарном транспортном акте. Установлено, что для однозарядных ионов щелочных металлов определяющей является водородная связь, а для многозарядных катионов вклады водородной и ионной связи близки по величинам.

Ключевые слова: коэффициенты самодиффузии, подвижности, ионообменник, электропроводность, квантово-химический метод

Introduction

Researches in chemistry can be viewed as fundamental if they study the chemical bonds between atoms in the emerging compounds. In ion-exchanger, the issue of chemical bond has been given little attention. According to IUPAC nomenclature the ion-exchanger is defined as a solid or liquid, inorganic or organic material containing ions, exchangeable with other ions of the same charge sign present in a solution in which the exchanger is supposed to be insoluble. The most common type of ion exchangers are polymers containing a fixed ion in their matrix that unable to exchange with other ions. In accordance with the condition of electro-neutrality, the charge of fixed ion is compensated by the charge of movable counter ion that can be taken place in the exchange process which has the same charge sign. Atoms in the polymer matrix of the ion-exchanger are connected by strong covalent bonds, which do not participate in the ion exchange process. Ion exchange is a process of exchanging ions between a solution and ion-exchanger in which the forming and braking of ionic bonds are taken place. In this regard, ion exchange process can be considered as a process of breaking one and forming other ionic bond [1].

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Like counter ions, fixed ions can also form hydration with some water molecules in which the hydrogen bonds are formed between their hydration shells. In the study of ion exchange process and electro-migration of the alkali metal cations, it was found that an ionic bond is much weaker than hydrogen bond; this is because of the increase in the distance between the charges and the dielectric permittivity of inter-ionic space during hydration. Due to this the conclusion has been made that hydrogen bond plays the determining role in ion exchange processes [2, 3]. The aim of the current work is to study the problem of cation exchange process of multiply-charged counter ions, which have large values of the electrostatic interaction with the fixed ions in comparison with the singly charged alkali metal cations [4]. This allowed us fundamentally to understand the relationship between chemical bonds arising from the ion exchange processes. For this study, different methods have been used to understand the chemical bonds affecting the transport of ions in ion exchange membrane, like theoretical methods based on quantum-chemical calculations and the experimental method based on conductometry, that allow us to judge about the mobility and self-diffusion coefficients of counter ions in the cation exchanger.

Experimental

There are three method of measuring the electrical conductivity of ion-exchange membranes. The first one is the difference method which is based on measuring the electrical resistance of the cell with membrane in equilibrium with a solution and the equilibrium solution itself separately. The difference of the two determines the true value of the electrical resistance of the membrane [5]. This method allows measuring precisely the electrical conductivity of the membrane in equilibrium with the medium and concentrated solutions of electrolytes. In dilute solutions, this method leads to significant measurement errors, since it is necessary to determine the difference between two large quantities. However, it is in very dilute solutions, the real conductivity of the membrane can be measured, because in the medium and concentration solutions the exchanger comprises non exchangeable adsorbed electrolyte (Gibbs equilibrium - Donnan) and therefore the electrical conductivity of electrolyte solution is preferably measured rather than the membrane.

Contact method is another method that measure conductivity of membrane in measuring directly the electrical resistance of the membrane which comprises the conductivity of electrodes [6]. It has been found that the contact method involves a large electrical resistance of the electrode - solution phase boundary that leads to the dependence of the electrical conductivity on the frequency of the alternating current used for the conductometric measurements [7].

In this paper contact-difference method was applied [8], in which electrical resistance of one and two membranes were measured. By finding the difference of the two, the true conductivity of a membrane which does not depend on the frequency of the alternating current was obtained. Fig. 1 shows a sample cell of contact-difference method that is applied in this work.

Measurements were carried out using Tesla 507 impedancemetry, which can measure the total impedance Z and the phase angle φ. The magnitude of Z is plotted in the coordinates of Nyquist Im(Z) - Re (Z) at an angle φ. From the resulting vector impedance value, the line is drown perpendicular to the Re (Z) axis, which makes it possible to determine the magnitude of the real electrical resistance R. The vector subtraction between resistances of one and two membranes gives the true electrical resistance (R) of the

membrane. From the obtaine value of the real electrical resistance of the two and one membrane, the specific conductivity of the membrane (κ) was determined as indicated by equation (1).
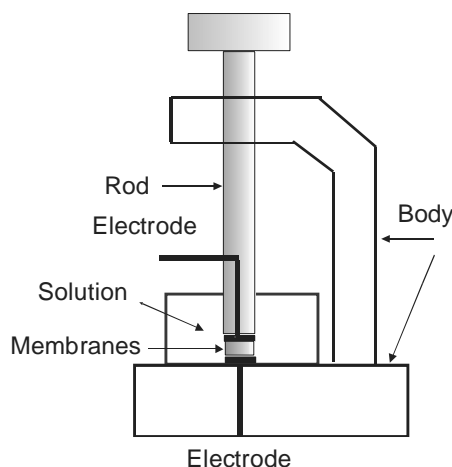

Fig. 1. Sample cell used for measuring the electrical conductivity of membranes by contact and contact-difference methods

$$R = \frac{d}{\kappa S}, \tag{1}$$

where d - membrane thickness, S - area of the membrane or electrode. The electrical mobility u of ions has been calculated by using equation (2).

$$u = \frac{\kappa}{Fc}, \tag{2}$$

in which F - Faraday's constant, c - the concentration of ions in the membrane (mol /dm^3). To determine the concentration of ions in the membrane, first the massive capacitance E of the membrane is measured (meq/g), and then the membrane density γ (3).

$$c = \frac{z_i E \gamma}{1000} \tag{3}$$

To determine the density of the membrane a simple and quick method has been applied.

A weighed sample of the membrane was cut into small pieces and placed in a cylinder in which a previously known liquid non-electrolyte that has lower density than that of the membrane (toluene). Then into the cylinder containing membrane and less dense liquid non-electrolyte, another non-electrolyte solution denser than the membrane was poured drop wise from the burette (carbon tetrachloride). When the density of mixture of non-electrolyte solutions was reached equal to the density of the membrane, the pieces of membrane started floating and hovered in the volume of the cylinder container, somewhat like particles "fluidized" layer. Then the density of the mixture was measured with a hydrometer which is assumed to be equal to the density of the membrane. The self-diffusion coefficient of ions in the ion exchange membrane D was calculated using the Nernst-Einstein equation (4)

$$D_i = kTu, \tag{4}$$

where k - Boltzmann constant, T - absolute temperature. The temperature dependency of the measured self-diffusion coefficients of the fluid in the cylinder container of the cell shown in Fig. 1 that was placed in heat exchangers coupled with ultra-thermostat. This allows us to measure the diffusion coefficients at a given temperature.

Results and discussions

Self-diffusion coefficients of the condensed bodies is determined by the equation (5)

$$D_i = \frac{\delta^2}{6t_o} exp\left(-\frac{E_a}{kT}\right), \tag{5}$$

in which δ - a path in which the particle passes in an elementary act of transport, t_o - the time of single oscillations in a potential well, E_a - activation energy. After dividing the self-diffusion coefficients obtained at various temperatures, we obtain (6)

$$D_2 = D_1 exp \frac{E_a(T_2 - T_1)}{kT_1T_2} \tag{6}$$

the energies of activation which was determined using the equation (7)

$$E_a = \frac{kT_1T_2 \cdot ln(D_2/D_1)}{T_2 - T_1} \tag{7}$$

was experimentally measured using the temperature dependence of electrical conductivity of ion exchange membrane MC-40, which was produced from sulfo-cation exchanger KU-2. The experimental results are calculated by equations (1-4) in the form of temperature dependency of self-diffusion coefficients, membranes were first transferred into a salt forms, prior to measurement of electrical conductivity and then they were put in distilled water that brought it in equilibrium with pure water. The results are shown in Figure 2. The calculation of the effective activation energy in equation (7) is shown in Table 1.

To determine the energy of electrostatic interaction between counter and fixed ions, the quantum – chemical method was used by optimizing the structural fragment of cation exchange membrane in the form of singly charged sodium, doubly charged magnesium and triply charged aluminum ions. The calculation was done using MMMO method by stepwise doing the molecular mechanics (MM) in the first step and the molecular orbital (MO) method in the second step. The method of molecular mechanics allows us to calculate the covalent bonds in cation exchange membrane made of sulfonated polystyrene cross linked with divinylbenzene. The linear combinations of atomic orbitals (LCAO MO) method was used to calculate the ionic and hydrogen bonds in the hydrated form of the cation exchanger. Finally the structural optimization of cation exchanger was performed using 6-31 G basis functions to calculate the structure of the cation exchanger in the form of singly charged sodium and STO - 3 G to calculate the structure of the cation exchanger in the form of multiply charged ions of magnesium and aluminum. The structure of cation exchanger in the form of magnesium ion was presented in previous work [4]. Fig. 3 shows the optimized structure of the cation exchanger in the form of triply charged aluminum ion.

The quantum - chemical calculation method yielded the values of inter-ionic distances and that of the effective charges of fixed and counter ions as shown in Table 1. The necessary parameter for the calculation of the Coulomb's interaction energy between fixed and counter ions in the ion exchange membrane is the value of dielectric permittivity of the system, which was calculated by using the modified Debye equation [9,10] as shown in equation (8).

$$\varepsilon(r) = 78 - 77\left(\frac{r}{2.5}\right)^2 \frac{e^{r/2.5}}{(e^{r/2.5} - 1)^2} \tag{8}$$
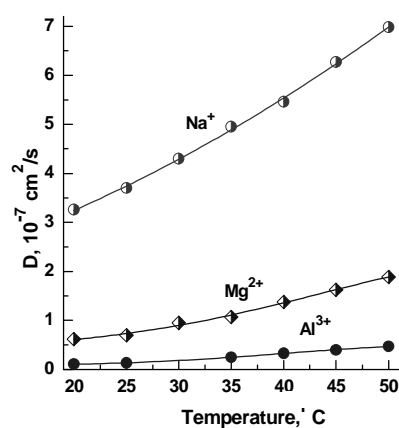
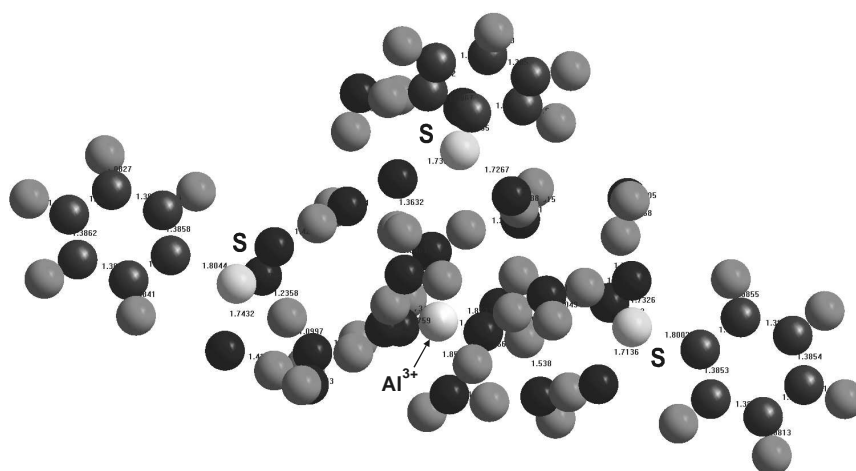Fig. 2. Dependence of self-diffusion coefficients of ions in the cation exchange membrane on temperature

Fig. 3. Fragmental structure of sulfo-cation exchange membrane in the form of aluminum ion (aluminum cation and sulfur atoms are shown by symbols)

To calculate the electrostatic interaction energy of counter ions with fixed ion in ion-exchanger, the integral form of Coulomb's law was used (9).

$$E_{el} = \frac{z_+ z_- e^2}{\varepsilon r}, \qquad (9)$$

where z - effective number of charges of the ion, e - electron charge, ε - dielectric constant, r - distance between the charges. The result of calculation of the electrostatic interaction energy of the counter and fixed ions is given in Table 1.

Table 1. The results of conductometric measurements and quantum - chemical calculations

Counter ions	r, Å	ε	z_+	E, kJ/mol			
				E_a	E_{el}	E_H	E_H/E_{el}
Na^+	4.36	17.5	0.55	19.7	3.8	15.9	4.2
Mg^{2+}	4.70	19.3	1.02	29.0	12.8	16.1	1.3
Al^{3+}	4.84	20.2	1.36	37.4	20.8	16.6	0.8

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If the activation energy is considered as an overall amount of energy necessary to overcome the potential barrier of counter ion in ion-exchanger, then it is possible to provide the approximate estimation of hydrogen bond dissociation energy by taking the difference in the activation energy and Coulomb's interaction energy of fixed and counter ions. These values are given in Table 1. Energy of formation and breaking of hydrogen bonds are hardly dependent on the charges of counter ions, however, there has been possible to note some increment in its value with increasing charges of counter ions. Comparing the energies of the hydrogen bond in water 16.7 kJ / mol [11] and in the ion-exchange membranes (Table 1), it can be noted that the obtained values of hydrogen bond energies are more or less closer to the literature value.

Conclusion

The obtained results allow us to compare the contributions of ionic and hydrogen bonds to the activation energy of the system which is considered as potential barrier of transport of ions. For singly charged ion sodium, the ratio of hydrogen bond to the ionic bond is 4.2, this leads to the valid conclusion that the hydrogen bond can play a dominant role in the ion exchange process and electro-migration of ions in their transport through ion exchange membrane [3]. For doubly charged magnesium ion, the contribution of the hydrogen bond energy is slightly higher than the contribution of the electrostatic interaction energy between fixed ion and counter ion, so that the dominant role of hydrogen bond is not significant in case of magnesium. For triply charged aluminum ion, the hydrogen bond contribution is even smaller than the contribution of the ionic bond between the counter ion and the fixed ion. Therefore, this study indicates that the necessity of considering both the role of hydrogen and ionic bonds in ion-exchange processes and electro-migration, and it was found that with increasing charge of counter ion, the role of hydrogen bonding decreases in ions transport trough ion exchange membrane where as the role of the electrostatic interaction between fixed and counter-ions increases. The main conclusion is that both the hydrogen and ionic bonds are highly considered in ion-exchange process and electro-mass transport of ions through ion-exchange membrane during electrodialysis.

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