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ELECTRICAL CONDUCTANCE STUDIES ON ION EXCHANGE MEMBRANE USING CONTACT-DIFFERENCE METHOD

Tolera Seda Badessa[a,*], Vladimir Alexeevich Shaposhnik[b]

[a] Department of Chemistry, College of Natural Science, Arba Minch University, P.O.Box 21, Arba Minch, Ethiopia
[b] Department of Analytical Chemistry, Faculty of Chemistry, Voronezh State University, Universitetskaya Sq. 1, 394006 Voronezh, Russia

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ABSTRACT

Comparisons of contact-difference and contact methods for the measurement of membrane conductivity were made. It was found that the conductivity of the ion exchange membrane at infinite dilution can be accurately measured only by contact-difference method (CDM) in equilibrium with highly diluted electrolyte solutions. The dependence of the measured specific electrical conductivity and impedance of ion exchange membranes on the concentration, temperature, charges of counter ions and frequency of an electric field was discussed. Good agreement was found between the experimentally determined activation energy of ion-exchange membranes in the form of ions of different charges and the calculated activation energy using ab initio quantum chemical method.

1. Introduction

Ion exchangers, in the forms of membranes and granules are conductors of the second kind. In extremely dilute solutions, ion exchange membranes contain only one kind of mobile ions (counter ions) and are unipolar conductors of electricity. However, in solutions of medium and high concentrations, non-exchangeable adsorption of electrolyte takes place, and the ion exchanger becomes a complicated system described by the Gibbs – Donnan equilibrium [1,2]. With increasing the concentration of the solution in which the membrane is present, its selectivity decreases and the conductivity value is attributed not only to the membrane, but also to the conductivity of non-exchangeable sorbed ions of the electrolyte.

The difference and contact methods of measuring the electrical conductivity of membrane were widely used in different research works. For the first time in 1929, the difference method was used to measure the electrical conductivity of collodion membranes [3]. In this method, the difference of the measured electrical resistance of a cell filled with solution containing membrane and without membrane was conducted and converted into membrane conductivity. G. Manecke [4,5] measured the conductivity of anion and cation exchange membranes for the first time using a difference method. The method gives reproducible results when the concentration of external solution is not lower than 0.01 mol/L. However, measuring the conductivity of membrane in dilute solutions by this method gives large difference between two values of the resistances and results in a significant reduction in the reproducibility (precision) of the method. For membrane conductivity testing, the concentration of the solution used is usually closer to seawater. For example, the French standard for testing the conductivity of ion-exchange membranes uses the equilibrium concentration of 0.5 mol/L and that of Russian standard uses 0.6 mol/L, due to their proximity to the ocean water [6,7]. At this concentration the membrane contains not only the mobile counter ions but also the Donnanian sorbed electrolyte, in which the concentrations of co-ions and counter ions are higher than in dilute solutions. In the medium to high concentrated solutions, electrical conductivity is largely a function of the concentration and mobility of the Donnanian sorbed electrolyte, and not a function of the concentration of counter-ions. In this connection it is possible to conclude that the electrical conductivity measurement of ion exchange membrane by the difference method in both concentrated and at infinite dilution does not yield the correct result. Differential difference method [8] gives better results as compared to the traditional difference method for measuring conductivity; however, it also does not allow correct measurement of the

* Corresponding author.
E-mail address: toleraseda@yahoo.com (T.S. Badessa).

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electrical conductivity of the ion exchange membrane in extremely dilute solutions. Another type of the difference method is with a cell made of electrical insulating material having electrodes on the inner surface [9]. This method has the advantage of measuring membrane conductivity very fast.

Contact method is another type of measuring the conductivity of a membrane. It was used for the first time to measure the electrical resistance of longitudinal ion-exchange membranes [10]. In this method, the measurement was conducted with the electrodes directly connected to a strip of the ion exchange membrane. Although this method has the advantage of a rapid measurement, it also has a disadvantage. Shunting of the membrane with the film of the solution during measurement of the electrical conductivity of homogeneous ion exchange membranes and the effect of reinforcing fabric on the electrical conductivity of heterogeneous ion-exchange membranes are the main problems of the method.

In the measurement of the transversal conductivity of a membrane using the contact method, the strip of the membrane is placed between two planar platinum electrodes and the resistance of the membrane is measured and then converted to conductivity [11]. The flow of electrical current during electrodialysis with ion exchange membranes is due to the movement of ions through cross section of the membrane. Therefore, it is practically important to measure only transversal electrical conductivity of the membrane. The main drawback of this method is the compression of the membrane, in which the deformation of the membrane occurs during the measurement. To prevent the problem of deformation, mercury electrode is commonly used [12]. However, the contact – mercury method has its own drawbacks associated with the formation of capacitance and electrical resistance of the solution film between mercury electrode and membrane [13]. Other disadvantages of the mercury method are related to the toxicity of mercury vapor and the effect on the reproducibility results from the permissive velocity of the membrane in the cell. It has been found that the time between removal of the sample from the solution, and immersing it in mercury should not exceed 6 to 8 seconds [14].

The results of conductivity of ion exchange membranes that were measured by different methods have been compared in [15]. It is worth mentioning that the results of measurements by different methods are significantly different. Except mercury-contact method, all methods indicate that the membrane specific conductivity increases with increasing concentration of the solution in which the membrane is immersed. In mercury-contact method, however, the conductivity increases with decreasing concentration. The increase in the electrical conductivity of the membrane with decreasing concentration of the electrolyte solution is contrary to the logic of Gibbs – Donnan equilibrium [1,2] and casts doubt on the validity of the method for measuring membrane conductivity. In [16] the electrical conductivity of the membrane was measured using a mobile electrode for membrane characterization. The resistance of membrane was also measured as a function of concentration in [17]. In these papers, the electrical conductance and resistance of only monovalent ions were measured as a function of concentration. A new method of measuring the conductivity of ion exchange membranes was introduced in [18]. The method focuses only on measuring the lateral resistance of the membrane for a wide range of concentration without contact between membrane and electrode. The purpose of the current work is primarily to analyze the dependence of electrical conductivity of ion exchange membranes on the concentration of the equilibrium solution of electrolyte, the AC frequency, temperature and charges of counter ions, as well as to show the optimal method of measuring membrane conductivity at infinite dilution.

2. Instrumentation, material and methods

2.1. Contact – difference method (CDM)

CDM combines the well-known methods mentioned above. It consists of contact and difference methods in which electrical resistance of two membranes and one membrane is measured and then their difference is the actual resistance of the membrane. In this case the measured resistance of the membrane is independent of the resistances of the solution film between electrodes and the membrane. Differential contact – difference method was developed for inclusion in the parallel arms of the cell with one membrane and two membranes. In the current work, CDM was used to investigate the concentration, temperature and frequency dependences of electrical conductivity of membrane, whereby the membrane and electrodes were placed in the thermostatic glass cylinder with heat exchangers connected by a rubber tube to the ultra-thermostat [19]. Edge effect has an impact on the electrical conductivity of solution at concentrations above the iso-electrical conductance. To prevent this effect, at higher concentration of the designed experiment we measured the conductivity of the membrane by releasing the rod-containing electrode on membrane with ring plexi-glass that screens current lines coming from solution. Fig. 1 shows the general view of the cell, which was used for measuring the electrical conductivity both by the contact method and CDM.

During the measurement, one or two membranes are placed between the electrodes. To do this, the rod is raised up and released down after putting the membrane between the electrodes. The weight is placed on top of the platform to maintain membrane-electrode contact. For the measurement of membrane conductivity using CDM, initially two membranes and then one membrane were placed between the two electrodes, the electrical resistances were measured, then their difference R2 – R1 is the resistance of the membrane, which is finally converted to specific conductivity κ calculated by the equation (1).

$$\kappa = \frac{d}{(R_2 - R_1)S} \quad (1)$$

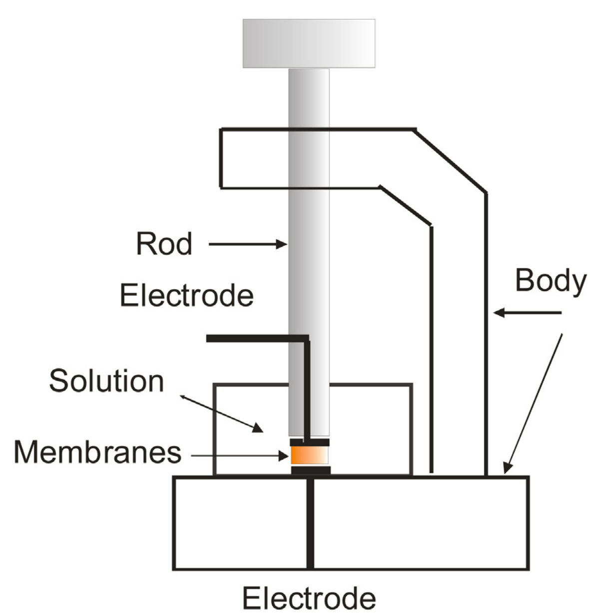

Fig. 1. The Sample cell for measuring the electrical conductivity of membrane by contact and contact – difference methods.