Journal of Membrane Science 498 (2016) 86–93

Contents lists available at ScienceDirect

Journal of Membrane Science

journal homepage: www.elsevier.com/locate/memsci

The electrodialysis of electrolyte solutions of multi-charged cations

Tolera Badessa*, Vladimir Shaposhnik

Department of Analytical chemistry, Faculty of chemistry, Voronezh State University, Universitetskaya pl. 1, Voronezh 394006, Russia

ARTICLE INFO

Article history:
Received 28 February 2015
Received in revised form
9 September 2015
Accepted 11 September 2015
Available online 22 October 2015

Keywords:
Multi-charged cations
Cation-exchange membrane
Electrodialysis
Generation of hydrogen ions
Quantum chemical method

ABSTRACT

The quantum chemical calculation of the structure of ion exchange membrane in the form of differently charged cations was performed. The contribution of ionic and hydrogen bonds to the activation energy during the ion transport was investigated. The obtained results show that the energy of ionic bond increases with increasing the charges of cations while the energy of hydrogen bond remains the same. In singly charged cation, the hydrogen bonding plays the determining role in the ion transport, in doubly charged cation the energy of ionic bond is half of the energy of hydrogen bond and hence electrostatic interaction also has a significant role in the transport of ions. For triply charge cation, both ionic bond and hydrogen bond energies are of comparable values and hence they equally contribute to the magnitude of the potential barrier in the transport of ions through membrane. To see these effects practically, the electrodialysis of electrolyte solutions of differently charged cations was studied and their fluxes were investigated. Fluxes of cations through cation exchange membrane in the electrodialysis of electrolyte solutions of multi-charged cations were found to decrease with increasing charges. The generation of hydrogen ions on the interface of solution and cation exchange membrane was also studied and interpreted.

1. Introduction

The base for any science related to pure or applied chemistry is the nature of chemical bonds. In the membrane science a little attention has been given to this problem. Previous works [1,2] on ion-exchange membranes in solutions of alkali metal salts, show that hydrogen bond has the main role in the ionic transport in the membrane. And it was shown that the activation energy of the ionic transport is almost equal to the energy required to break the hydrogen bonds. The current work focuses to investigate the transport of cations with different charges through cation exchange membrane during electrodialysis. Since multiply charged cations have more energy of electrostatic interaction than singly charged cation, we expected to get an answer to the question of the relationship between the energies of hydrogen and ionic bonds during the electromigration of ions through the membrane. This problem is common also for analyzing the selectivity of ion exchangers and in the reverse osmosis.

In addition, the transports of multiply charged ions during electrodialysis with alternating cation and anion exchange membranes have practical importance because the underground and mine water contain alkaline earth metal cations and cations of triply charged iron and aluminum. In this regard, one of the goals of the work was to study the process of irreversible dissociation of water molecules in the overlimiting current density, which has been the cause of precipitation of these ions in concentrate cells.

Among the main methods of electrochemistry of membrane processes, electrodialysis with ion-exchange membranes is the most economical for the desalination of brackish water with a concentration of less than 8 g/L [3,4]. During the electrodialysis of brackish water in the region of intensive current density, the phenomenon of irreversible dissociation of water molecules takes place [5]. This leads to a generation of hydrogen ions at the interface of solution-cation exchange membrane, the hydroxyl ions on the boundary layer of anion exchange membrane and the solution [6]. Kressman and Tye [7] introduced the concept of the limiting current density with electro-migration of ions through ion-exchange membranes. Application of intensive current modes, when current density is above its limiting value, increases the rate of electrodialysis process [8,9]. B. A. Cooke in his work indicates that the flux of hydroxyl ions through anion exchange membrane is substantially greater than the flux of hydrogen ions through cation exchange membrane [10]. The difference in the rates of generation of hydrogen and hydroxyl ions in the boundary layer of solution-anion exchange membrane and solution-cation exchange membrane leads to an increase in the pH of solutions of concentrate cells of electrodialyzer. In the electrodialysis of an electrolyte solutions containing singly charged cations, principally the change in pH does not affect the process, but in the electrodialysis of the solutions containing doubly and triply charged cations, the

---

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

http://dx.doi.org/10.1016/j.memsci.2015.09.017
0376-7388/

change in pH leads to the formation of sparingly soluble hydroxides in the concentrate cells of the electrodialyzer, which blocks the surface of anion exchange membranes, increases the electrical resistance of the electro-membrane system and contributes to the termination of transport process.

In the study of the processes taking place in electrodialysis beyond the limiting current density, there was a problem of neutralization of hydrogen ions by hydroxyl ions in solutions of concentrate cells. In such studies, the pH measurement gives information only about the flux of hydrogen ions through the cation-exchange membrane that have not been neutralized by hydroxyl ions and distorts the information about the flux of hydrogen ions partially entering into the neutralization reaction with hydroxyl ions. Previously, a method was proposed that allows measuring the fluxes of hydrogen ions through cation-exchange membrane and hydroxyl ions through anion exchange membrane in electrodialysis of solutions of singly charged ions [5]. The study indicates that there is no passivation of the surface of a membrane. The dependence of fluxes of salt ions and ions of water molecule through ion-exchange membrane under electrodialysis on ion-exchange membrane composition was studied for singly charged ions in the work [11]. There are a number of research works related to transports of ions through ion exchange membranes during electrodialysis, which are mostly focused on the theory of electrodialysis and transports of singly charged and in some cases doubly charged ions[12–23]. The transport of triply charged ions, which is the main focuses of our current study was not reported. In general there is no detailed studies have been documented on the nature of chemical bonds and the transport of doubly and triply charged cations through cation exchange membrane during electrodialysis of their salt solutions at current density above the limiting values. This is mainly because of the lack of adequate research methods to protect the blockage of membrane by the precipitates of sparingly soluble electrolytes of these cations.

2. Experimental method

2.1. Chemicals and reagents

All chemicals and reagents used were of analytical reagent grade unless otherwise stated. Distilled-deionized water was used for the preparation of solutions. The chloride forms of sodium, calcium and aluminum were used to prepare electrolyte solutions of the cations for the electrodialysis. Buck scientific company (USA) 1000 ppm standard solutions of sodium, calcium and aluminum were used to prepare a series of working standard solutions for the calibration of the instruments. The triammonium salt of aurintricarboxylic acid (Aluminon) was used as compelexing agent for the determination of aluminum ions in sample solutions. 10% NaOH and 10% HCl were used for the preparation of membranes that were used in electrodialysis.

2.2. Instruments and apparatus

Apparatus such as volumetric flasks (both glasses and plastics), measuring cylinders, bottles, and beakers were washed with detergents and tap water, rinsed with distilled water, soaked in concentrated nitric acid, then rinsed with distilled water, dried and kept in clean place until needed for use.

Fig. 1 shows a schematic diagram for the continuous direct flow electrodialysis process. It contains 7 cells separated alternatively by cation exchange membrane MK- 40 and anion exchange membrane MA-41 brands made up of polymethylmethacrylate produced by JSC “Shchekinoazot.” The cells were bounded by pins. Heterogeneous cation exchange membrane is composed of 3/2 sulfo-cation exchanger KU-2 and polyethylene. The mixture was compressed between reinforcing Dacron fabrics. The cation exchanger KU-2 was obtained by sulfonation of polystyrene. To create a three dimensional structure of the membrane, 8% divinylbenzene was added during the synthesis as a cross agent. Anion-exchange membranes were prepared by compressing strongly basic anion exchanger AV-17, polyethylene and lavsan polyester reinforcing fabric. The electrodes of electrodialysis were made of platinum, which prevent both electrochemical and chemical dissolution of electrodes in acids and alkalies solutions that are formed during electrode reactions. The source of direct current was AIP-D5, which provides the terminals of the apparatus with a constant electric current. The galvanostatic mode was used to supply the apparatus with a constant electric current. A high resistance voltmeter V7-15 was used to measure the electrical potential difference between the terminals of the electrodialyzer. Anion-exchange membranes were prepared by compressing a mixture of a highly basic anion exchanger AV-17, having benzyl trimethyl ammonium ion as a fixed group (2/3), and polyethylene as inert filler material. Cation-exchange membranes were prepared by compressing strongly acidic cation exchanger KU-2, having a sulfo-cation exchanger as a fixed group (2/3), and polyethylene as inert filler material.

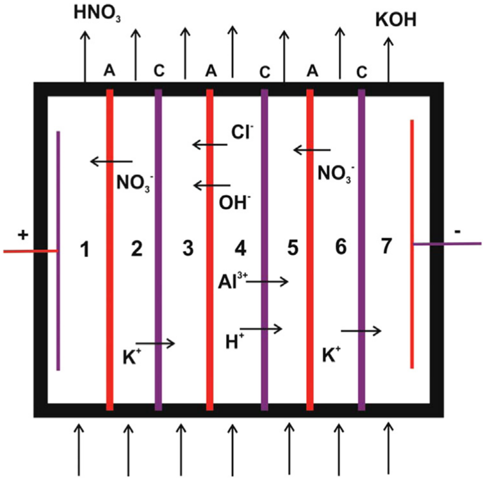

Fig. 1. Schematic diagram of electrodialyzer with alternating anion-exchange (A) and cation-exchange (K) membranes, 1- 7-number of cells.

For the analysis of sodium and calcium ions in test solutions that were collected during electrodialysis, flame emission photometer of model PAZH-1 (Russia) was used. And for the determination of aluminum ion, direct spectrophotometer model FTC.2. YXL42 No. 913136 having external wavelength filter (Russia) was used. The pH of the medium was measured by direct potentiometry using ion meter EV-74 connected to glass electrode ESR-10101 as indicator and silver chloride electrode as reference.

2.3. Preparation of ion exchange membranes

Preparation of membrane MK-40 and MA-41 to use in the apparatus of electrodialyzer was performed in the following steps. The surface of the membranes was rubbed with cotton moistened with CCl_4 to remove the oily film then it was immersed in ethanol for 6 h in separate containers. It was then immersed consecutively in saturated, 100 g/L and 30 g/L of NaCl solutions for 24 h. After immersing the membranes in distilled-deionized water for 48 hours, cation-exchange membrane (MK-40) was immersed in 10% HCl and anion-exchange membrane (MA-41) was in 10% NaOH solutions for 48 h. Again immersing the membrane in distilled-deionized water for 48 h, the cation exchange membrane was