The Proton Leakage Through Polyether-Sulfone Anion Exchange Membrane

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Abstract

The proton leakage through polyether sulfone anion exchange membrane was investigated. In the system containing hydrochloric acid or sulphuric acid on the cathodic side and the mixture of acid with alkali salt solutions on the anodic side was performed. The effect of alkali salt solutions was examined as a function of mole fraction in the anodic side. The proton leakage on the membrane is quantified from proton transport number value. The proton leakage was found to be higher for sulphuric acid compared with hydrochloric acid.

Key Words: Proton leakage, polyether-sulfone, anion exchange membrane, membrane transport, acid recovery.

Introduction

Recovery of acids from wastewater or industrial effluents is very important because of environmental protection as well as economy in resources [1-10]. Today, treatment of the waste acidic solutions is a serious recovery problem and they are either purified or discarded. In general, purification is preferable from the point of recovery of resources, but disposal is often chosen as the less expensive alternative method. Electromembrane process is a favourable method in the recovery of acids from waste effluents or the regeneration of acids or bases from salts [11-15]. In the process of bleaching wood pulp, H_2SO_4-Na_2SO_4 solutions were treated in order to reconconcentrate H_2SO_4, to obtain pure Na_2SO_4 [15]. The concentration of H_2SO_4 from the alkali sulphates was studied with throcompartment electrolytic cell by using anion and cation exchange membranes [16-17]. The optimum operating conditions for recovering sulphuric acid from acidic wastewater released in metallurgic industry were determined for electrodialysis process [18]. Classical anion exchange membranes for electrodialysis processes are not suitable for acid recovery due to high proton leakage through these membranes. The proton has specific properties due to its mobility and non-conformist structure and migrates generally by a mechanism which is different from the other ions. From this point, the proton leakage phenomena are the main problem encountered during the acid recovery. Acid recovery from electromembrane process is performed by either electrodialysis, on bipolar membrane or electro-electrodialysis. In this process, limiting current efficiency is also important for electro transport of acids through anion exchange membrane.

The aim of this work was to examine the possible use of SB-6407 anion-exchange membrane in recovering inorganic acids from waste effluent by electro-electrodialysis and focused experimental determination of the proton leakage through anion exchange membrane separating an inorganic acid on one side and acid-salt solution on the other. The inorganic acids chosen were H_2SO_4 or HCI mixed with their monoacid alkaline salts.

Experimental

All chemicals were purchased from Merck and were reagent grade. The membrane studied (SB-6407), is strongly basic anion-exchange

membrane and was obtained from Gelman Sciences Neosepta-AMH anion-exchange membrane was used for comparison, obtained from Eurodia (Tokuyama Soda Co. Ltd.). The ion exchange capacities of SB-6407 and Neosepta-AMH membranes are 2.15 and 1.90 mmolg^{-1} and thicknesses are 0.152 and 0.260 mm respectively. Before use, the membranes were pre-treated in boiling water for 1 hr, then conditioned by a cycle of equilibrations with in turn, concentrated HCl, distilled water, NaOH, distilled water and finally kept in 1M HCl or H$_2$SO$_4$ solution for 24 hr.

The proton leakage measurements

The proton leakage through membranes was performed by electro-electrodialysis (EED) measurements made in symmetric Teflon cell that consists of two chambers of equal volume separated by a membrane with an active area of 7 cm^2 between two smooth Pt electrodes. The schematic description of the cell is presented in Figure 1. The anodic chamber contained 40 mL of a mixed solution [xH$_2$SO$_4$-(1-x) M$_2$SO$_4$ or xHCl-(1-x) MCL], M: Na or K$^+$, the molarities of the acid and salt solutions was 0.1 mol/L.
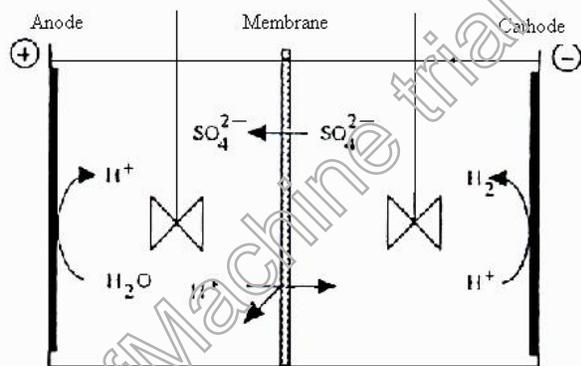

Fig. 1. Experimental description for the proton leakage measurements.

The cathodic chamber was filled with 0.1 M HCl or H$_2$SO$_4$. The concentration of two acids was taken constant in order to compare the proton leakage of the membranes for the two acids. In the literature [3], free proton concentrations for 1 M H$_2$SO$_4$ and 1 M HCl are given as 1.20 M and 1 M, respectively. The applied current density was 2 mA cm^{-2} and duration of electrolysis was 30 min. After

electrolysis, the proton concentration in both chambers was determined by acid-base titration. The concentrations of alkali cation in the cathodic chambers were determined by flame-photometry (Corning). All measurements were carried out at room temperature and determinations were repeated three times for each set of experimental conditions.

Results and Discussion

The amount of transported proton from anodic chamber to cathodic chamber was determined by acid-base titration. The transported proton was performed by applying the current, when one faraday current crosses the membrane; one mole of proton is reduced at the cathode while a certain amount E_{H+} mole of proton is transferred from anode chamber. The transported proton is called as "apparent" transport number of proton, which is performed by different mechanisms, ionic migration, electrolyte diffusion, and electro osmotic flow etc. The proton transport number was calculated by using the following equation;

$$E_{H^+} = \frac{(C_f V_f - C_i V_i)F}{I.t}$$

where C_i and C_f the initial and final concentration of proton, V_i and V_f the initial and final volume of the cathodic chambers, respectively, I the current density, F, the faraday constant and t is electrolysis time. Electrolysis time was taken as 30 min, and it was decided with preliminary experiments that after 30 min of electrolysis, further transport was not significant due to reduction of H$^+$ in the cathodic electrodes.

The variation of proton transport number was presented as a function of mole fraction of H$_2$SO$_4$-K$_2$SO$_4$ or Na$_2$SO$_4$ and HCl-KCl or NaCl mixtures for SB-6407 and Neosepta-AMH membranes in Figure 2 and Figure 3, respectively. It is seen from both figures that, the proton leakage values of H$_2$SO$_4$ mixtures were found to be higher than those of HCl for both membranes. The proton transport number values were obtained as 0.11±0.01 for H$_2$SO$_4$-K$_2$SO$_4$ and 0.08±0.01 for H$_2$SO$_4$-Na$_2$SO$_4$ mixtures for molar fraction of 0.5. The transport number values for Neosepta AMH membrane were found as 0.11 and 0.09 for H$_2$SO$_4$-K$_2$SO$_4$ and H$_2$SO$_4$-Na$_2$SO$_4$ mixtures for the same

mole fraction, respectively. The proton leakage was slightly increased with increasing acid concentration for H_2SO_4-K_2SO_4 mixture and this is not remarkable for H_2SO_4-Na_2SO_4 mixture. In case of HCl mixture, the values of proton transport were lower than those of H_2SO_4 and these results are in agreement with the data in the literature.
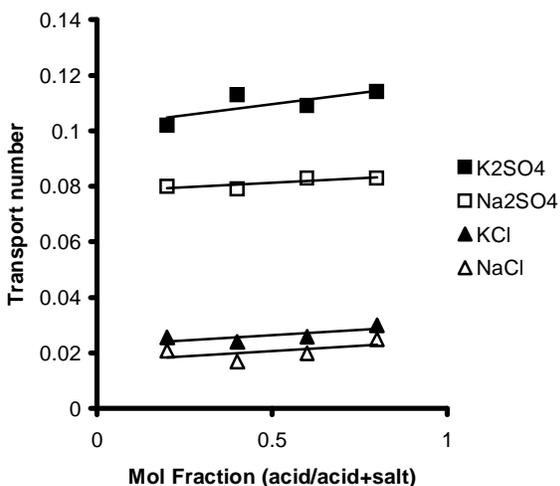

Fig. 2. Transport number of the proton (proton leakage) through SB-6407 anion exchange membrane as a function of acid concentration.

When the proton transport numbers obtained were small when compared with the literature. The present work in paper, the applied current efficiency was 2mA cm^{-2} which is small when, compared with the literature (70 or 100 mA cm^{-2}) [3]. The current efficiency was kept as lower because of the reduction of hydrogen in the cathodic electrode. In preliminary experiments, the current was directly applied to the chambers, and when the current efficiency was greater than 2mA cm^{-2}, air bubbles were observed at the electrode. Therefore, current efficiency was kept as 2mA cm^{-2} during the experiments.

Alkali cation transport was also measured in the cathodic chambers. However, the measured alkali cation in the cathodic chambers was not significant and it is difficult to explain the obtained values at this applied current efficiency. In this paper the aim was to find the effect of alkali salt solutions and the effect of H_2SO_4-K_2SO_4 mixture was found to be higher than that of H_2SO_4-Na_2SO_4 mixture on the proton leakage. In this work, only the effects of K and Na cations were investigated.

Generally, smaller ions have larger heats of hydration and a small ion contains more concentrated charge, leading to a greater electrostatic interaction between the ion and polar water molecules. The hydration number is directly proportional to the charge and inversely proportional to the size of ion. The hydration number of Na is higher than that of K ion [19]. So the higher hydration (Na ion) increases the mobility of proton from anodic chamber to the cathodic chamber.
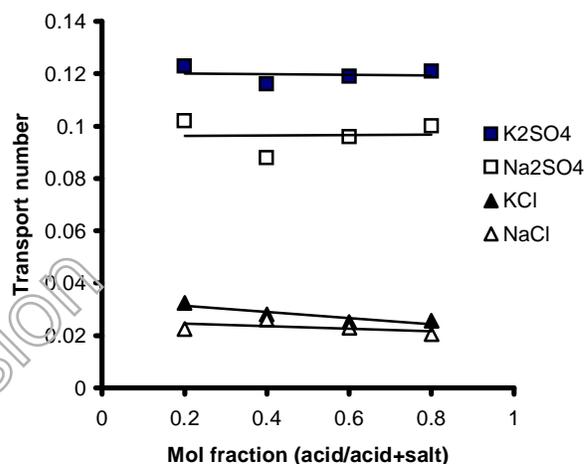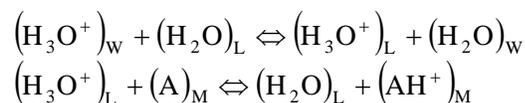

Fig. 3. Transport number of the proton (proton leakage) through Neosepta AMH anion exchange membrane as a function of acid concentration.

Two different proton transport models for anion exchange membranes were proposed [3]. The first one is called the Grotthus mechanism which describes the migration of H_3O^+ by succession of proton hopping steps. The proton hops from H_3O^+ ion to a neighbouring H_2O and it propagates to another. In the second mechanism which is called the Bjerrum fault, the proton transfer occurs by a succession of molecular rotations such a way that all protons progress by one small distance in a given direction.
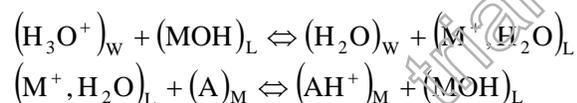
These two mechanisms have been applied to membranes by Nagle et al. [20]. In the anodic side, the cations are not transferred but, are present at the solution-membrane interface. The presence of M-OH groups at the membrane-solution interface is related to polarising power of cation. It was reported that the polarising power of K$^+$ is negligible. In case of Na$^+$ from NaOH is present in the interfacial layer. According to two

mechanisms, the proton transport can be described according to the following reactions. At first, the transport is mediated with water molecules and secondly, it introduces the polarising cations in to the layers in contact with the membrane. Here the electrical field in the interfacial layer is important. The dissociation power of NaOH increases with respect to Wien effect [21]. The transfer reactions one represented as follows;

$$\left(H_3O^+\right)_W + \left(H_2O\right)_L \Leftrightarrow \left(H_3O^+\right)_L + \left(H_2O\right)_W$$
$$\left(H_3O^+\right)_L + \left(A\right)_M \Leftrightarrow \left(H_2O\right)_L + \left(AH^+\right)_M$$

where, W, L, and M represents the anodic aqueous solution, interfacial layer, and membrane phase, respectively. A is one of proton acceptors, either H_2O or charged group and promotes the proton transport within the membrane. When the aqueous solution contains sulphuric acid or HCl A is SO_4^{-2}, or Cl^-.

According to two mechanisms, the transport can be mediated by the hydrated polarising cation present in the interfacial layer with a two-step exchange reaction as follows;

$$\left(H_3O^+\right)_W + \left(MOH\right)_L \Leftrightarrow \left(H_2O\right)_W + \left(M^+, H_2O\right)_L$$
$$\left(M^+, H_2O\right)_L + \left(A\right)_M \Leftrightarrow \left(AH^+\right)_M + \left(MOH\right)_L$$

Therefore the flux of proton leakage is related to the polarising power of a cation present in the interfacial layer.

Conclusion

The proton leakage through anion-exchange membranes was investigated as a function of acid and alkali cation concentration for electromembrane process, which is specially designed in acid media. When the proton leakage of H_2SO_4 and HCl were compared, the proton leakage obtained was always higher for H_2SO_4 as presented for free proton concentration in the solution. The effect of alkali cation was found to depend on the hydrating number in the order of K>Na. However, the effect of hydration number should be investigated for all alkali cation series.

The proton leakage slightly increases when the proportion of salt decreases in the anodic chamber.

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