

초청강연 I

Anion Exchange Membrane Having Permselectivity for specific Anion in Electrodialysis

Toshikatsu Sata

Faculty of Engineering, Yamaguchi University,

Registered Consulting Engineer,

Ohoshima Ohara 89-57, Tokuyama City,

Yamaguchi Prefecture, 745 0803, Japan

Abstract

To change permselectivity between anions through the anion exchange membrane in electrodialysis, the various modified anion exchange membranes were prepared: highly crosslinked anion exchange membranes, anion exchange membranes having benzyl trialkylammonium groups with different carbon number of alkyl chain as anion exchange groups and anion exchange membranes having pyridinium groups with a hydrophilic or hydrophobic substituent at a different position as anion exchange groups. It became clear from the evaluation of these membranes that the degree of the hydrophilicity of the anion exchange membranes greatly affects the permselectivity between two anions. To increase the hydrophilicity of the anion exchange membranes further, electrodialysis was carried out in the presence of ethylene glycols and the permeation of strongly hydrated anions increased and that of less-hydrated anions decreased. It became clear that the change in the permselectivity between two anions is due to the change in the affinity of anions to the membranes, not the change in mobility ratio of the anions in the membranes phase.

I. Introduction

The ion exchange membranes are one of the most advanced separation membranes and have been used in various industries: electrodialysis to concentrate or deionize electrolyte solutions, diffusion dialysis to recover acid or alkali from waste acid and alkali solutions, as a separator for electrolysis as in chlor-alkali production, etc. The ion exchange membrane is a polymeric membrane having cationic or/and anionic charges and can basically separate cations from anions or anions from cations. Though the performance of the ion exchange membranes has been vastly improved, the membranes cannot separate ions with the same sign. Namely, when given specific ions should be

concentrated or removed from a solution, conventional ion exchange membranes are ineffective. For this reason, several specific ion exchange membranes were developed, e.g., monovalent cation or anion permselective membranes[1], anti-organic fouling membranes[2], proton permselective ion exchange membranes[3].

In recent years, the concentration of nitrate ions in groundwater has greatly increased due to excess use of artificial fertilizers. This is a serious problem because nitrate ions are harmful to human health. European Community proposed that the concentration of nitrate ions in drinking water should be below 25 ppm. However, the concentration of nitrate ions in groundwater of some places exceeds 50 ppm. On the other hand, there is some places where the concentration of fluoride ions in groundwater is high and many people has been suffered from the fluoride ions[4]. Electrodialysis is one of the promising methods to remove harmful ions if ion exchange membranes having permselectivity for specific ions were developed. Thus, it is desirable to establish the preparation method of ion exchange membranes having permselectivity for specific ions or electrodialysis method to permeate specific ions. The permselectivity of specific ions in ion exchange membranes is governed by the difference of the mobility of each ions in the membrane phase and the affinity of the ions to the membrane (ion exchange equilibrium constant) similar to other non-porous separation membranes such as gas separation membranes and membranes for pervaporation process.

In this work, anion exchange membranes having permselectivity for specific anions and electrodialysis method to permeate specific ions through the membranes were summerized from our recent studies.

II. Experimental

1. Preparation of anion exchange membranes and electrodialysis method.

1) Anion exchange membranes with high crosslinkage[5].

A copolymer membranes composed of chloromethylstyrene and divinylbenzene(divinylbenzene: 10%) reacted with N,N,N',N'-tetramethylethylenediamine, N,N,N',N'-tetramethyl-1,3-propanediamine or N,N,N',N'-tetramethyl-1,6-hexanediamine to form high crosslinkage and to introduce quaternary ammonium groups in the anion exchange membranes.

2) Introduction of benzyl trialkylammonium groups with different carbon number of alkyl chain into a crosslinked membrane as anion exchange groups[6].

A copolymer membrane prepared from chloromethylstyrene and divinylbenzene(divinylbenzene: 10%) reacted with various amines,

4 한국막학회 98년도 춘계 학술발표회

trimethylamine, triethylamine, tri-n-propylamine, tri-n-butylamine and tri-n-pentylamine, to obtain anion exchange membranes with different hydrophilicity.

3) Anion exchange membranes having various pyridinium groups with a substituent on the pyridinium as anion exchange groups[7].

A copolymer membrane prepared from chloromethylstyrene and divinylbenzene(divinylbenzene: 10%)reacted with various pyridine derivatives (ethyl pyridines, pyridine ethanols,etc.). The ethyl pyridines and pyridine ethanols used have a substituent at the 2-,3- and 4-position.

4) Electrodialysis in the presence of ethylene glycols using anion exchange membranes[8].

After ethylene glycols (ethylene glycol, diethylene glycol, triethylene glycol, tetraethylene glycol, etc.) had been adsorbed on th anion exchange membranes, electrodialysis was carried out using th mixed salt solution containing the ethylene glycols of various concentrations because alcoholic groups and ether bonds are hydrophilic.

2. Measurements.

A four compartment cell[6] with Ag-AgCl electrodes was used to evaluate the transport number of various anions relative to chloride ions in electrodialysis (amount of solution in each compartment: 100 cm³; effective membrane area: 10 cm²). The anion exchange membrane to be measured to be measured was placed at the center of the cell and the anolyte and catholyte were separated from two middle compartments by cation exchange membranes (sodium choride solution was used as the anolyte and catholyte). The transport number of anions A relative to chloride ions was measured using a 1:1 mixed salt solution: sodium sulfate and sodium chloride, sodium nitrate and sodium chloride, sodium bromide and sodium chloride or sodium fluoride and sodium chloride. The transport number of anions A relative to chloride ions was defined by the eqution: $P_{Cl}^A = (t_A/t_{Cl})/C_A/C_{Cl}$: t_A and t_{Cl} are transport numbers of A^- and Cl^- in the membrane phase, C_A , C_{Cl} average concentrations of A^- and Cl^- during electrodialysis, respectively. The current efficiency was also measured by the amount of transported anions through the membrane and electricity measured with a coulometer.

III. Results and Discussion

1. Permselectivity between various anions and chloride ions of highly crosslinked anion exchange membranes.

In general, larger ions become difficult to permeate through the ion exchange membranes with increasing crosslinkage. N,N,N',N'- tetramethyl

alkylenediamines were reacted with chloromethyl groups of a membrane crosslinked with divinylbenzot to form high crosslinkage. Permeability coefficient of urea (Stokes radius: 3.3Å) through the membranes was about 100 times lower than that of the membrane with benzyl trimethylammonium groups. Sulfate and fluoride ions became difficult to permeate through the membranes and nitrate and bromide ions became easy to permeate through the membranes with increasing number of methylene groups of the diamines. Because sulfate and nitrate ions are apparently larger than chloride ions, the results were opposite to what was expected (the pore size of the membranes is expected to increase with increasing number of methylene groups). Permselectivity between anions was governed by not only the degree of crosslinkage of the membranes, but also carbon number of alkyl groups.

2. The effect of carbon number of alkyl chain bonded to ammonium groups on the permselectivity between two anions.

It is expected from the above result that less-hydrated anions easily permeate through the anion exchange membranes and strongly hydrated anions permeate through the membrane with difficulty with increasing carbon number of alkyl chain bonded to ammonium groups. Namely, because the hydrophilicity of the anion exchange membranes is thought to affect the permselectivity between two anions, transport numbers of anions relative to chloride ions were examined using anion exchange membranes with different anion exchange groups (from benzyl trimethylammonium groups to benzyl tri-n-pentylammonium groups). With increasing chain length of alkyl groups bonded to ammonium groups, the permeation of strongly hydrated anions compared with chloride ions, sulfate and fluoride ions, decreased and that of less-hydrated anions, nitrate and bromide ions, increased. A relationship between the Gibbs hydration energy of anions and the transport numbers of various anions relative to chloride ions was recognized (e.g., Gibbs hydration energies of sulfate, fluoride, chloride, bromide and nitrate ions: -1000, -434, -317, -303 and -270 kJ/mol, respectively). It was confirmed from mobility ratios between anions in the membrane phase and ion exchange equilibrium constants between them that permselectivity between two anions is due to the change in the affinity of respective anions to the membranes, not the change in mobility ratio of anions in the membrane phase[6].

3. The effect of a hydrophilic or hydrophobic substituent on pyridinium groups on the permselectivity between two anions[7].

The effect of a hydrophilic or hydrophobic group near ammonium groups on

the permselectivity between two anions was examined using anion exchange membranes having pyridinium with a substituent at the 2-, 3- and 4-position as anion exchange groups. When a hydrophilic group, -OH, existed at the 2-position of the pyridinium groups, the permeation of sulfate ions increased and that of bromide ions was decreased. On the other hand, the permeation of bromide and nitrate ions was enhanced with ethyl groups at the 2-position of the pyridinium groups. Atmosphere around the anion exchange groups clearly affected the permselectivity between two anions depending on the hydration degree of anions.

4. Electrodialysis of the mixed salt solution in the presence of ethylene glycols[8].

The backbone polymer of ion exchange membranes is basically hydrophobic due to existence of many aromatic groups. To increase hydrophilicity of the anion exchange membranes further, electrodialysis was carried out in the presence of ethylene glycols in the mixed salt solution after the glycols had been adsorbed on the membranes. With increasing concentration of the ethylene glycols, the permeation of sulfate and fluoride ions increased and that of nitrate and bromide ions decrease. This is also based on the change in ion-exchange equilibrium constants between each anions and chloride ions in the presence of the glycols, not the change in mobility ratio of in the membrane phase. [8].

IV. References.

1. T. Sata and R. Izuo, *J. Membrane Sci.*, 45, 209 (1985); R. Yamane, Y. Mizutani, H. Motomura and R. Izuo, *Denki Kagaku*, 32, 277 (1964), etc.
2. T. Sata, *Colloid Polym. Sci.*, 256, 62 (1978).
3. Y. Yamane, R. Izuo and Y. Mizutani, *Denki Kagaku*, 33, 589 (1965),
4. *Drinking Water Atlas of China*, Institute of Environmental Health Monitoring, Chinese Academy of Preventive Medicine, China Cartographic, Peking, China, 1994, p.147, 149.
5. T. Sata, K. Teshima and T. Yamaguchi, *J. Polymer Sci., Polym. Chem. Ed.*, 34, 1475 (1996).
6. T. Sata, T. Yamaguchi and K. Matsusaki, *J. Phys. Chem.*, 99, 12875 (1995).
7. T. Sata, Y. Yamane and K. Matsusaki, *J. Polymer Sci. A. Polym. Chem.*, 36, 49 (1998).
8. T. Sata, K. Mine and M. Higa, *J. Membrane Sci.*, 141, 137 (1998).