No 9501

Studies on Anion Exchange Membranes having Permselectivity between Halogen Ions

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Summary

One of the unsolved problems in ion exchange membranes is a lack of permselectivity of a specific ion though ions with different valence can be separated to some extent. In recent years, requirements for ion exchange membranes to separate ions with the same sign and same valence have been increasing: removal of nitrate ions from groundwater, decreasing permeation of bromide ions through the anion exchange membrane in sea water concentration, etc. In this work, trials to change permselectivity between halogen ions through the anion exchange membranes from their intrinsic values were made because most of anion exchange membranes selectively permeate bromide ions compared with chloride ions and fluoride ions are difficult to permeate through the membranes.

Though anion exchange groups of conventional anion exchange membranes are mainly benzyltrimethyl ammonium groups or N-methyl-pyridinium groups. Pyridinium groups are expected to make specific interaction between halogen ions. Thus, permselectivity between bromide ions and fluoride ions relative to chloride ions was examined by following membranes: 1) copolymer membranes of vinylpyridines-divinylbenzene (2-vinylpyridine-divinylbenzene, 2-vinylpyridine-4-vinylpyridine-divinylbenzene, 4-vinylpyridine-divinylbenzene) which were alkylated with different alkyl halides, and 2) copolymer membranes of chloromethylstyrene and divinylbenzene which reacted with pyridine derivatives such as ethylpyridines, pyridine methanols and 4-alkyl pyridines.

The anion exchange membrane from 4-vinylpyridine-divinylbenzene alkylated with methyl iodide showed the lowest permeation of bromide ions and the highest for fluoride ions among the anion exchange membranes of vinylpyridines-divinylbenzene. As the alkyl agent of pyridinium groups became hydrophobic, bromide ions easily permeated through the membranes. Crosslinking between pyridine unites with propyl dibromide did not decrease permeation of bromide ions.

The anion exchange membranes prepared from a membranous copolymer of chloromethylstyrene and divinylbenzene, and pyridine derivatives revealed that when hydrophilic groups such as methanol groups existed near pyridinium groups, fluoride ions easily permeated through the membranes compared with the membrane of which methanol groups existed in 4-position of pyridine, and bromide ions selectively permeated through the membranes in which hydrophobic groups such as ethyl groups existed near pyridinium groups.

From above results, permeation of anions through the anion exchange membranes was mainly controlled by balance of hydrophobicity and hydrophilicity of the ion exchange membranes with hydration of anions. To permeate selectively fluoride ions and bromide ions through the anion exchange membranes compared with chloride ions, the membrane should be strongly hydrophilic.

It is concluded that a new hydrophilic material except styrene-divinylbenzene copolymers should be explored for the matrix of the anion exchange membrane to achieve these selectivity.