

DOCTORAL THESIS

Synthesis, characterization of poly(amidesulfonamide)s (PASAs) and their applications in reverse osmosis and pervaporation processes

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**Synthesis, Characterization of Poly(amidesulfonamide)s
(PASAs) and Their Applications in Reverse Osmosis and
Pervaporation Processes**

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Abstract

Ten homopolymers and fifteen copolymers of poly(amide sulfonamide)s were synthesized by low-temperature polycondensation of five different diamino monomers with isophthaloyl chloride/terephthaloyl chloride in *N,N*-dimethylacetamide. The general reverse osmosis (RO) performance of these new membrane materials was investigated by using a systematic screening test which used 270 ppm nickel ion industrial waste as the feed solution. A copolymer series based on 2,5-dimethylpiperazine, 1,3-diaminopropane and terephthaloyl chloride emerged as the best polymer system in terms of RO separation characteristics. The RO tests for the membrane were performed at 20 kg cm⁻² operating pressure on three different feed solutions. Membranes showed salt rejection of up to 98.6 and 94.3% at a flux of 13 cm per day, respectively, for nickel and sodium ion feeds.

Seven poly(amidesulfonamide) homopolymers were selected for the preparation of pervaporation membranes. During the pervaporation of 90 wt.% aqueous solution of methanol, ethanol, 1-propanol, and 2-propanol, all the membranes were preferentially permeable to water. Their separation factors were mainly dependent on the molecular weight of the solvent. The exact structure of the PASAs had a profound effect on their pervaporation characteristics. Some of the selected PASAs materials demonstrated a higher transporting selectivity for water (relative to ethanol) but a low permeating flux (< 10 g m⁻² h⁻¹). Furthermore, symmetric nonporous membranes were fabricated from the five poly(amide sulfonamide)s derived from five different diamino monomers and isophthaloyl chloride. The transportation mechanism in the pervaporation process of ethanol/water mixtures was deduced. It was found that water preferentially permeated through all the PASA

membranes in all ranges of feed compositions. The dependence of the permeation rate on the feed composition was explained by the "fixed-carrier mediated" mechanism. The coupling interaction among water, ethanol and membranes affects the preferential sorption as well as the diffusion processes.

In order to improve the permeability of PASA membranes, PASA_{PM} polymerized from *N,N*-bis(4-aminophenylsulfonyl)-1,3-diaminopropane and isophthaloyl chloride was selected for the chemical modifications. Under basic conditions, the reaction of PASA_{PM} with a variety of alkylating agents gave five new *N*-alkylated derivatized polymers which were subsequently characterized by IR, ^1H -NMR and ^{13}C -NMR spectroscopic methods and thermal analysis. After the introduction of a alkyl pending group to the polymer backbone, all the modified membranes showed an enhancement in permeation flux and a variation of the separation factor in the pervaporation of aqueous alcohols. In the dehydration of ethanol, several modified membranes possessed separation characteristics superior to that of the parent membrane in terms of the pervaporation separation index (PSI).

The addition of zeolite fillers into the PASAs membranes is also a viable method to improve the permeation flux of the PASA membrane in the water/ethanol mixture pervaporation process. A more elaborate study will be required to verify the feasibility of improving the membrane separation characteristics through the zeolite modification.

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