CHAPTER-IX

SUMMARY

The present thesis addresses study on composite polymeric membranes for the pervaporation separation of different aqueous-organic mixtures. The goal of this thesis is to achieve a comprehensive understanding of separation characteristics of a hydrophilic polymer such as NaAlg and its modified forms by incorporating different particulate fillers. Such a study is very important and useful in many engineering areas. Composite polymeric membranes are able to offer enhanced flux and selectivity data for water in particular, which can be used successfully in separation and purification technology. The pervaporation-aided esterification was also studied for the conversion of ethanol and acetic acid to ethyl acetate. The present thesis comprises of nine chapters discussing about various aspects pervaporation membranes and the binary systems.

Chapter I presents a general introduction to the field of pervaporation and details of the historical perspective as well as literature search on different types of sodium alginate (NaAlg) membranes used in pervaporation separation. Up to date information is given.

In Chapter II, details of experimental protocols used are given. Procedure for the preparation of composite membranes filled with many different types of particulates systems have been presented. The details of pervapotation technique and esterification modules have been discussed. Many types of characterization techniques used for the newly developed membranes are presented.

In Chapter III, sodium alginate (NaAlg) and mesoporous molecular sieve (MCM-41)-filled NaAlg nanocomposite membranes prepared by solution casting and crosslinked with glutaraldehyde have been used in pervaporation separation of isopropanol at 30°C. A feed composition of 10-50 weight % water for the membrane containing 20 weight % MCM-41-loaded NaAlg membrane gave the highest...
selectivity ranging between 29,991 and 3332 for the feed water compositions of 10-50 weight %. Flux of the plain NaAlg membrane ranged between 0.067 and 0.340 kg/(m² h), while for 20 weight % MCM-41-filled NaAlg membrane, the flux increased from 0.110 to 0.555 kg/(m² h). To the best of our knowledge, this was the first study reported so far in the literature using an admixed hybrid composite of a mesoporous molecular sieve (MCM-41) with NaAlg for dehydration of isopropanol.

In Chapter IV, composite membranes of NaAlg prepared by solution casting method after incorporating with SBA-15 and Fe-SBA-15 molecular sieves have been crosslinked with glutaraldehyde. These membranes were tested for PV dehydration of isopropanol and 1,4-dioxane from their aqueous solutions at ambient temperature (30°C) to judge their performance capabilities over that of pristine NaAlg membrane. Infinite selectivity values with moderate fluxes have been observed for composite membranes in the feed compositions of 10-20 wt. % of water. A complete removal (100 wt. %) of water was achieved on permeate side with a slight compromise in flux. For the range of feed water compositions investigated, fluxes of the composite membranes have been slightly lower than the pristine NaAlg membrane. Pristine NaAlg could remove up to a maximum of 97 wt. % of water at higher feed water concentrations with the considerably much lower values of selectivity. Dual pore system of SBA-15, having both hydrophilic micropores and hydrophobic mesopores, in addition to its molecular sieving effect as well as its interaction with the NaAlg matrix were responsible for such an increased performance of the composite membranes.

In Chapter V, novel hybrid composite membranes have been prepared by incorporating 5 and 10 wt. % of sodium montmorillonite (Na⁺MMT) clay particles into NaAlg and crosslinked with glutaraldehyde. The PV separation performance of the hybrid composite membranes was investigated for dehydration of isopropanol, 1,4-dioxane and tetrahydrofuran (THF) from their aqueous solutions at 30°C. The effect of Na⁺MMT in NaAlg membrane was investigated and it was found that driving force for Na⁺MMT adsorption is entropic, which involves at least partial replacement of water of hydration associated with exchangeable cations in the clay galleries. The results of PV experiments demonstrated that addition of Na⁺MMT clay
particles would help to increase the selectivity to water over that of pristine NaAlg membrane by pushing its limit to infinity, giving a moderate flux. Permeation fluxes of the hybrid composite membranes were lower than those observed for plain NaAlg membrane.

Microporous materials are known to exhibit pronounced molecular sieving effect and selective adsorption capacity, the incorporation of which into NaAlg membrane was used to tailor the material intrinsic properties such as mechanical strength and separation performance. These data are discussed in Chapter VI. The filler used was microporous alumino-phosphate (AIPO₄-5), which was loaded into NaAlg to prepare composite membranes by the solution casting; membranes were further cross-linked with glutaraldehyde and tested for PV dehydration of azeotropic mixtures of aqueous isopropanol (12.6 wt. % water), 1,4-dioxane (18.1 wt.% water), THF (6.7 wt. % water) and ethanol (4 wt.% water) at 30, 40, 50, 60 and 70°C. The PV dehydration experiments at the feed compositions from 5 to 20 wt. % were performed for pristine NaAlg and 20 wt. % AIPO₄-5-loaded composite membranes at 30°C. The activation parameters of permeation were evaluated. The PV results have shown a simultaneous enhancement of flux and selectivity near the azeotropic compositions of all the feed mixtures as a result of adding varying amounts (5, 10, 15 and 20 wt.%) of AIPO₄-5 into NaAlg-based matrix. Flux and selectivity increased simultaneously for all the feed mixtures with increasing loadings of AIPO₄-5 at 30°C. Selectivity to water was higher for water-isopropanol azeotrope, but flux was more in case of water-1,4-dioxane and water-THF azeotropes. Selectivity to water was smaller for water-THF and water-ethanol azeotropes as compared to water-isopropanol and water-1,4-dioxane azeotropes. Pervaporation results have been discussed in terms of sorption-diffusion principles. Molecular sieving effect due to uniform distribution of microporous molecular sieve particles, and hydrophilic characteristics of the alumino-phosphate molecular sieve in addition to its interaction with the hydrophilic NaAlg matrix are responsible for such an appreciable increase in membrane performance over that of pristine cross-linked NaAlg membrane. Composite membranes of this study have shown better mechanical strength properties than the pristine cross-linked
NaAlg. The present membranes could withstand the repetitive cyclic PV processes when tested on a laboratory scale module.

In Chapter VII, PV separation performances of ZSM-5 and Na-Y type zeolite-filled NaAlg membranes were compared with those of pure NaAlg for the dehydration of acetonitrile. PV separation characteristics of the zeolite-filled membranes showed a dependence on the nature of zeolites. The variation of acidity function of ZSM-5 zeolite had an influence on flux and selectivity of the membranes when compared to the unfilled membranes. The crosslinked membranes were characterized by differential scanning calorimetry, X-ray diffraction, scanning electron microscopy, and Fourier transform infrared spectroscopy. Among the NaAlg membranes, plain NaAlg membrane showed the highest selectivity of 414 at 30 mass % water in the feed mixture, whereas Na-Y- and ZSM-5 (40)-filled NaAlg membranes exhibited much lower values of selectivity i.e., 7.3 and 4.3, respectively for 30 mass % water in the feed. When flux and selectivity data of ZSM-5 (250)-filled NaAlg membranes were compared with that of Na-Y or ZSM-5 (40)-filled NaAlg membranes, a noticeable increase in selectivity for ZSM-5 (250)-filled NaAlg membrane was observed, but a somewhat smaller flux was observed as compared to plain NaAlg membrane.

In Chapter VIII, the filled matrix membranes of NaAlg have been prepared by solution casting followed by in situ incorporation of 4A zeolite particles in 5 and 10 wt. % with respect to the weight of NaAlg. The membranes were crosslinked with glutaraldehyde and tested for PV dehydration of acetic acid and ethanol mixtures at 30°, 40° and 50°C. Infinite separation factors and moderate fluxes were achieved with the filled matrix membranes over the studied feed composition range of 10-30 wt. % water at 30°C with a complete removal (100 wt. %) of water on permeate line with a slight compromise in flux. The 4A zeolite, with its high hydrophilic nature as well as molecular sieving effect and its favorable interaction with the hydrophilic NaAlg, is responsible for such an improvement in PV dehydration performance. With increasing temperature, flux increased, but the amount of water extracted in permeate line was decreased. Arrhenius parameters for permeation have been calculated and these data are found to depend upon the type of membrane matrix used.
Pervaporation-aided catalytic esterification of acetic acid with ethanol was attempted at 70°C, which led to a considerable increase in ethyl acetate conversion with a reduction in reaction time due to the continuous removal of water permeating through the barrier membrane.

The research findings of the present thesis have been published in international journals of high impact factors and also accepted in national conferences. These details are given under publication record. In future, there is ample opportunity to continue this type of research by developing different types of membranes for attacking other mixture separation problems.