Summary

This thesis explained preparation, characterization and PV applications of organic/inorganic hybrid mixed matrix membranes prepared by solution casting technique. Different types of organic polymeric materials like sodium alginate, PVA, PVP, Chitosan and HEC incorporated with inorganic heteropolyacids such PMA, PWA, SWA and $\text{H}_{14}\text{P}_5$ were used in order to develop organic/inorganic hybrid mixed matrix membranes. Fabricated hybrid membranes were characterized by using FTIR spectroscopy, XRD study, TGA-DSC study, SEM and AFM analysis, Contact angle measurement and PALS analysis and used in separation of azeotropic mixtures of isopropanol and ethanol. These membranes were able to enhance the selectivity towards water with reasonable flux, which is an important task in many industries. The research carried out in this thesis is an effort to study the various aspects of polymeric membranes for pervaporation separation of binary systems.

Chapter 1:

Chapter I present a general introduction to the field of pervaporation separation. Details of the historical perspective as well as literature search have been given.

Chapter 2:

This chapter gives the details regarding the experimental protocols used in the present research. Preparation of polymer membranes is given. Procedures for the preparation of blend and mixed matrix membranes with different heteropolyacid fillers have been presented. The details of pervaporation techniques have been discussed. Theoretical aspects and different types of characterization techniques used for the membranes are presented.
Chapter 3A:

This chapter presents PV Separation of isopropanol–water mixtures using mixed matrix blend membranes of poly(vinyl alcohol)/poly(vinyl pyrrolidone) loaded with 0, 4, 8 and 12 wt.% phosphomolybdic acid (PMA). Membranes were characterized by FT-IR, XRD, DSC, DMTA, SEM and contact angle measurement. PV performance of the membranes was investigated in terms of flux and selectivity at different experimental conditions. Among the all prepared MMMs 4 wt.% PMA filled membrane (M-4) have shown better water selectivity than other MMMs (M-8 and M-12) and plain PVA/PVP (M-0) membrane. M-4 has shown 29991 separation factor with 0.036 kg/m²h flux. Whereas, M-8 and M-12 membranes have shown separation factors 12848 and 8172 respectively. Flux of M-8 and M-12 increased as compared to M-4. With increasing feed water composition, membrane performance affected markedly in accordance with the swelling results, which also supports the findings of increase of separation factor with a decrease in flux. The near azeotropic composition of water-IPA mixture (10 wt. % feed water) could be efficiently separated using the water-selective M-4 membrane. Solubility selectivity being higher than diffusion selectivity, suggests that separation is dominated by solubility. Flory-Huggins theory enabled to satisfactorily explain the thermodynamic processes involved in PV separation. PV performance was also evaluated by varying the feed temperature and found that PV performance of all membranes diminishes with increased feed temperature. Temperature effect study is supported by Arrhenius activation energy values calculated from Arrhenius plots which showed that MMMs exhibited significantly lower activation energies for water than IPA with a negative heat of sorption which indicates easy permeation of water than IPA.
Chapter 3B:

Chapter 3B deals with pervaporation (PV) separation of water + acetic acid mixtures, has been attempted using the blend MMMs of PVA and PVP loaded with phosphomolybdic acid. These results have been compared with the PV performance of plain PVA/PVP membrane. Both plain PVA/PVP and MMMs have been crosslinked with glutaraldehyde in an acidic medium. Pervaporation separation experiments have been performed at 30°C for 10, 20, 30 and 40 wt. % of feed water mixtures containing acetic acid. M-4 membrane has shown a separation factor of 17991 for 10 wt. % of water in water + acetic acid. For all the feed mixtures, selectivity for the MMMs was higher than that observed for plain PVA/PVP membrane, but flux of the MMMs was lower than that observed for the plain PVA/PVP membrane. Membranes of this study are able to remove as much as 99.95 wt. % of water from the feed mixtures of water + acetic acid. Flux of water increased for all the feed mixtures, while the selectivity decreased at higher feed water concentrations. The same trends were observed for effect of feed temperature study. Permeation flux followed the Arrhenius trend over the range of temperatures investigated. It was found that by introducing a hydrophilic PMA into PVA/PVP blend, the selectivity increased dramatically, while flux decreased compared to plain PVA/PVP.

Chapter 3C:

This chapter addresses the application of 4 wt.% PMA loaded PVA/PVP membrane (M-4) in esterification reaction between ethanol and acetic acid. The membrane was found to selectively dehydrate ethanol, IPA and acetic acid from ethanol-water, IPA-water, acetic acid-water mixtures respectively. Since, the membrane was highly selective for water; We thought to use M-4 membrane for shifting the esterification equilibrium of acetic acid with ethanol towards the product side by removing the water generated from the reaction
mixture through pervaporation. The esterification of acetic acid with ethanol was carried out with Dowex-50 as the external heterogeneous catalyst. The % conversion of acetic acid for ethanol: acetic acid mole ratio of 0.5 was found to be 26.41, 51.12 and 60.65 respectively for the esterification carried out without pervaporation, with pervaporation by plain PVA-PVP membrane and by M-4 membrane. Effect of variation in mole ration of reactant was also studied and we found higher % yield at 3:1 mole ratio of ethanol to acetic acid; due to excess alcohol in feed mixture. The mixed matrix membrane incorporated with phosphomolybdic acid efficiently enhances the esterification through pervaporation removal of water from the reaction mixture at ambient temperature. Therefore, highly water selective nature of the mixed-matrix blend membrane incorporating PMA can be successfully employed for the pervaporation assisted esterification of acetic acid with ethanol at ambient temperature.

Chapter 4:

Chapter 4 discusses preparation of nanocomposite membranes (NCMs) of sodium alginate (NaAlg) loaded with 0, 6, 8 and 10 wt.% preyssler heteropolyacid (H$_{14}$-P$_5$) for sorption and permeation studies for water + isopropanol mixtures. Sorption, diffusion and permeation properties of NCMs were studied at different experimental conditions. Results of sorption study were confirmed by evaluating different thermodynamic parameters. Higher values of sorption selectivity than diffusion selectivity clearly indicates that sorption plays major role in the PV. Flory-Huggins theory was used for determination of the interaction parameters and solubility parameters which are useful to study the thermodynamic processes involved in PV dehydration of IPA. PV separation of IPA was studied by varying the filler concentration, feed water composition and feed temperature. It was observed that incorporation of
Summary

**Chapter 7**

Hydrophilic H$_{14}$-P$_5$ nanoparticles boost the sorption and PV performance of the membranes. Separation factor 530 for pristine NaAlg membrane increased up to 71960 for NCM-6 for azeotropic composition at 30°C. But separation factor was lowered for further filler loading i.e. NCM-8 and NCM-10, may be due to agglomeration/clustering of filler nanoparticles at 8 and 10 wt.% filler loading. Flux of the NCMs increased considerably with increased filler loading. PV performance of the NCMs is gratefully affected by feed water content; increase in feed water content leads to poor PV performance. Similar trend of results was obtained for increased feed temperature. PV performance of the NCMs diminishes with increased feed temperature from 30°C to 60°C. The NCMs exhibited lower Arrhenius values for water than IPA (calculated from Arrhenius equation), suggesting the higher water selective nature of the NCMs. Diffusion coefficients values calculated by using Fick’s law also proves the water selective nature of the NCMs.

**Chapter 5:**

Chapter 5 describes development of novel type of MMMs from the blend polymers of chitosan and hydroxyethylcellulose, incorporated with hydrophilic PWA nanoparticles and used for effective ethanol dehydration. Prepared membranes were characterized by different physicochemical parameters like FT-IR, XRD, DSC, SEM, AFM and contact angle measurement. PV performance of MMMs was investigated in terms of flux, permeance, separation factor and selectivity. The boost in PV performance of the MMMs was observed as compared to plain CS/HEC membrane attributed to hydrophilic-hydrophilic interactions between the filler nanoparticles and water. The values for separation factor, selectivity, permeance and flux were found to be 129, 20, 1.56 x 10-8 kg/m$^2$s and 0.057 kg/m$^2$h respectively for plain CS/HEC membrane which were increased to 39976, 3847, 2.77 x 10-8
kg/m$^2$s and 0.098 kg/m$^2$h respectively for CS/HEC-2. At higher loadings of PWA nanoparticles i.e. for CS/HEC-4 and CS/HEC-6, declined PV performance was observed as compared to CS/HEC-2, may be due to the aggregation of PWA particles in membrane matrix. The flux and permeance values increased with increasing feed water composition while selectivity and separation factor decrease with increased feed water composition. Sorption and diffusion data suggest that membrane selectivity is mainly governed by sorption selectivity. Flux and selectivity data shown a decrease with increasing temperature; the temperature dependence of PV results followed the Arrhenius trend. Activation parameters of permeation for MMMs revealed the requirement of a lesser activation energy for water molecules to transport across the barrier membranes than ethanol, suggesting higher water selective nature of the developed MMMs.

Chapter 6:

Chapter 6 addresses application of organic-inorganic hybrid MMMs of poly(vinyl alcohol) PVA/tetraethylorthosilicate (TEOS) prepared by incorporating silicotungstic acid (SWA) nanoparticles. PV separation performance for ethanol-water mixture was studied for MMMs and compared with the performance of plain PVA/TEOS membrane. It was observed that, Incorporation of SWA could dramatically improve separation abilities of MMMs. PV performance was investigated in terms of separation factor and permeation flux. Separation factor was increased with increased SWA loading at the expense of permeation flux. 15wt. % SWA loaded membrane i.e. MMM-15 has shown better PV performance as compared to MMM-5, MMM-10 and plain PVA/TEOS membrane. Highly water selective nature of MMM-15 was confirmed by estimating F-H interaction parameters which revealed favorable interactions between water and membrane as compared to the interactions
between ethanol-membrane. Optimum PV performance was determined by varying the experimental conditions like concentration of filler particles, variation of feed water composition and variation in feed temperature. Increase of concentration of SWA nanoparticles in the PVA/TEOS matrix caused the matrix to be rigid with a decrease in free volume parameters, but at the same time creating possible water channels for effective ethanol dehydration. Separation factor 365 of plain PVA/TEOS membrane increased to 8622 for MMM-15, while flux of PVA/TEOS decreased from 0.066 kg/m²h to 0.034 kg/m²h for MMM-15. Physicochemical characterizations of the membranes revealed adequate film properties such as free volume, crystallinity, thermal properties, surface free energies and morphology that are essential to explain the PV results. Degree of swelling of all the membrane increased comprehensively with increased feed water content, but overall swelling of the membranes decreases with enhanced incorporation of SWA nanoparticles in membrane matrix. PV performance of MMMs declined at higher feed water content due to plasticization effect of membranes. Permeation flux of the MMMs increased with feed water content which is in accordance with swelling results. Increased feed temperature also reduces the separation factor of the membranes. Effect of temperature was explained on the basis of diffusion coefficients and Arrhenius activation parameters. Diffusion coefficients values for water and ethanol showed the highly water selective nature of MMMs and lower Arrhenius activation energies for water as compared to ethanol proved the easy permeation of water.

Chapter 7:

This chapter provides the summary of the research findings of the present work. The research findings of this thesis have been published and communicated to reputed international journals. In future, there is vast scope
on preparation of organic/inorganic hybrid mixed matrix membranes for use in
dehydration of organic solvents. Prepared membranes are also proved to be
important in membrane catalyzed reactions like esterification between
carboxylic acid and alcohol.