**Separation Science and Technology**
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

# Dehydration of Acetic Acid, Alcohols, and Acetone by Pervaporation Using Acrylonitrile-Maleic Anhydride Copolymer Membrane

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**To cite this Article** Ray, S. and Ray, S. K.(2005) 'Dehydration of Acetic Acid, Alcohols, and Acetone by Pervaporation Using Acrylonitrile-Maleic Anhydride Copolymer Membrane', Separation Science and Technology, 40: 8, 1583 — 1596
**To link to this Article: DOI:** 10.1081/SS-200053321
**URL:** http://dx.doi.org/10.1081/SS-200053321

*Separation Science and Technology*, 40: 1583–1596, 2005

ISSN 0149-6395 print/1520-5754 online
DOI: 10.1081/SS-200053321

# Dehydration of Acetic Acid, Alcohols, and Acetone by Pervaporation Using Acrylonitrile-Maleic Anhydride Copolymer Membrane

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**Abstract:** Pervaporative dehydration of acetic acid, ethyl alcohol, isopropyl alcohol, and acetone over the entire concentration range of 0–100 wt% is studied using acrylonitrile-maleic anhydride copolymer membrane. The membrane exhibits reasonable performance with respect to both separation factor and permeance (11.0 and 279.4 g/m$^2$.hr./bar, respectively, at 92 wt% feed conc. of water) for acetone dehydration. Dehydration performances of acetic acid and ethyl alcohol are comparable (permeance and separation factor of water for its mixture with acetic acid is 119.5 gm/m$^2$.hr./bar and 2.4, respectively, while the same for its mixture with ethyl alcohol is 125.4 gm/m$^2$.hr./bar and 2.5, respectively, at 50 wt% feed) over the whole concentration range. Isopropyl alcohol shows the best separation factor for water at very low alcohol concentration (8.7 at 2.5 wt% feed) with lowest permeance among the four systems of separations.

**Keywords:** Pervaporation, dehydration, acetic acid, alcohols, acetone, poly(acrylonitrile-co-maleic anhydride)

## 1. INTRODUCTION

Dehydration of acetone, organic acids, and alcohols by pervaporation is important since most of these compounds form azeotrope or yield a pinch

Received 26 August 2004, Accepted 9 December 2004

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on the vapor-liquid equilibrium curve (1, 2). These compounds are among the top 20 organic intermediates used (1) in the chemical industry, and their mixture with water is encountered in the preparation of several important intermediates and bio-products (1, 3). Since membrane processes are generally operated at ambient temperature and the separation is achieved by physical means, the various components of the mixture are not subjected to any thermal stress or chemical alteration (4). Further, the mass separation properties of membranes can be adjusted over a wide range of specific requirements and their use is relatively economical with little effect on scale of operation. As an alternative candidate, pervaporative dehydration is energy saving and economically more viable. The most important application of pervaporative separation is observed in different bio-chemical reactions, especially where continuous removal of bio-solvents with inhibitory effects on the production rate such as ethanol, butanol, acetone, etc. (4) from fermentation broths are needed. As the last downstream processing step after separation of the microorganisms, dehydration of these organics demands highly selective pervaporation membranes even at the cost of low permeance (4).

In recent years, a number of new polymers have been tried as membrane materials for pervaporative separation, but very few of these are effective for dehydration of organic compounds (5, 6). The first commercial pervaporation membrane, a composite of poly-acrylonitrile support with polyvinylalcohol (PVA) top layer from G.F.T. shows high separation factor and permeance for alcohol dehydration but negligible separation factor for other acids and acetone (7). The poor performance and collapse of PVA membrane in acetic acid dehydration is attributed to the gradual hydrolysis of the ether linkage, which is formed by reaction of PVA with its crosslinker. Polyacrylic acid is much more hydrophilic than PVA, but its mechanical strength is very poor. Crosslinking by a metal ion for polyacrylic acid as used by Huang et al. (8) collapses with time and thus reduces the membrane performances. Polyacrylonitrile (PAN) is a film-forming polymer with very high mechanical strength because of its high $T_g$ and good chemical resistance. However, presence of one nitrile functional group in its repeating unit is not sufficient to make it hydrophilic enough for use in pervaporative dehydration. The membrane shows a high separation factor with negligible permeance during dehydration (1). Water absorption value of pure PAN has also been found to be much less (1–1.5%) than its copolymer (around 95%) with other hydrophilic monomers (1, 9). Hence, in the present work, the PAN membrane has been modified to a strongly hydrophilic membrane by copolymerizing acrylonitrile with maleic anhydride containing two strongly polar carboxylic groups. This copolymer membrane has been studied over 0–100 wt% water in feed for pervaporative dehydration of the said organic solvents i.e., acetone, acetic acid, ethanol, and isopropyl alcohol.

## 2. EXPERIMENTAL

### 2.1. Materials

L.R. grade of Acrylonitrile, maleic anhydride, sodium lauryl sulfate, and potassium peroxodisulfate obtained from E. Merck (India) Ltd., Mumbai, were used for synthesis of the membrane polymer. Acrylonitrile monomer was freed from its inhibitor by washing with 5% aqueous sodium hydroxide solution and then with distilled water to remove traces of alkali. It was then kept over fused $CaCl_2$ overnight and distilled under vacuum before use. Maleic-anhydride, sodium lauryl sulfate, and potassium peroxodisulfate were used as obtained without any further purification.

### 2.2. Synthesis of Polymer

Copolymerization of acrylonitrile with maleic-anhydride was carried out by emulsion polymerization in a three-necked reactor at 70°C for 6 hr. The reactor was fitted with a stirrer, a thermometer pocket, and a condenser. Water was used as the dispersion medium. Sodium lauryl sulfate and potassium peroxodisulfate was used as the emulsifier and initiator, respectively. After polymerization, the polymer was precipitated by using sodium chloride and washed repeatedly with distilled water, toluene, and ethyl acetate to remove unreacted monomer and emulsifier. The purified copolymer was then dried at 70°C for 4 hr in a vacuum drier.

### 2.3. Membrane Casting

The copolymer (2.1 gm) was first completely dissolved in dimethyl formamide (30 gm) by continuous stirring until a clear solution of required viscosity was obtained. Membrane was prepared by casting from dimethyl formamide (DMF) solution of the copolymer with an applicator on a clean and smooth glass plate and dried at 60°C for 2 hr under vacuum. Subsequently, the membrane was annealed at 80°C for an additional 6 hr. The thickness of the copolymer membranes were maintained at $\sim$30 micron. The thickness was measured by Test Method ASTM D 374 using a standard dead weight thickness gauge (Baker, Type J17).

### 2.4. Copolymer Composition

Copolymer membranes with varied performance characteristics based on different comonomer compositions are quite unlikely in our system, as the product of reactivity ratios of both acrylonitrile and maleic anhydride has been reported to be zero (10). This always results in a copolymer with a close tendency of 1:1 alternate comonomer composition (11). Hence, membranes with other comonomer compositions were not tried for our system, as it would result in copolymers of almost the same compositions, varying little in its pervaporation performances. The copolymer poly(acrylonitrile-co-maleic anhydride) as obtained from the above experiment (given under section 2.2 and 2.3) was characterized by the following methods.

## 2.5. Copolymer (Membrane) Characterization

### 2.5.1. FT-IR Studies

The FT-IR spectra of poly(acrylonitrile-co-maleic anhydride) was recorded on a Jasco (model no 460) FT-IR using a thin film of the polymer.

### 2.5.2. Intrinsic Viscosity Studies

The intrinsic viscosity of the copolymer were determined using an Ubbelohde type viscometer. Four dilute solutions of the polymers (0.25, 0.5, 0.75, and gm/dL) in DMF were taken in the viscometer and specific viscosities were determined from the relative times taken by the polymer and the solvent itself in the viscometer. Reduced viscosity, which is specific viscosity for unit concentration, was plotted against concentration of the polymer solution, and from the plot intrinsic viscosity of the copolymer membrane was obtained by extrapolating to zero concentration.

### 2.5.3. Glass Transition Temperature ($T_g$)

$T_g$ was measured by a differential scanning calorimetry analyzer (Mettler-Toledo model no. DSC882$^e$).

### 2.5.4. Mechanical Strength

The tensile strength and elongation at break of the polymer film was determined by an Instron-Tensile tester (model no. 4301). The experiment was performed according to ASTM D 882-97. In our system, length of the specimens was 250 mm, the thickness of the specimens was around 0.1 mm, and the thickness was uniform to within 5% of the thickness between the grips. The width of the specimens was 20 mm and edges were parallel to within 5% of the width over the length of the specimen between the grips.

The same tests were also performed with the sorbed membranes.

## 2.6. Sorption Studies

Membranes of known weights were immersed in different known concentrations of aqueous acetic acid, ethyl and isopropyl alcohols, and acetone solutions and were allowed to equilibrate for 96 hours at 30°C. These membranes were taken out from the solutions and weighed after the superfluous liquid was wiped with tissue paper. The increment in weight is equal to the total weight of water and organic solvents sorbed by the membrane.

## 2.7. Permeation Studies

Pervaporation experiments were carried out in a batch stirred cell (Fig. 1) with adjustable downstream pressure that was maintained at 1 mm Hg by liquid (mercury) column method using a manometer. The feed compartment of the pervaporation cell was equipped with a pitched bladed turbine type agitator to ensure adequate mixing of the liquid feed so as to eliminate any concentration or temperature gradient (12). Effective membrane area in contact with the feed mixture was 19.6 $cm^2$ and the feed compartment volume was 150.0 $cm^3$. Pervaporation experiments were carried out at constant temperature of 30°C. The water content of the permeate was determined by an

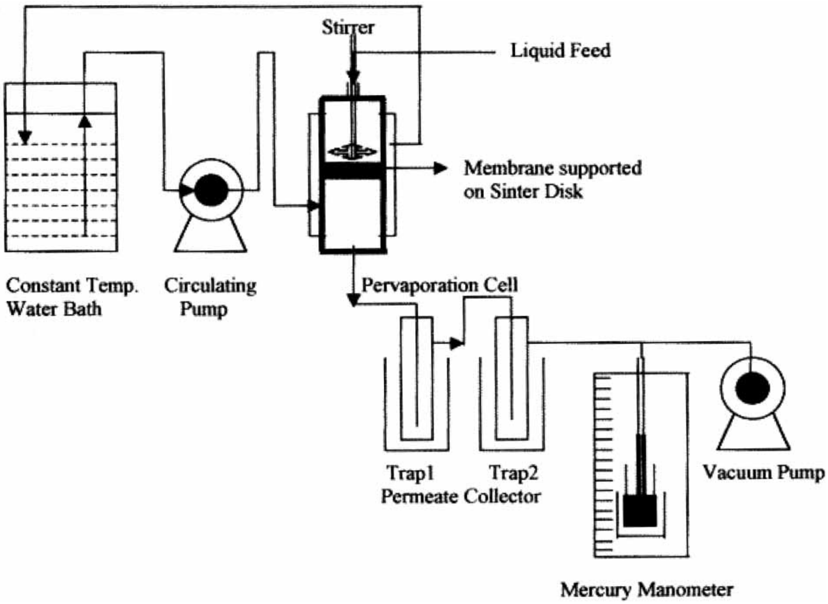

*Figure 1.* Schematic diagram of permeation setup.

Abbe type Refractometer. The binary separation factor ($\mu_{ij}$) for dehydration is defined as

$$\alpha_{water-organic} = \frac{y_{water}/y_{organic}}{x_{water}/x_{organic}}$$

where $y_I$ and $x_I$ are weight fraction of component i in permeate and feed, respectively.

## 3. RESULTS AND DISCUSSION

### 3.1. Synthesis of Polymer

Maleic anhydride can be copolymerized with vinyl comonomers (13). Free radical and UV-initiated bulk and solution copolymerization of maleic anhydride with acrylonitrile have been reported (13, 14) to yield random, nonequimolar polymers. However, in this study, copolymerization of acrylonitrile with maleic-anhydride was carried out by emulsion polymerization method. In bulk polymerization, viscosity builds up rapidly at low conversion (15), leading to a low molecular weight gelled polymer from which membrane preparation is impossible. In bulk polymerization, control of reaction also becomes difficult due to poor dissipation of high heat of vinyl polymerization in the absence of any other solvent, resulting in a runaway reaction. Solution polymerization also requires highly polar solvents like DMF, DMSO, NMP, etc. where the reaction is sluggish in nature due to interaction of these solvents with the propagating polymer chain (16). In contrast, in emulsion polymerization, an easy dispersion medium like water leads to a high molecular weight polymer with minimum contamination (17). In emulsion polymerization, apart from a high molecular weight product, a polymer with low polydispersity is obtained, resulting in a membrane of better mechanical strength and consistent permeation behavior. In this study, acrylonitrile was thus copolymerized with maleic anhydride by emulsion polymerization to get the pervaporation membrane of desired qualities.

### 3.2. Copolymer (Membrane) Characterization

#### 3.2.1. FT-IR Study

The FT-IR spectra of poly(acrylonitrile-co-maleic anhydride) was obtained by using a very thin film of the polymer. The FT-IR of the polymer is given in Fig. 2. It transpires from the figure that the bands appearing at 1094 $cm^{-1}$, 1434 $cm^{-1}$, and 2240 $cm^{-1}$ are due to acrylonitrile comonomer while the bands of 1781 $cm^{-1}$ and 1242 $cm^{-1}$ are due to maleic anhydride comonomer of the copolymer membrane. The strong bands at 2240 $cm^{-1}$

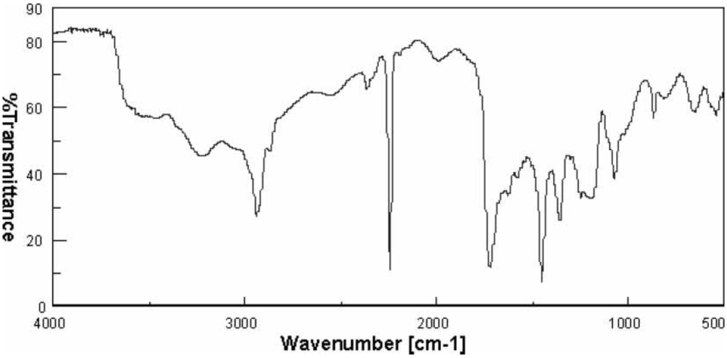

***Figure 2.*** FT-IR spectra of poly(acrylonitrile-co-maleic anhydride) coploymer.

correspond to CN of acrylonitrile and bands at 1742 $cm^{-1}$ correspond to anhydride of maleic anhydride (18). These apart, the strong band of 780 $cm^{-1}$ and 2900 $cm^{-1}$ are due to ($-CH_2-$) methylene (19) and C–H alkane group of the copolymer membrane (20).

### 3.2.2. Intrinsic Viscosity Studies

The intrinsic viscosity of the copolymer as obtained from Fig. 3 was 1.99 dL/gm. The viscosity average molecular weight of the copolymer could not be measured because of the nonavailability of the Mark-Houwink constants for this system. However, from the literature, intrinsic viscosity of polyacrylonitrile has been found to be 1.97–6.87 dL/gm, corresponding to a viscosity average molecular weight of 53,000. Comparing this value with the

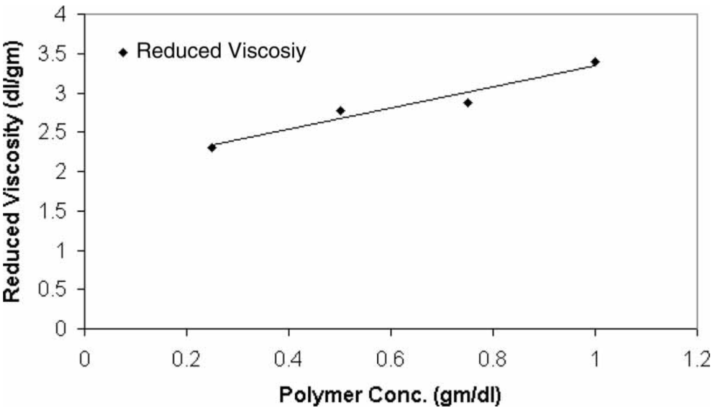

***Figure 3.*** Reduced viscosity vs. polymer conc. at 30°C.

experimental value, it is evident that the membrane copolymer was of high molecular weight (21).

### 3.2.3. Glass Transition Temperature ($T_g$)

$T_g$ plays an important role in determining the membrane performance, as high and low $T_g$ makes a polymer tough and rubbery, respectively, which affects differently the permeability of membrane. Polyacrylonitrile is a glassy polymer with $T_g$ as high as 95°C. Apart from increased hydrophilicity, incorporation of maleic anhydride also enhances permeability of the resulting copolymer membrane through intramolecular plasticization. It is also apparent from the reduced $T_g$ (68°C) of the copolymer as obtained from its DSC curve (Fig. 4).

### 3.2.4. Mechanical Strength

Too high tensile strength (TS) or elongation at break (EAB) result in poor quality membrane. For a good membrane, there should be an optimum balance between TS and EAB. The copolymer membrane synthesized for this study was found to have better tensile strength and EAB (5.6 MPa and 6.9%, respectively) in comparison to homo polyacrylonitrile (2.3 MPa and 9.3%, respectively) at dry condition. At sorption condition, tensile strength decreases to 5.2 MPa and EAB increases to 7.6%.

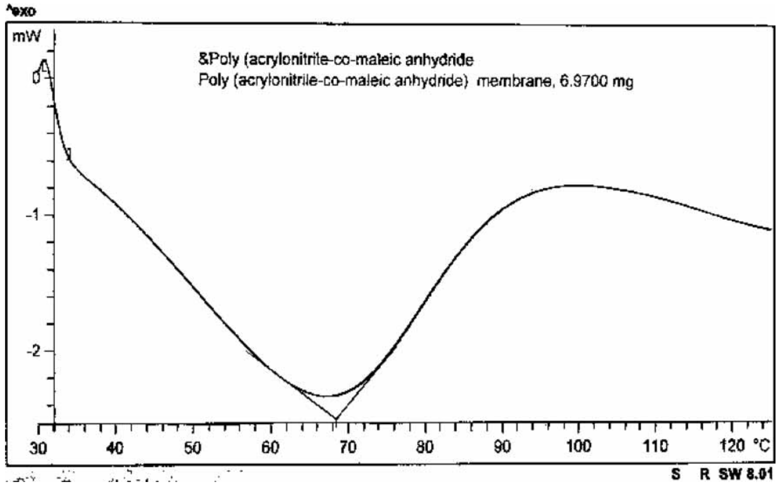

*Figure 4.* Thermal (differential scanning calorimetry, DSC) curve of poly(acrylonitrile-co-maleic anhydride).

## 3.3. Sorption Studies

Figure 5 shows the variation of total of water and organic material sorption of the copolymer membrane with the corresponding feed concentration of water at 30°C. It is evident from the figure that these sorption isotherms closely resemble Rogers Type-III sorption. The drastic increase of sorption at around 40 wt% water content as shown in the figure may be ascribed to the mutual interaction of the sorbed particles, which is greater than their interaction with the polymer, and these particles form a cluster within the polymer matrix (22).

## 3.4. Permeation Studies

### 3.4.1. Effect of Feed Composition on Dehydration

Figure 6 shows the variation of wt% of water in the permeate against wt% of water in the feed for dehydration of acetone, isopropyl alcohol, ethyl alcohol, and acetic acid with poly (acrylonitrile-co-maleic anhydride) membrane. It appears from these McCabe-Thiele type xy diagrams that the membrane shows measurable dehydration characteristics over the entire concentration range without any pervaporative azeotrope. It is evident that at low water % in feed (up to 15 wt%), separation performances of the membrane are similar for all the four systems of separation, but with increasing water % in feed, acetone shows much better dehydration in comparison to alcohols or acetic acid. This may be attributed to the difference in extent of

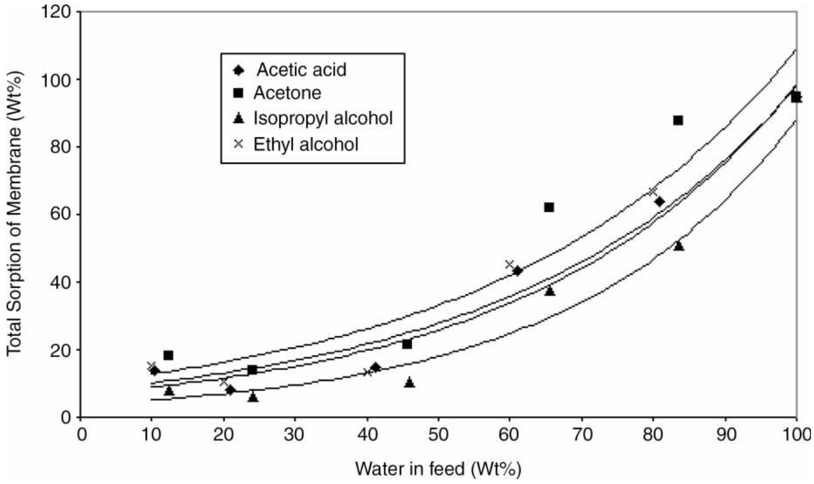

***Figure 5.*** Sorption isotherm of the membrane at 30°C.

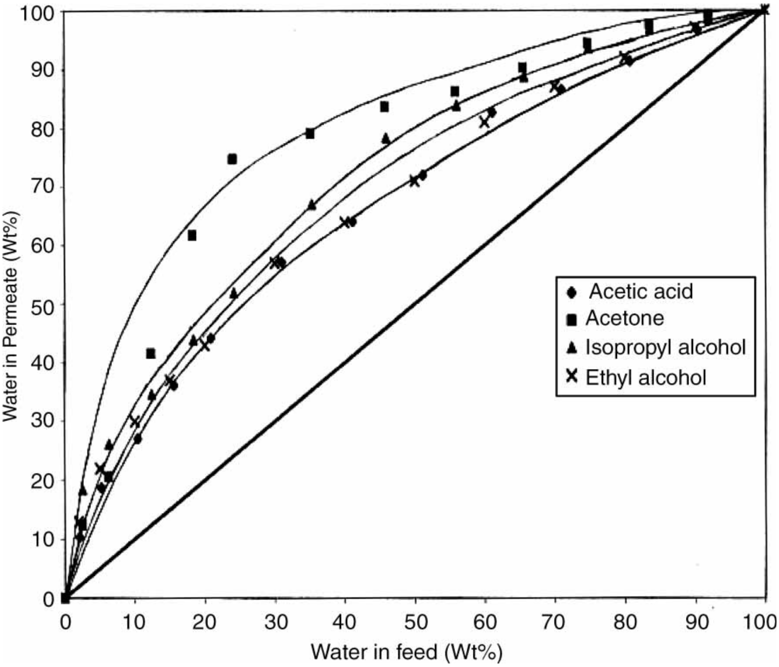

***Figure 6.*** Variation of permeate conc. of water with its feed conc. at 30°C.

hydrogen bonding between water and the other component in the different binary systems.

### 3.4.2. Effect of Feed Composition on Permeance and Separation Factor

Figures 7 and 8 show the effect of feed concentration of water on its permeance and separation factor, respectively, for the said alcohols, acetone, and acetic acid with the copolymer membrane. It appears from the figures that with increase in water concentration in feed water, permeances increase at the cost of separation factor except for acetone where separation factor for water increases up to a certain feed concentration (around 25 wt% water in feed) and then decreases like the other systems. The observed abnormal trend for the acetone-water system may be due to less plasticization of the membrane in comparison to other systems of separation. The decrease in separation factor with increase in water concentration in the feed for all the binary mixtures may be attributed to the plasticization of the hydrophilic membrane at high water content in the feed. However, at high dilution of water in the feed (above ~60%), dehydration separation factors increase for all the four systems of separation. This may be ascribed to the presence of

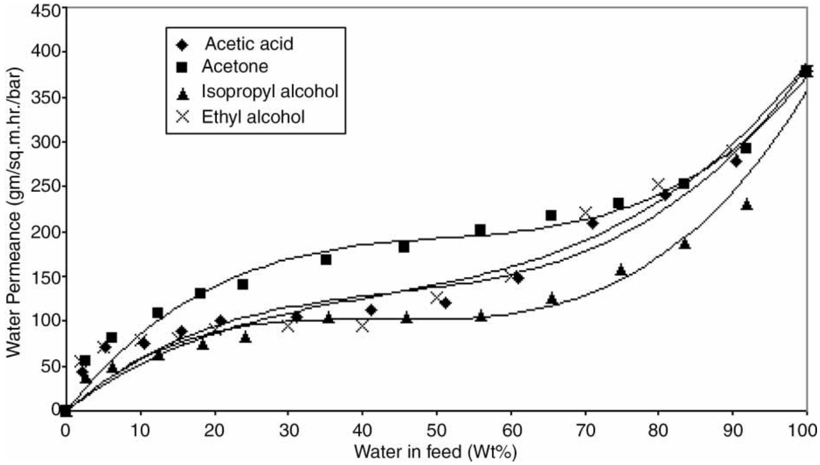

*Figure 7.* Variation of water permeance of membrane with feed conc. of water at 30°C.

hydrophilic anhydride group in the membrane, which forms preferential hydrogen bond with the sorbed water molecule (1). The relative performance of different membranes used for dehydration of alcohol, acetic acid, and acetone are given in Table 1. From this result it transpires that the performance of the present membrane in terms of both permeance and separation factor are comparable to those reported for the same systems.

## 4. CONCLUSIONS

Pervaporative dehydration of volatile organics like alcohols and acetone or corrosive acids like acetic acid demands a membrane of excellent mechanical

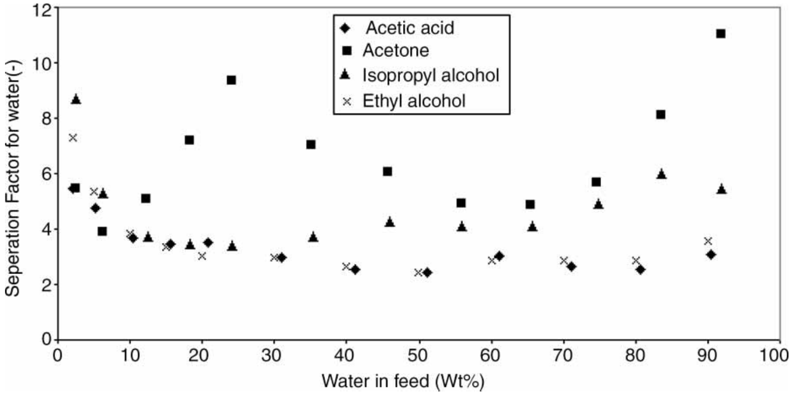

*Figure 8.* Variation of separation factor of membrane with feed conc. of water at 30°C.

***Table 1.*** Comparison of dehydration performance of various pervaporation membranes

| Separation system A/B in wt% | Membrane used | Flux (kg/m$^2$ · hr) | $a_{B/A}$ | Ref. |
|---|---|---|---|---|
| Ethanol/water (1:1) | Poly(vinylidenefluoride) | 0.45 | 1.0 | 23 |
| | Poly(phenyleneoxide) | 0.08 | 23 | 24 |
| | Poly(acrylonitrile-co-maleicanhydride) | 0.18 | 2.7 | Present work |
| Acetic acid/water 90:10 | Poly(vinylalcohol)/poly(N-vinyl-2-pyrrolidone) blend | 0.80 | 2.8 | 25 |
| | Poly(vinylalcohol)/poly(ethylenimine) | 1.40 | 2.0 | 25 |
| | Poly(acrylonitrile-co-maleicanhydride) | 0.26 | 3.9 | Present work |
| Acetone/water 90:10 | Poly(acrylonitrile-co-maleicanhydride)[a] | 0.34 | 5.4 | Present work |
| Isopropyl alcohol/water 85:15 | Poly(tetrafluroethylene)-poly(4-vinyl pyridine) grafted polymer | 4.3 | 0.77 | 26 |
| | Poly(tetrafluroethylene)-poly(N-vinyl pyrrolidone) grafted polymer | 8.9 | 12.2 | 27 |
| | Poly(acrylonitrile-co-maleicanhydride) | 0.21 | 3.8 | Present work |

[a] No other reference was found.

strength, acid resistance, and hydrophilicity. The high molecular weight pervaporation membrane as obtained from solution casting of copolymer of acrylonitrile with maleic anhydride showed high tensile strength. The membrane showed reasonable permeance and separation factor over the entire concentration range for dehydration of acetone, ethyl alcohol, isopropyl alcohol, and acetic acid. At low feed concentration of water, the membrane showed similar dehydration characteristics for all the systems of separation while showing the best result in terms of both permeance and separation factors for dehydration of acetone.

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