



# Analysis of sorption and permeation of acetic acid–water mixtures through unfilled and filled blend membranes



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## ABSTRACT

A systematic method was employed for making blend membranes from two different hydrophilic polymers. Accordingly, blend membranes of polyvinyl alcohol (PVA) and sodium carboxy methyl cellulose (CMC) at three different wt ratio i.e. PVA:CMC wt ratio of 1:0.25, 1:0.5 and 1:0.75 were prepared. These blend membranes were designated as PC1, PC2 and PC3, respectively. Each of these membranes was crosslinked with 2 wt% (of total polymer) maleic acid. These membranes were used for pervaporative (PV) separation of acetic acid–water mixtures at different feed compositions and temperatures. PC2 membrane showing optimum flux and water selectivity was further filled with 1, 2 and 3 wt% (of total polymer) hydrophilic bentonite filler to produce three different filled membranes i.e. B1PC2, B2PC2 and B3PC2, respectively. These filled membranes were also used for separation of acetic acid–water mixtures. Both unfilled and filled membranes were characterized by FT-IR and UV spectroscopy, SEM, XRD, DSC and mechanical properties. Sorption of the membranes was analyzed by Flory–Huggins thermodynamics. Partial permeability of water and acid through the membranes were determined. Diffusion coefficient of permeants was also determined using a model based on free volume theory. Among these six membranes B2 PC2 membrane showed optimum performance in terms of flux and selectivity.

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## 1. Introduction

Pervaporation (PV) is a widely used technique for organic solvent dehydration. Various hydrophilic and hydrophobic polymers have been used for making PV membranes including those of chemically modified or filled polyvinyl alcohol (PVA), copolymer, interpenetrating network, blends of two or more polymers, filled polymers, etc. [1–7].

Membranes made from blend of different polymers are more versatile since properties of the constituent polymers are integrated in the resulting membranes. Further, several membranes may be obtained by varying blend compositions. However, permeability of a blend membrane depends highly on the degree of molecular interaction between the constituent polymers [5,8]. Solubility parameter values of two polymers should be close to each other for good molecular interaction and thermodynamic compatibility [5]. Membrane made from thermodynamically incompatible polymers shows poor interfacial adhesion properties and unstable phase morphology [9]. Poor interfacial adhesion or coarse morphology within the membrane matrix results in low selectivity of the desired solvent during PV. Among the various techniques of making blends, solution blending of two or more polymers by dissolving the polymers in a common solvent is an

easy but effective way of making a stable blend. Because of strong polymer–polymer interaction this kind of blend shows excellent permeability and selectivity for different solvents [5]. This apart, type and amount of crosslinker and fillers also influence permeability of a membrane [10]. Thus, by varying the blend composition, concentration of filler and crosslinker it is possible to prepare a filled and crosslinked membrane showing optimum performance for flux and selectivity. In the present work a systematic method was employed for preparing blend membrane. In one of our previous works type and amount of a crosslinker and filler was varied to produce filled and crosslinked PVA membrane showing optimum flux and selectivity for dehydration of isopropyl alcohol [10]. Blend and filled membranes made from synthetic and natural polymers have also been used for pervaporative separation [11–14]. In the present work blend and filled membrane from PVA and CMC were produced and used for separation of acetic acid–water mixtures over the concentration range of 81–98 wt% acid in water including pure (100 wt%) water and pure (100 wt%) acetic acid. A systematic method was employed to obtain composition of membrane showing optimum flux and selectivity.

## 2. Experimental

### 2.1. Materials

High purity analytical grade acetic acid used for this study was purchased from Merck (India) Ltd., Mumbai. Polyvinyl alcohol

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## Nomenclature

$A$	area ( $\text{m}^2$ )
$A_d$	free volume parameter
$a$	absorbance of the membrane
$B_d$	free volume parameter
$B$	generalized $B_d$
$D$	basic diffusion coefficient ( $\text{m}^2/\text{s}$ )
$D_T$	thermodynamic diffusion coefficient ( $\text{m}^2/\text{s}$ )
$E_d$	absorption edge (eV)
$E$	activation energy (kJ/K mol)
$f$	fractional free volume
$f(0, T)$	free volume parameter
$f(1, T)$	free volume parameter
$J$	permeation flux ( $\text{g}/\text{m}^2 \text{ h}$ )
$M$	molecular mass ( $\text{g}/\text{mol}$ )
$m$	mass fraction in membrane
$R$	universal gas constant (kJ/K mol)
$T$	temperature (K or $^{\circ}\text{C}$ )
$T_g$	glass transition temperature ( $^{\circ}\text{C}$ )
$T_m$	melting temperature ( $^{\circ}\text{C}$ )
$t$	time of experiment (h)
$V$	molar volume ( $\text{m}^3/\text{mole}$ )
$v$	volume fraction (-)
$v_s$	specific volume ( $\text{m}^3/\text{g}$ )
$W$	total permeate mass (g)
$X$	mass fraction in feed
$x$	mole fraction in feed

$Y$	mass fraction in permeate
$y$	mole fraction in permeate

### Greek letters

$\alpha_{pv}$	separation factor
$\alpha_s$	sorption selectivity
$\beta_i$	proportionality constant
$\gamma_m$	activity coefficient in membrane
$\chi$	interaction parameter
$\Phi$	volume fraction in binary mixtures
$\Phi_c$	crystallinity of the polymer
$\phi$	volume fraction in ternary mixtures
$\eta$	viscosity (cp)
$\rho$	density ( $\text{g}/\text{cm}^3$ )

### Subscripts

1	water
2	acetic acid
$f$	feed
$i$	component $i$ (water)
$j$	component $j$ (acetic acid)
$m$	membrane
$p$	permeate
$u$	upstream

(PVA) of number average molecular wt 125 KDa and degree of hydrolysis of 98–99% was obtained from S.d. fine chemicals, Mumbai. Sodium salt of carboxy methyl cellulose (CMC, pH 6–8, viscosity 1100–1900 cp for 1% w/v in water) and maleic acid was procured from E. Marck, Mumbai and were used as obtained. Hydrophilic bentonite filler (50–75 micron particle size, Amricon Petroleum Institute (API) grade) was kindly given by Amricon pte. Ltd., Kolkata. Deionized water, having a conductivity of 20  $\mu\text{S}/\text{cm}$ , was produced in the laboratory itself from a reverse osmosis (RO) module. This water was used for polymer and membrane feed solutions.

## 2.2. Preparation, crosslinking and casting of blend membranes

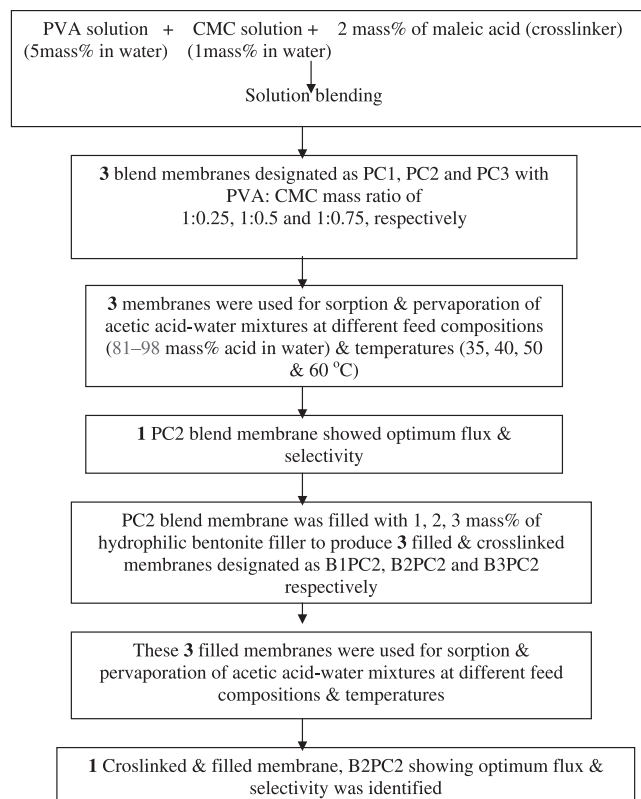
### 2.2.1. Preparation of blend solution

5 wt% PVA solutions were made in deionised water in a 250 ml glass beaker by gradual addition of required amount of PVA to boiling water in several intervals with constant stirring to obtain a viscous clear PVA solution. 1 wt% CMC solution was made in deionised water in a 500 ml conical flask following the same procedure. The clear and homogeneous CMC solution was then mixed with aqueous solution of PVA for making unfilled membranes from this mixture. For filled membranes, required amounts of hydrophilic bentonite filler were added and stirred with magnetic stirrer for 8 h to get filler incorporated stable polymer dispersion. The systematic method employed to obtain composition of membrane showing optimum flux and selectivity is shown in Scheme 1.

### 2.2.2. Preparation of membrane

The aqueous blend solutions of PVA and CMC were mixed with required amounts of maleic acid (2 wt% of polymer blend) and stirred for 3 h at room temperature. These solutions were then cast on a clean and smooth glass plate covered with polyethylene sheet, dried at ambient temperature for 24 h and then peeled off. These were then cured at 110  $^{\circ}\text{C}$  for 3 h in a hot air oven for crosslinking

reaction [15]. Subsequently, the membranes were annealed at 80  $^{\circ}\text{C}$  for an additional 3 h. The thickness of the unfilled and filled



**Scheme 1.** Flow sheet of a systematic method for obtaining filled and crosslinked blend membrane showing optimum flux and selectivity.

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