# Pervaporative recovery of acetone from water using mixed matrix blend membranes

Himadri Sekhar Samanta, Samit Kumar Ray *

*Department of Polymer Science and Technology, University of Calcutta, 92, A.P.C. Road, Kolkata 700009, India*

A B S T R A C T

Several organophilic blend membranes were prepared by solution blending of polyvinyl chloride (PVC) and polystyrene (PS). Mixed matrix membranes were also prepared from PVC and PS by incorporating organophilic clay in these blends. These filled (mixed matrix) and unfilled blend membranes were characterized and used for pervaporative recovery of 5–25 wt.% acetone from water. The filled blend membrane containing 2 wt.% clay was observed to yield the best result, i.e., a flux of 0.042 kg/m$^2$ h and acetone selectivity of 10.6 at 30 °C for 5 wt.% acetone in water. The permeability, intrinsic membrane selectivity and concentration average diffusion coefficients of the solvents were also determined.

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## 1. Introduction

Pervaporation is a promising membrane technology used for separating solvent mixtures. The major application of pervaporation to biotechnology is the recovery of acetone–butanol–ethanol (ABE) from fermentation broth [1–3]. However, product induced inhibition and thus, low concentration (around 2 wt.% with average weight ratio of acetone:butanol:ethanol of 3:6:1) of the solvents in the broth raises the energy cost for separation and recovery of the products [2,3]. Thus, to make this bio separation route economically feasible and competitive with the alternating petrochemical route, the ABE recovery should be coupled to an effective product recovery technique to remove the inhibitory products [1]. There will be massive energy consumption for concentrating these heavily diluted solvents by conventional distillation. Thus, other product recovery techniques such as crystallization [4], adsorption [5], liquid–liquid extraction [6,7], gas stripping [8], membrane distillation [9], reverse osmosis [10], ultrafiltration [11], perstraction [12] and pervaporation [1–3] have been tried.

Amongst these various separation techniques membranes based pervaporation is preferred because it is more selective than non membrane processes [2]. In distillation separation is dependant on the vapor–liquid equilibrium of the solvent mixtures. In contrast, in pervaporation, separation takes place by preferential sorption and diffusion of the solvent. The solvent diffuses from the upstream to downstream side of the membrane because of the gradient in chemical potential maintained by applying negative pressure on the downstream side by using vacuum pump or sweeping gas. Further, only the solvents diffusing through the membrane undergo phase change and thus pervaporation needs much lower energy and hence, lower cost than distillation. In fact, the main capital cost of pervaporation is governed by its membrane unit. A membrane with high selectivity and flux needs low cross sectional area and thus the cost is reduced. The objective of the present work was to synthesize a suitable membrane for pervaporative recovery of one of the important organics of ABE, i.e., acetone from water.

Acetone is an organic ketone. It is extensively used as solvent in paints, varnishes and ink industries and also as a precursor for preparing monomers like methyl methacrylate and bis phenol-A [13]. The annual consumption of acetone is around 6 million ton [13]. Although there are a good many number of reports on the dehydration of acetone [13–17] but there are few reports on the recovery of acetone using a suitable pervaporation membrane [18,19]. Acetone is miscible in all proportion with water. It is also comparable in molecular size and polarity with water. Thus, it is difficult to recover acetone from water by pervaporation using a selective membrane. A hydrophobic but polar membrane with solubility parameter value close to the solubility parameter of acetone is required for selective removal of acetone from water. In the present work polyvinyl chloride (PVC) and polystyrene (PS) have been chosen as membrane forming polymers.

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* Corresponding author. Fax: +91 33 351 9755.
  *E-mail address:* samitcu2@yahoo.co.in (S.K. Ray).

PVC or polystyrene are low cost commodity thermoplastic widely used for making different plastic products. The solubility parameter of PVC (19.5 MPa$^{0.5}$) or polystyrene (18.7 MPa$^{0.5}$) is very close to the solubility parameter of acetone (19.7 MPa$^{0.5}$) [20]. The unfilled and filled membranes made from PVC and also from its blend with other polymers have been used for recovery of benzene from benzene–cyclohexane mixtures [21–23], toluene from toluene-n heptane mixtures [24] and bromoform from bromoform–water mixtures [25]. Similarly, in the present work several blend membranes were prepared from PVC and PS. Membranes were also prepared by incorporating organophilic clay fillers in the blends of PVC and PS. These unfilled and filled blend membranes were used for pervaporative recovery of acetone from acetone–water binary mixtures containing 5–25 wt.% (1.6–9.4 molar%) acetone.

## 2. Experimental

### 2.1. Materials

PVC resins in powder form (M$_w$ 565,000/mole) were procured from Georgia Gulf Co. and polystyrene (PS) (M$_w$ 528,000/mole) resin in bead form was purchased from EniChem, India. The analytical grade solvents acetone and tetrahydrofuran (THF) were purchased from Sigma Aldrich Co, India. The organophilic montmorillonite clays (OMMTs), Cloisite 15A was kindly gifted by Southern Clay Products, Kolkata and used as obtained. The specification of this organophilic clay is shown in Table 1. Distilled water was used for making water–acetone mixtures for sorption and pervaporation experiments.

### 2.2. Method

#### 2.2.1. Membrane preparation
The blend and filled membranes were made by solution casting method. The required amounts of PVC and PS were separately dissolved (3%, $w/v$) in the common solvent THF by high speed mechanical stirring for around 8 h till a clear solution is obtained and the two polymer solutions were mixed and further stirred for 1 h for uniform mixing. The polymer blend solution was then kept overnight for removing the entrapped air bubbles. This solution mixture was cast on a clean and smooth glass plate to obtain the blend membrane. For making the filled blend membranes similar method was applied but in this case the required amount of the organophilic clay was further dispersed for around 3 h in the polymer blend solution before casting. After casting on the glass plate the membranes were dried at ambient condition to remove the volatile solvent (THF). The membrane thickness was around ~50 µm.

#### 2.2.2. Membrane characterization
The blend and filled membranes were characterized by mechanical properties, Fourier transform Infrared spectroscopy (FTIR), scanning electron microscopy (SEM), X-ray diffraction profile (XRD), differential thermal analysis (DTA) and also the thermogravimetric analysis (TGA). For mechanical properties, the tensile

strength (TS) and elongation at break (EAB) of the polymer membranes were determined by a Lloyd-UTM (Lloyd instruments, England) as per ASTM D 882-97 for polymeric film. The FTIR spectra of the membrane samples were recorded on a Perkin Elmer, model-Spectrum-2, (Singapore) spectroscope. The morphology of the unfilled and filled membranes were observed by using SEM (model no. S3400N, VP SEM, Type-II, made by Hitachi, Japan) with the accelerating voltage set to 3 kV. The wide angle XRD of the unfilled and filled blend membranes were studied at room temperature with a diffractometer (model: X'Pert PRO, made by PANalytical B.V., The Netherlands) using Ni-filtered Cu Kα radiation ($\lambda$ = 1.5418 Å) and a scanning rate of 2°/s. The DTA-TGA of the membrane samples were carried out in a Perkin Elmer instrument in nitrogen atmosphere at the scanning rate of 10 °C per minute in the temperature range of 60–600 °C.

#### 2.2.3. Sorption and permeation study
The sorption and pervaporation experiments with the blend and filled membranes were carried out with feed mixtures of varied wt.% of acetone in water. For sorption experiments the blend and filled membranes samples of known weight were immersed in acetone–water binary mixtures of known concentration (5–25 wt.% acetones in water). The membrane samples were allowed to equilibrate for 96 h at 30 °C. Each sample was weighed periodically until no weight change was observed. The membranes were then taken out from the solution and weighed after the superfluous liquid was wiped out with tissue paper. The increment in weight is equal to the total sorption (S) of acetone and water mixtures by the membranes. For determining sorption selectivity, the swelled membranes were taken in a conical flask connected to a vacuum pump [26]. The solvent mixtures (S) absorbed by the membranes were collected in a trap immersed in liquid nitrogen using this vacuum pump and it was analyzed by a digital refractometer (Anton Paar, model – Abbemat-HP). The molar sorption ($N_t$) by these membranes were determined using the following Eq. (1) [27]

$$N_t = \frac{S}{x_{im}M_i + (1 - x_{im})M_j} \tag{1}$$

where $M_i$ and $M_j$ are molecular weight of the component $i$ (acetone) and $j$ (water), respectively, $x_{im}$ is mole fraction of the preferentially sorbed component $i$ (acetone) in membrane. Similarly, sorption selectivity ($\alpha_s$) for acetone was obtained from membrane phase and feed concentration of acetone using the following Eq. (2)

$$\alpha_S = \frac{\frac{y_{im}}{y_{jm}}}{\frac{x_{if}}{x_{jf}}} \tag{2}$$

Here $y_{im}$ and $x_{if}$ are weight fraction of component $i$ in the membrane and feed, respectively. The permeation studies were carried out by pervaporation experiments in a batch stirred cell [26] with adjustable downstream pressure that was maintained at 1 mm Hg. Effective membrane area (A) in contact with the feed solution was 19.6 cm$^2$ and the feed compartment volume was 150 cm$^3$. The acetone–water mixtures in contact with the membrane were allowed to equilibrate for around 3 h for the first experiment and 1 h for the subsequent experiments with different feed compositions. The PV experiment was performed at a constant temperature by circulating constant temperature water around the jacket of the PV cell for different feed compositions. At steady state permeates was collected in traps immersed in liquid nitrogen. The pervaporation results of acetone–water mixtures were reproducible, and the errors inherent in the pervaporation measurements were less than 1.0%. The weight of permeate was determined by a digital electronic balance. Permeation flux (J) was calculated by dividing the amount of total permeate (W) by the time (t) of the experiment and the area (A) of the membrane from the following Eq. (3).

**Table 1**
Specification of the organo clay (Cloisite 15A).

| Organic modifier | Dimethyl-dihydrogenated tallow quaternary ammonium salt |
|---|---|
| Modifier concentration | 125 meq/100 g clay |
| Particle size of clay | 90–95 nm |
| Density | 1.66 g/cm$^3$ |
| Basal spacing | d$_{001}$ is 3.15 nm |