



Separation of benzene–cyclohexane mixtures by filled blend membranes of carboxymethyl cellulose and sodium alginate



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ABSTRACT

Blend membranes were prepared by solution blending of sodium alginate (SA) and sodium carboxymethyl cellulose (CMC) in water with varied compositions. One of the blend membranes containing 25% SA and 75% CMC was found to show optimum flux and benzene selectivity for 19.6 wt% benzene in cyclohexane. This unfilled blend membrane designated as F0 was further filled with 2, 4, 6 and 8 wt% organophilic bentonite filler to obtain four filled membranes designated as F2, F4, F6 and F8, respectively. These five (one unfilled and four filled) membranes were characterized by various conventional methods like FTIR, XRD, DTA (for unfilled blend membranes) and SEM (for filled membranes). These membranes were used for pervaporative separation of benzene from its mixtures with cyclohexane over the concentration range of 0.5–20 wt% benzene. The filled F8 membrane showed lower flux (35.65 kg $\mu\text{m}^2/\text{h}$) than the unfilled F0 membrane (77 kg $\mu\text{m}^2/\text{h}$) but separation factor for benzene of the F8 membrane (212) was much higher than the F0 membrane (88.7).

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1. Introduction

In pervaporation hydrophilic membranes are used for dehydration while organophilic membranes are employed for removal of traces of organics from water. This straightforward approach of membrane selection for preferential permeation of water or organics from water–organic mixture is not applicable for organic–organic separation. The choice of an organophilic membrane for selective removal of an organic from its mixture with another organic depends on relative solubility parameter of the membrane polymer and the permeants. The permeant with solubility parameter close to that of the membrane polymer will selectively permeate through the membrane. Among the various aromatic–aliphatic mixtures, membrane based separation of low concentration of benzene from its mixtures with cyclohexane is important. Cyclohexane is industrially produced by hydrogenation of benzene under Ni or Pt catalyst. The removal of the unreacted benzene from the reaction mixtures is difficult by conventional distillation process since benzene and cyclohexane have close boiling points (benzene 80.1 °C and cyclohexane 80.7 °C). Presently, instead of normal distillation, azeotropic or extractive distillation is practiced for separation of benzene–cyclohexane mixtures [1]. However, these separation processes are more complex and also very expensive because of requirement of high energy. As a low energy alternative

candidate membrane based separation of benzene–cyclohexane mixtures by pervaporation have been tried by many researchers. Unlike distillation, separation efficiency of pervaporation does not depend on relative volatility of the components to be separated. Instead, separation potential of pervaporation depends on preferential sorption and diffusion of the desired component present in low concentration, i.e., benzene in the present case. Between benzene and cyclohexane, benzene has smaller size (benzene 89.4 cm^3/mol , cyclohexane 108.7 cm^3/mol) and collision diameter (benzene 89.4 nm, cyclohexane 0.606 nm) [1]. Thus, under the same concentration gradient benzene is likely to show preferential diffusion by moving at a faster rate than cyclohexane. Being aromatic with pi electron conjugation, benzene also shows electrostatic interaction with polymer having reactive functional groups. Depending on this electrostatic interaction a good many number of polymers show varied degree of swelling and even complete solubility in benzene. Thus, highly benzene selective membrane may be made from polymer having high affinity for benzene. Based on this concept membrane made from organophilic polymers like polypropylene, low density polyethylene, polyvinylidene fluoride (PVDF), blend of polyvinyl chloride and ethylene vinyl acetate [1,2], functional polymers having varied degree of swelling in benzene, i.e., polyvinyl alcohol and its blend with other polymers and adsorptive fillers [1,3–7], cellulose based polymers i.e. cellulose acetate, tosylcellulose butyryl cellulose [1,8,9], various copolymers, i.e., copolymers of acrylonitrile, polyacrylonitrile–polymethyl acrylate block polymer [1,10], acrylate and styrene

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grafted polyamide [11], polyether block amide (PEBA) [12], semi-fluorinated aromatic, poly(ether amide) [13], aromatic polyamide [14], polyurethane, polyoxytetramethylene based polyurethane [1,15], nañon-117 containing silver and sodium metal [16], substituted polyacetylene [17], etc., and also various elastomers showing swelling in benzene like polydimethyl siloxane rubber [18], styrene butadiene rubber (SBR) [19], etc. were tried for separation of low concentration of benzene from its mixtures with cyclohexane. In the present work several blend membranes have been synthesized from CMC, SA and organophilic bentonite filler. These membranes were used for pervaporative separation of benzene from its mixtures with cyclohexane over the concentration range of 0.5–20 wt% benzene in cyclohexane.

2. Experimental

2.1. Materials

Natural polymer sodium alginate (SA, average molecular weight 500,000 and degree of deacetylation 84%) was procured from E. Merck, Mumbai and used as it is without any further purification. Sodium salt of carboxymethyl cellulose (CMC, pH 6–8, degree of substitution 1.8 and molecular weight 20,000) was also procured from E. Marck, Mumbai and was used as obtained. Organophilic bentonite filler (API grade, residue of diameter >75 micron or 200 mesh is 3.5%) was kindly given by Amrfe o pte. Ltd., Kolkata. High purity, HPLC grade benzene, cyclohexane and crosslinker glutaraldehyde (25% aqueous solution) was purchased from s.d. fine-chem, Mumbai, India. For making polymer solution deionized water, having a conductivity of 20 μ S/cm, was produced in the laboratory itself from a reverse osmosis module.

2.2. Preparation, crosslinking and casting of blend membranes

Polymer solutions were made in deionised water in a 250 ml glass beaker by gradual addition of required amount of CMC or sodium alginate (1% m/v) to boiling water in several intervals with constant stirring to obtain a viscous clear polymer solution. Two solutions were then mixed with addition of required amount of filler. It was stirred with magnetic stirrer for 8 h to get filler incorporated stable polymer dispersion. Crosslinking of CMC and sodium alginate blend by glutaraldehyde was carried out at a certain pH maintained by adding sulfuric acid (10 wt% in water), acetic acid (10 wt% in water) and methanol (50 wt% in water) in the blend solution like crosslinking of polyvinyl alcohol [20]. Membrane was prepared by casting this aqueous dispersion of the blend with an applicator on a clean and smooth glass plate. It was kept overnight at room temperature and then dried at 60 °C for 2 h under vacuum. Membrane thickness was maintained at \sim 50 μ m. The thickness was measured by Test Method ASTM D 374 using a standard dead weight thickness gauge (Baker, Type J17).

2.3. Membrane characterization

2.3.1. Fourier transform infrared spectroscopy (FTIR)

The FTIR spectra of the thin film (\sim 10 μ m) of the polymer samples were carried out in a Perkin Elmer (model-Spectrum-2, Singapore) spectroscope.

2.3.2. X-ray diffraction (XRD)

The wide angle X-ray diffraction (XRD) of the polymer samples was carried out in a diffractometer (model: X'Pert PRO, made by PANalytical B.V., The Netherlands). For XRD Ni-filtered Cu K α radiation with wavelength (λ) of 1.542 Å was used. The scanning rate was fixed at 2 deg/s.

2.3.3. Differential thermal analysis and thermogravimetric analysis (DTA–TGA)

The DTA and 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.

2.3.4. Scanning electron microscopy (SEM)

For studying morphology of the blend samples SEM (model No. S3400N, VP SEM, Type-II, made by Hitachi, Japan) of the gold coated polymer samples was carried out at accelerating voltage of 15 kV.

2.4. Total sorption and membrane phase concentration

Sorption experiments were carried out by immersing known weight (m_d) of dry membrane samples in mixtures of benzene and cyclohexane of varied compositions. The membranes immersed in the solvent mixtures were allowed to equilibrate for 96 h at 30 °C. Each sample was weighed periodically until no weight change was observed. The swollen membranes were taken out from the solution and weighed (m_e) after the superfluous liquid was wiped out with tissue paper. The total sorption (S_t) of benzene and cyclohexane mixtures by the membranes (g/g dry membrane) is obtained as

$$S_t = \frac{m_e - m_d}{m_d} \quad (1)$$

Partial sorption of benzene and cyclohexane was obtained by multiplying total sorption weight (S_t) with membrane phase solvent concentration viz. weight fraction of benzene and cyclohexane in swollen membranes. For determining concentration of benzene and cyclohexane in swollen membrane, the total amount of solvents sorbed by the membrane (S_t) was collected in a trap immersed in liquid nitrogen and connected to a vacuum pump. The composition of benzene and cyclohexane in membrane was analyzed by a digital refractometer (Anton Paar, model – Abbemat-HP).

2.5. Permeation studies

Permeation studies of solvent mixtures were carried out by pervaporation experiment in a stirred batch cell. The membrane was inserted in the stainless-steel stirred cell. Effective membrane area (A) in contact with the feed solution was 19.6 cm² and the feed compartment volume was 150 cm³. Downstream pressure was maintained at \sim 1 mmHg by a vacuum pump. The feed 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 pervaporation experiment was performed at a constant temperature by circulating constant temperature water around the jacket of the pervaporation cell for different feed compositions. The solvent vapors coming out from the membrane on its downstream side at low pressure were collected in traps immersed in liquid nitrogen. Pervaporation experiments were reproducible and the errors inherent in the measurements were less than 1.0%.

2.5.1. Total and partial flux

From the permeation data, total flux (J , as g/m²h) was obtained using the following equation

$$J = \frac{W}{At} \quad (2)$$

Total molar flux (J_m , mole/m² h) was obtained as

$$\frac{J}{M_{avg}} = J_m = \frac{J}{x_i M_i + (1 - x_i) M_j} \quad (2a)$$

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