Separation of toluene–methanol mixtures by pervaporation using filled elastomeric membranes

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ABSTRACT

Hybrid type elastomeric membranes were prepared by mixing natural rubber (NR) with 10 wt% of (of rubber) three different types of organophilic fillers, *i.e.*, carbon black, organophilic clay and organophilic zeolite. These elastomeric membranes were cured (crosslinked) by semi efficient vulcanization technique using sulfur (S) and zinc diethyl dithio carbamate (ZDC), an ultra fast room temperature curing accelerator to obtain three membranes designated as NRCB, NRC and NRZ, respectively. The membranes were characterized by crosslink density, FT-IR, SEM analysis, and mechanical properties and used for pervaporative removal of low concentration of toluene from its mixtures with methanol at different feed toluene concentrations and temperatures. The NRCB membrane was found to show the best result with respect to toluene flux and selectivity over the entire feed concentration of 3–40 wt% of toluene in methanol.

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1. Introduction

For pervaporative dehydration hydrophilic membranes are used while for pervaporative recovery/separation of a low concentration of an organic from water, an organophilic membrane may be used. However, for organic–organic separation the organophilic membrane should selectively permeate one organic while the other organic should be less permeable. In pervaporation separation takes place by a preferential sorption and diffusion mechanism. The preferential sorption depends on the relative solvent–membrane interaction which may be evaluated in terms of relative solubility parameter values of the solvents with respect to the membrane polymer. Thus, for organic–organic separation, the membrane material should be chosen in such a way that the solubility parameter of the organic to be preferentially permeated is very close to the solubility parameter of the membrane material [1]. Further, the organic to be preferentially permeated should have also smaller kinetic diameter than the other organic for preferential diffusion through the membrane. In the last ten years several polymer membranes were reported [2–17] for pervaporative separation of alkane–aromatic mixtures like separating thiophene from octane or heptane simulating model gasoline [2,3,4], toluene from n-heptane [5–8] and also for separation of aromatic-alcohol mixtures like benzene–methanol [9] and toluene–methanol [10–19].

In most of the above cases, clay filled hybrid type glassy [5–7,9,10] or elastomeric membranes have been tried [1,16,17] because of its integrity and high selectivity. However, the hybrid membranes prepared by incorporating clay in to a glassy thermoplastics show poor flux. On the other hand the membranes made from elastomers yield high flux but poor selectivity. In fact, the elastomeric membranes show preferential organic sorption but its high free volume and the flexibility of its long polymer chains results in high flux but poor selectivity. For improving selectivity, elastomeric membranes were suitably crosslinked [15], filled with adsorptive clay [16,17] and also blended with another glassy polymer [18,19]. Among the various organic mixtures, toluene-methanol binary mixtures are required to separate in many petrochemical and pharmaceutical industries. Both methanol selective [13,14] and toluene selective [5–12,15–19] membranes were reported for this separation. However, toluene forms an azeotrope with methanol at a composition of around 32% (w/w) toluene at atmospheric pressure [18]. Accordingly, separation of low concentration of toluene from its mixture with methanol using a toluene selective hybrid membrane is industrially more significant than selective methanol separation from this binary mixture using a methanol selective membrane. In our previous works hybrid type membranes prepared by incorporating carbon black in natural rubber and crosslinking these filled elastomer with sulfur were used for removal of organics from water [20] and also for the separation of aromatic-alcohol mixtures [15,16]. In continuation of this work, in the present case natural rubber was crosslinked with sulfur and zinc dithio carbamet (ZDC) by semi efficient

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method after incorporating three kinds of adsorptive fillers, *i.e.*, N330 carbon black, bentonite clay and also zeolite. These hybrid membranes were used for separation of toluene-methanol mixtures over the feed concentration of 3–40 wt% toluene in methanol.

2. Experimental

2.1. Materials

Solvents used for this study, *i.e.*, toluene and methanol of high purity analytical grade were purchased from M/s. E. Merck (India) Ltd, Mumbai. Natural rubber (NR) of grade RSS-4, sulfur, zinc dithio carbamate (ZDC, accelerator) and carbon black filler of N330 grade (BSS No. 325 sieve ~90%, Iodine Absorption Number 82 g/Kg, pore density 22 lb/ft³) were kindly given by Tyre Corporation of India, West Bengal. Smectone clay C (BSS No. 200 sieve ~90%, moisture content-4.0 %, specific gravity-1.7) and zeolite (moisture content-4.9%, specific gravity-2.2, thickness-4.5 μm) fillers were kindly supplied by Amrfeo pte. Ltd., Kolkata.

2.2. Preparation of filled and crosslinked natural rubber membranes

The filled natural rubber membranes were prepared by similar method as reported elsewhere [13]. Natural rubber (NR) of RSS-4 grade was masticated and cut in to small pieces. It was then swelled in toluene for 24 h followed by an addition of the required amounts (10 wt%) of the three different organoselective fillers in portions with mechanical stirring of the dispersion for 24 h. Sulfur (crosslinker) and ZDC (accelerator) were then added in 1:1 ratio and the dispersion was stirred for another 8 h. From this rubber dispersion membrane was cast on a smooth and clean glass plate and it was air dried overnight at ambient condition. The air dried membrane on a glass plate was then taken in a hot air oven and the membrane was cured (crosslinked) at 110 °C for 40 minutes. The cured membrane on glass plate was then cooled, immersed in cold water and the membrane was peeled out from the glass plate. Preparation of these filled NR membranes is shown in Scheme-1. The thickness of the filled NR membranes was maintained at ~160 micron. 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. FTIR spectroscopy
The FTIR spectra of the membrane samples were recorded on a Perkin Elmer (model-Spectrum-2, Singapore) spectroscope using a thin film (~10 μm) of the membrane.

2.3.2. Mechanical strength
The tensile strength (T.S.) and elongation at fracture (E.A.F) of the filled NR membranes were determined in by an Instron-Tensile tester (Instron 4301, Instron Limited, England). The experiment was performed according to ASTM D 882-97.

2.3.3. Morphology of the filled NR membranes by scanning electron microscopy (SEM)
The membrane samples were coated with gold (Au). The morphology of the unfilled and the filled membranes were analyzed by SEM (Scanning electron Microscope, model no. S3400N, VP SEM, Type-II, made by Hitachi, Japan) with the accelerating voltage set to 15 kV.

2.3.4. Measurement of crosslink density by chemical and mechanical method
The crosslink density of the filled NR membranes was measured by both chemical and mechanical method.

2.3.4.1. Measurement of crosslink density by chemical method. The cured natural rubber membrane was weighed and then immersed in pure toluene and kept for 72 h till equilibrium sorption was attained. When the sorption equilibrium was attained, there was no further increment of weight between two successive readings of sample weights at different times. Chemical crosslink densities of the cured membrane were determined from the following Flory–Rehner Eq. (1) [21].

$$\nu = \frac{1}{V_s}\left[\frac{\ln(1 - \nu_r) + \nu_r + \chi \nu_r^2}{\nu_r^{1/3} - \frac{1}{2}\nu_r}\right] \tag{1}$$

where ν, V_s and V_r is the crosslink density, molecular volume and volume fraction, respectively, of the rubber membrane while χ is the interaction parameter between the solvent and the membrane.

2.3.4.2. Measurement of crosslink density by mechanical method. The crosslink density of the cured membrane was also determined by mechanical method using the following Eq. (2) based on the kinetic theory of elasticity in its simplest form [21].

$$\sigma = RT\nu\left(\lambda - \frac{1}{\lambda^2}\right) \tag{2}$$

Here, σ is the tensile stress required to extend the crosslink rubber sample to an extension ratio of λ, R is the universal gas constant, T is the absolute temperature and ν is the number of crosslinks per cubic cm of the membrane sample.

2.4. Sorption studies

The transport of solutes through the membrane is governed by a preferential sorption and diffusion due to the concentration gradient from the bulk feed to the downstream side of the membranes. The relative separation performances of the membranes were evaluated by pervaporation (PV) experiments. However, PV is a dynamic process combining both sorption and diffusion. The evaluation of the membranes by sorption is important to find out the operating condition for pervaporation [22].

2.4.1. Total and partial sorption
For sorption experiments the membrane samples of known weights were immersed in several toluene-methanol mixtures of known concentrations and allowed to equilibrate for 96 h at 30 °C. Each sample was weighed periodically until no weight change was observed. After sorption, these membranes were taken out from the solution and weighed after the superfluous liquid was wiped out with a tissue paper. Total sorption % (S_t) of toluene and methanol mixtures by the membranes (%) is obtained as

$$S_t = \frac{w_i - w_d}{w_d} x 100 \tag{3}$$

where w_d and w_i are the weight of the membranes before and after immersion in toluene–methanol mixtures.

2.4.2. Sorption selectivity
The membrane phase composition of toluene and methanol was determined by analyzing the sorbed liquid from the swollen membrane. The swollen membranes were taken in a conical flask which was connected to a vacuum pump through a cold trap immersed in a liquid nitrogen cryo can as shown in Scheme 1f. By applying vacuum, the liquid, *i.e.*, total amount of toluene and methanol sorped by the swollen membrane were collected in the cold trap and analyzed by a digital refractometer (Anton Paar, model – Abbemat-HP, precision up to 5 decimal). From the mass of total sorption and