



Pervaporative recovery of tetrahydrofuran from water with plasticized and filled polyvinylchloride membranes



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ABSTRACT

Plasticized polyvinyl chloride (PPVC) membranes were prepared by incorporating 20, 25 and 30 wt% of dioctyl phthalate (DOP) plasticizer in the matrix of PVC. Filled PPVC membranes were prepared by incorporating 1, 2 and 3 wt% bentonite clay in the PPVC membrane containing 25 wt% of DOP. The membranes were characterized by FTIR, DTA-TG, XRD, SEM and mechanical properties. These membranes were used for sorption and pervaporation of 1–18 wt% tetrahydrofuran (THF) in water. The preferential sorption of the organophilic membranes were analyzed in terms of thermodynamic interaction parameters. The permeability and the diffusion coefficient of the solvents were determined.

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Introduction

Pervaporation may be used for the removal or recovery of low concentration of an organic especially volatile organic compound (VOC) from water [1]. The direct discharge of the aqueous waste containing the low concentration of a VOC to a treatment process such as incineration makes it less economic because of the high transport and treatment cost. However, the aqueous waste may be concentrated before the discharge by pervaporation or if the organic pollutant is an expensive VOC it may also be recovered from the diluted feed by pervaporation. For concentration or recovery of an organic, pervaporation may be a better candidate than the conventional distillation or steam stripping since the cost of pervaporation increases linearly with the system capacity whereas the cost of the other conventional separation process such as steam stripping is proportional to the 0.6–0.7 power of its capacity [2]. Thus, pervaporation is quite economic for a small to medium sized stream containing a low concentration of an organic like VOCs. In contrast, the distillation would be highly expensive for these processes. Further, the separation characteristic of the pervaporation does not depend on the vapor liquid equilibrium and thus, the azeotrope of distillation is not encountered in

pervaporation. Unlike distillation the low energy pervaporation process may be carried out at a low temperature and the selectivity of the pervaporation is much higher than the selectivity of distillation [3]. Thus, in recent years several organophilic membranes were tried for the pervaporative recovery/removal of a VOC [4].

Various crosslinked and filled elastomers such as polydimethyl siloxane (PDMS) [5], natural rubber [6], styrene butadiene rubber [7], ethylene propylene rubber [8], etc., were tried as organophilic membranes for the pervaporative separation of an organic from water. However, rubber or elastomers are amorphous in nature and thus contain a large amount of a free volume. Thus, most of the rubber membranes show high flux but poor organic selectivity [9]. On the other hand non rubber polymers such as thermoplastic or thermoset polymers are glassy in nature with only 0.2–10% free volume in its structure [10]. The diffusion of the solvents through a glassy polymer is more complex than its diffusion through a rubbery membrane [10]. These non rubber polymers are reported to yield a poor flux for the recovery of an organic from water [11]. In this case, the permeability and the selectivity of the solvent depend on the closeness of the solubility parameters of the membrane material with the solvent to be preferentially permeated. The objective of the present work was to prepare an organophilic membrane for the pervaporative recovery of a low concentration of an organic solvent from water.

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Amongst the various organic solvents, the volatile tetrahydrofuran (THF) is chosen since it is an expensive solvent used for the synthesis of various organics. The mixture of THF-water is used in different chemical processes and thus the separation of these mixtures is important. It also forms an azeotrope with water. Further, THF easily forms the peroxides with oxygen and the distillation of peroxide containing THF may lead to the risk of serious explosion [12,13]. There are many reports on the dehydration of THF by a hydrophilic membrane [14–22] but the recovery of a low concentration of this VOC from water using an organophilic membrane is also important. There are few reports on the recovery of THF from water. Claes et al. [23] crosslinked poly[1-(trimethylsilyl)-1-propyne] (PTMSP) with 3,3'-diazido-diphenylsulfone and used the resulting crosslinked membrane for the removal of THF from water. The PTMSP membrane crosslinked with 15 wt% 3, 3'-diazido-diphenylsulfone concentrated 10 wt% THF in feed to 84 wt% THF in the permeate [23].

In the present work, PVC was chosen as the membrane material since it is easily available and not expensive. After polyethylene, PVC is the most widely used thermoplastic [24]. This film forming polymer repels water and because of its low degree of crystallinity (~10%), additives such as plasticizer and adsorptive fillers can be easily incorporated in its matrix. Thus, unfilled and filled PVC and its blend with other polymers were reported as an organophilic ultrafiltration [25] or pervaporation membrane [11,26–29]. In one of our previous works organophilic membranes made from the blend of PVC and polystyrene, unplasticized PVC and the PVC containing 5 wt% dioctyl phthalate (DOP) as the plasticizer were used for the removal of THF from water by pervaporation [11]. Amongst these three kinds of membranes, the unplasticized PVC membrane showed the highest selectivity but lowest flux of only 4.7 g/m² h for a feed containing 0.4 wt% THF in water at 30 °C. In this work, the PVC and DOP plasticizer (20 wt% of PVC) was blended at low temperature (30 °C) and thus plasticized PVC was not formed. The plasticized PVC (PPVC) is prepared by incorporating a large amount (20–50 wt%) of a primary plasticizer in its matrix by heating above its gelling temperature. The inherent rigidity of unplasticized PVC due to its high glass transition temperature (T_g) limits its applications. In contrast, plasticized PVC (PPVC) is soft and flexible due to lowering of its T_g . In fact, PPVC occupies 30% of total PVC market [30]. About one third of disposable medical devices including blood and intravenous storage bags are made from PPVC due to its structural flexibility and excellent plasticizer-PVC compatibility [30]. In PPVC the amorphous part of the polymer is solvated with the plasticizer while its small crystalline parts act as a physical crosslinker in the PPVC gel formed by heating a mixture of PVC and plasticizer above its gelling temperature [31]. The membranes made from PPVC are being extensively used for potentiometric ion sensors [32] and multi-barrier containment systems [33]. However, so far there is no report on use of PPVC as an organophilic pervaporation membrane.

Thus, in the present work PPVC membranes were prepared by incorporating varied amounts of a primary plasticizer DOP in PVC and heating the blends above its gel temperature to form PPVC. The PPVC membranes were further filled with bentonite clay to increase its organophilicity. These membranes were used for pervaporative separation of THF from water over the feed concentration of 1–18 wt% THF in water.

Experimental

Materials

High purity analytical grade THF used for this study was purchased from M/s. E. Merck (India) Ltd., Mumbai. The emulsion

grade polyvinyl chloride (PVC) with K value of 65 was kindly supplied by Reliance Industries, Mumbai. The plasticizer dioctyl phthalate (DOP) was purchased from E. Merck (India) Limited, Mumbai. The stabilizer Lead nitrate (pure) was purchased from Loba chemical Pvt. Ltd., Mumbai. Finely divided powder of Smectone clay C filler (particle size ± 200 mesh, i.e., around 74 μm , specific gravity 1.7, moisture content 4) was kindly gifted by City Cat Overseas Chemicals Ltd., Mumbai, India. Deionized water, having conductivity of 20 $\mu\text{S}/\text{cm}$, was produced in the laboratory itself from a RO module using polyamide reverse osmosis (RO) membrane and it was used for sorption and permeation experiments.

Methods

Preparation of the membranes

The membranes were made from a solution of the PVC in tetrahydrofuran (THF) by a similar method as described elsewhere [11]. The PVC powder was first dissolved in THF (5 wt% solution) by stirring with a magnetic stirrer to obtain a clear viscous solution followed by the addition of the lead nitrate stabilizer (2 wt% of PVC). For preparing the PVC-plasticizer blend, the plasticizer DOP was first added to the PVC solution (20, 25 and 30 wt% of PVC) with stirring for 5 h at 30 °C. For preparing the clay filled polymer mixture the required amounts of the organophilic clay filler was added and stirred with a magnetic stirrer for 8 h at 30 °C to get the filler incorporated stable polymer dispersion. The PVC-DOP and the PVC-DOP-clay solution mixture was then cast on a smooth and clean glass plate covered with a polyethylene sheet and air dried overnight at ambient condition followed by drying in a vacuum oven to remove the residual solvent (THF). The membranes were then further heated to 150 °C in an oven to produce the plasticized membranes [34]. The membranes were then peeled off from the glass plate by immersing in cold water. The thickness of the unfilled and the filled membranes was maintained at ~50 μm . The thickness was measured by the Test Method ASTM D 374 using a standard dead weight thickness gauge (Baker, Type J17).

Membrane characterization

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 polymer. The thermal properties of the membranes were determined by DTA-TGA. DTA and TGA of the membrane samples were carried out in a Perkin Elmer instrument in nitrogen atmosphere with a flow rate of 150 ml/min at the scanning rate of 10 °C per minute in the temperature range of 60–600 °C. The wide angle X-ray diffraction profile of the unfilled and the filled membranes were studied at room temperature with a diffractometer (model: X'Pert PRO, made by PANalytical B.V., The Netherlands) using Ni-filtered Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$) and a scanning rate of 2°/s (2 θ /s). For studying the surface morphology of the unfilled and the filled membranes by SEM (Scanning electron Microscope, model no. S3400 N, VP SEM, Type-II, made by Hitachi, Japan), the membrane samples were coated with gold (Au) and the accelerating voltage was set to 10 kV. The tensile strength (T.S.) and the elongation at fracture (E.A.F) of the unfilled and the filled PVC membranes were determined by an Instron-Tensile tester (Instron 4301, Instron Limited, England). The experiment was performed according to ASTM D 882-97.

Sorption and permeation by pervaporation

The transport of the solutes through the membranes is governed by a preferential sorption and diffusion due to a concentration gradient from the bulk feed to the downstream side of the membranes. The relative performances of the membranes were evaluated by a pervaporation experiment. However, pervaporation is a dynamic process combining both

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