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Full Length Article

Phosphate barrier on pore-filled cation-exchange membrane for blocking complexing ions in presence of non-complexing ions

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ABSTRACT

In present work, an approach has been used to form a phosphate groups bearing surface barrier on a cation-exchange membrane (CEM). Using optimized conditions, the phosphate bearing monomer bis [2-(methacryloyloxy)ethyl] phosphate has been grafted on the surface of the host poly(ethersulfone) membranes using UV light induced polymerization. The detailed characterizations have shown that less than a micron layer of phosphate barrier is formed without disturbing the original microporous structure of the host membrane. The pores of thus formed membrane have been blocked by cationic-gel formed by in situ UV-initiator induced polymerization of 2-acrylamido-2-methyl-1-propane sulphonic acid along with crosslinker ethylene glycol dimethacrylate in the pores of the membrane. UV-initiator is required for pore-filling as UV light would not penetrate the interior matrix of the membrane. The phosphate functionalized barrier membrane has been examined for permselectivity using a mixture of representative complexing Am^{3+} ions and non-complexing Cs^{+} ions. This experiment has demonstrated that complex forming Am^{3+} ions are blocked by phosphate barrier layer while non-complexing Cs^{+} ions are allowed to pass through the channels formed by the crosslinked cationic gel.

1. Introduction

Polymeric membranes find wide range of applications in separations based on processes such as ion-exchange, Donnan dialysis, electrodialysis, etc. owing to their compact structure, low capital cost, low energy consumption and ease of operation. However, their industrial use is still limited by the tradeoff between permeability and selectivity [1]. Conventionally, a polymer membrane with high permeability is expected to have low selectivity for the desired moiety and vice versa. Enhanced selectivity with reasonable permeability has been achieved using facilitated transport membranes where the permeability of the desired moiety is increased owing to its transport by other mechanism in addition to the ordinary sorption-diffusion [2,3]. Biological membranes are ideal examples of facilitated transport where essential ions/molecules are transported by carrier proteins bound non-covalently to the underneath lipid bilayers present in these membranes [4]. The surface proteins act as barrier capable of recognition and traps for certain molecules and ions. The design and fabrication of the synthetic membranes that mimic the gating functions of biological ion channels has been a subject of continuous research due to immense potential of such materials for applications based on the selective separations [5–8]. A variety of such synthetic membranes have been synthesized using different strategies, like template-imprinted channel, size selective barrier, opposite-fixed charge barrier, dielectric barrier, etc., for achieving the desired selectivity [9]. One of the major approach of developing facilitated transport membranes is to introduce a “barrier” on the membrane surface, like surface proteins, which are selective for a target component of the feed. Surface protein based mimic membranes have been synthesized by modifying the membrane surface with carboxylic acid groups for immobilization of bio-functional macromolecules [10]. The template imprinted polymer membranes have also been developed for chemical separation of target ions and molecules [11,12]. Cs^{+} selective barrier has also been formed by immobilizing appropriate crown ether on the surface of the cation-exchange membrane [13]. In another approach to form a barrier, a thin dense layer of opposite fixed-charges have been formed on ion-exchange membrane to separate monovalent ions from multivalent ions [14–17]. These membranes work on the basis that Donnan exclusion of ions is higher for multivalent ions, and small monovalent ions can sneak through the barrier.

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Dielectric or hydrophobic barrier has also been used for separation of non-polar molecules from polar molecules or less hydrated ions from highly hydrated ions. For example, the gold nanotubule membranes modified with HS-$C_{16}H_{33}$ has been seen to transport preferentially hydrophobic permeant molecules [18].

The primitive technique of surface modification is physical application of surface-active agents such as surfactants or soluble polymers to a membrane surface prior to use. But this surface covering is temporary and restricts the membrane performance [19]. Membrane surface chemistry can also be permanently changed by chemical modification, plasma, gamma/electron beam irradiation and photochemical techniques [20–26]. The choice of a particular modification technique depends on the nature of the polymer matrix and the desired characteristics of the modified surface. Of these methods, photochemical grafting, done with UV irradiation has distinct advantages of being simple, less costly and being selectively absorbed by the monomers, with no adverse effect on the bulk polymeric matrix. Also, the UV grafting can be easily incorporated in the end stages of the membrane manufacturing process [24-25]. The technique has been used for the polymerization of a large number of monomers onto different polymeric matrices such as poly(propylene), poly(vinylidene fluoride), poly(ethylene terephthalate), poly(sulfone) and poly(ethersulfone). Of these matrices, poly(ethersulfone) (PES) is one of the most important polymeric materials and is widely used for membrane based separations. PES and PES-based membranes show outstanding oxidative, thermal and hydrolytic stability as well as good mechanical property. One of the unique feature of PES membrane is its light sensitivity in the UV range (200–320 nm). Due to this, the PES membranes do not need any initiating agent for radical production, i.e. they self-initiate and can produce sufficient radicals for vinyl grafting of various functional groups [27–35].

In the present work, an attempt has been made to synthesize functional groups barrier on the membrane surface to explore the possibility of blocking complexing ions and allowing non-complexing ions to pass through the cation-exchange membrane (CEM). Actinides (Am^{3+} and Pu^{4+}) has been taken as model complexing ions due to the general tendency of the actinide ions to complex and alkali metal ions (Cs^{+}) has been chosen as the non-complexing ions. The phosphate groups have been grafted on the surface of the UV-active poly(ethersulfone) (PES) membrane using monomer bis[2-(methacryloyloxy)ethyl] phosphate (MEP) dissolved in a mix solvent containing 1:1 (v/v) proportion of water and ethanol. The surface functionalization has been confirmed by alpha spectrometry and energy dispersive spectrometry (EDS) attached to field emission gun scanning electron microscope (FEG-SEM). Alpha radiography by solid state nuclear track detection has been used to image the distribution of grafted chains on the PES surface. It has been observed that the original microporous structure is not affected by the surface grafting. Therefore, the pores of the membrane have been blocked by pore-filling using UV-initiator induced polymerization of 2-acrylamido-2-methyl-1-propane sulphonic acid. The modified membranes have been subjected to permeation experiments using a feed containing representative complexing ions Am^{3+} and non-complexing ions Cs^{+}.

2. Experimental

2.1. Materials

The microporous host membranes used were poly(ethersulfone) (PES) membranes from Sartorius Stedim India Private Limited (pore size = 0.1 μm). The monomers Bis [2-(methacryloyloxy) ethyl] phosphate (MEP) and 2-acrylamido-2-methyl-1-propane sulphonic acid (AMPS), crosslinker ethylene glycol dimethacrylate (EGDMA), and UV-initiator 2,2′-dimethoxy-2-phenyl acetophenone (DMPA) were obtained from Sigma-Aldrich (Steinheim, Switzerland). The chemical structures of monomers and crosslinker used are shown in Fig. 1.

N,N’-dimethylformamide (DMF) and methanol were obtained from Merck (Mumbai, India). Deionized water (18 MΩ cm^{-1}) was used throughout the present work. Radiotracers ^{137}Cs and ^{241}Am were obtained from the Board of Radiation and Isotope Technology, Mumbai, India. The gamma activities of these radioisotopes in solution were monitored by well-type NaI(Tl) detector connected to a multi-channel analyzer.

2.2. Surface grafting

Grafting of MEP on surface of the PES membrane was carried out by dipping the membrane in a solution containing 0.1 mol L^{-1} MEP dissolved in ethanol and in a mixed solvent containing 1:1 v/v proportion of ethanol and water. The membrane sample in contact with a grafting solution was sandwiched between two Petridishes and irradiated with UV light (315–400 nm) for one hour as shown in Fig. 2. The box type UV multilamp photoreactor used was procured from Heber Scientific, Chennai, India fitted with two 20 watt UV lamps (Sankyo Denki, Japan) with radiation peaks at 352 nm and 368 nm, respectively. The irradiated samples were then washed with methanol repeatedly and dried in vacuum oven for 4–5 h.

The amount of surface grafting in a host membrane was determined gravimetrically using following equation:

$$\mathrm{Mass-gain} = (W_f - W_i)/W_i \tag{1}$$

where W_i and W_f are the dry weights of pristine and grafted sample, respectively.

2.3. Pore-filling

The pore-filling was carried out using a procedure described in our earlier work [36]. Briefly, the polymerizing solution was prepared by dissolving monomer AMPS (0.5 g), crosslinker EGDMA (5 mol% of monomer) and UV-initiator DMPA (2 wt%) in a mix solvent containing 1:1 v/v proportion of DMF and methanol. The PES membranes (with and without MEP surface grafted) were immersed overnight in a polymerizing solution for pore-filling. The membranes were then removed and excess of solution on surfaces was removed with a glass rod. These solution filled membranes were sandwiched between two transparent polyester sheets and exposed to 365 nm UV light for a period of 15 min in a multilamp photoreactor (model No. HML-SW-MW-LW-888, Heber Scientific, Chennai, India). This multilamp photoreactor contained eight lamps (8 watt, Sankyo Denki, Japan) in a circular ring. After exposure in a photoreactor, the membranes were washed thoroughly with a hot solution comprising of DMF, methanol and distilled water to remove unpolymerized components, and dried under vacuum at 60 °C for 4 h. The amount of crosslinked cationic gel filled in a host membrane was determined gravimetrically using Eq. (1).

2.4. Characterizations

The pore sizes of the pristine and grafted membranes were measured with capillary flow porometer (CFP) as described in our earlier publication [37]. The CFP model POROLUX™ 1000 procured from Benelux Scientific; Belgium was used. Porefil liquid (γ = 0.016 N m^{-1}) supplied by the manufacturer was used as a wetting liquid. For measurements, the membrane sample was wetted by immersing it in liquid for 1 h at room temperature. The wet membrane sample was mounted in a sample holder after removing