Separation and Purification Technology 167 (2016) 108–116

Contents lists available at ScienceDirect

Separation and Purification Technology

journal homepage: www.elsevier.com/locate/seppur

# Facile synthesis of pyridinium functionalized anion exchange membranes for diffusion dialysis application

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ARTICLE INFO

*Article history:*
Received 17 August 2015
Received in revised form 2 May 2016
Accepted 3 May 2016
Available online 4 May 2016

*Keywords:*
Anion exchange membrane
Diffusion dialysis
Acid recovery
Pyridinium
PVA

ABSTRACT

Pyridinium functionalized anion exchange membranes are prepared for diffusion dialysis using polyvinyl alcohol (PVA) as base material. Four membranes have been prepared by varying the content of pyridinium salt. The ion exchange (IEC), water uptake (WU), thickness and linear expansion ratio have been measured or calculated. These membranes have shown excellent thermal and chemical stabilities. When applied in diffusion dialysis with a simulated solution mixture of HCl and $FeCl_2$, the membranes show successfully good acid recovery and separation factor. The acid dialysis coefficients are in the range of 1.74–2.48 ($10^{-2}$ m/h) and separation factors in the range of 30.49–57.51. The obtained acid dialysis coefficients and separation factors are greater than that of the widely used commercial membrane DF-120 with ($U_H = 0.9 \times 10^{-2}$ m/h) and (S = 18.5). Hence, the results of this study suggest that the pyridinium functionalized AEMs can be potentially applied in diffusion dialysis process for acid recovery.


## 1. Introduction

With great increase of pollutants due to wastes and hazardous materials in nature, pilot plants and industries which deal with processes mainly biological, physical and chemical based-products have been requested to reuse and/or recycle the byproducts [1]. Waste water, beverages wastes, food residues processing plants/industries, etc. are already established in almost all countries to handle waste management related issues [2,3]. However, new technologies are required to yield in enough efficiency with low energy and related cost effectiveness during industrial processes. The membrane technology is today recognized as a tool of great significance that fits the desired requirements for industrial processes intensification [4].

In membrane technology, the separation processes such as electrodialysis, electro-electrodialysis, nanofiltration, and diffusion dialysis are used for acid or alkaline recovery [5–9]. Among others, diffusion dialysis is an attractive process that deals with acid or base recovery by saving energy consumption. The energy is only used in circulating solutions. Diffusion dialysis relies on the difference in chemical potential of species from one side to another. Particularly, the separation of acid from salts is achieved by using an anion exchange membrane and this allows the selective transport of anions across the membrane while other species remain impermeable in the membrane [10–12]. Interchangeably, ion mobility depends on size and ability of hydrated ion and this is also beneficial for diffusion dialysis application [13].

The anion exchange membranes which are concurrently used in various applications are quaternary ammonium based membranes but they occasionally exhibit low thermal and chemical stabilities [9,14]. Therefore, there is a need of the development of the new membranes that have good thermal and chemical stabilities [15].

To increase the thermal stabilities of anion exchange membranes, the incorporation of cross-linking agents in the membrane matrix is needed. Among others, aldehydes and alkoxysilanes were incorporated in polyvinyl alcohol (PVA) as base membrane [16,17]. The homogeneity of the membranes made by alkoxysilanes is also disturbed by entrapment of silica precipitates in polymer chain. Alternatively, it has been found that the attachments of pendant functional groups could increase the thermal stabilities [14]. However those membranes are not chemically stable due to the quaternary ammonium groups that are usually used during manufacturing process.

The development of aromatic functionalized groups containing nitrogen atom in the membrane structure could be the premising candidates for stable anion exchange membrane preparation. Also, the introduction of long chain alkyl spacers in the polymer

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http://dx.doi.org/10.1016/j.seppur.2016.05.006
1383-5866/

**Nomenclature**

*Abbreviations and acronyms*

| | |
|---|---|
| AEM | anion exchange membrane |
| ATR | attenuated total reflectance |
| DD | diffusion dialysis |
| DMA | Dynamic Mechanical Analysis |
| $E_b$ | elongation at break |
| FT-IR | Fourier Transform Infra-red |
| IDT | initial decomposition temperature |
| IEC | ion exchange capacity |
| LER | linear expansion ratio |
| NMR | nuclear magnetic resonance |
| PVA | poly vinyl alcohol |
| S | separation factor |
| SEM | scanning electron microscopy |
| TEOS | tetra ethyl ortho silane |
| TGA | thermo gravimetric analysis |
| TS | tensile strength |
| $U_{Fe}$ | dialysis coefficient of $FeCl_2$ |
| $U_H$ | dialysis coefficient of HCl |
| WU | water uptake |

backbone could result in membrane flexibility. On one hand, the stability is due to the sterical hindrance effect of substitution groups attached to aromatic group and the hyper-conjugative effect caused by conjugated aromatic ring [15,18]. On the other hand, the flexibility of the membrane is demonstrated by a significant variation of tensile strength and strain values of the membranes [19]. Imidazolium, guanidinium, pyridinium functionalized membranes with anion or cation groups, etc. have been potentially stable and efficient upon their properties and application [14,15,18,20–23]. Unfortunately, the chloromethylation as a toxic even carcinogenic source is one among the reaction steps during the preparation of such membranes.

Previous reports have studied the preparation of pyridinium anion exchange membranes for ion selective transport and have shown moderate properties [18,24]. Among others, bromomethylated poly (2,6-dimethyl-1,4-phenylene oxide) (BPPO) was used as a base membrane to form pyridinium groups. Those membranes which were crosslinked by either ammonia or trimethylamine have shown great stabilities compared to ones without crosslinking. This was due to bromomethyl residues of BPPO which were increasingly eliminated during the process [24]. However, such membranes present hydrophobicity behavior which can restrict ion permeability during diffusion dialysis process.

With ideas denoted above, it is worthy to avoid the use of toxic chemicals, complicated synthesis and expensive reagents. The anion exchange membranes with good hydrophilicity, thermal and chemical stabilities can be the promising candidates for acid recovery by diffusion dialysis process [25–27]. Our previous job was focusing on imidazolium functionalized AEMs where alkoxy groups were used to attached to the functional group; the dense, compact and homogeneous membranes could be obtained [28]. Such membranes present a rigidity behavior which turns to low flexibility due to the small interstices between the functionality and the polymer backbone. In the yet paper, pyridinium based membranes were prepared by alkylation of long chain hydrocarbons (11-Bromo 1-undecanol); therefore the flexible and homogeneous membranes are facilely synthesized. Herein, the alkylation of hydrocarbon with long chains has been chosen not only to form pyridinium salt but also to enhance the flexibility and chemical stability of the membrane [29]. The cross-linking agent TEOS is to guarantee the thermal and mechanical stability of the membrane by changing its morphological properties and hydrophilicity [30]. The PVA is not only used as a substrate but also as hydrophilic support even an agent for ion channeling transport [27].

In diffusion dialysis performance, the membrane properties must be taken into consideration. The fixed charged concentration is playing a major role in ion exchange capacity and water uptake of the membrane as result of membrane permeability [31]. Herein, different pyridinium salt contents have been used in membrane fabrication in order to balance its ion exchange capacity and swelling degree. Moreover, as the membrane matrix is totally hydrophilic while possessing ionic character due to pyridinium group, the water molecules absorbed in it may facilitate the ion mobility [10].

After designing such membrane with compatible properties, it has been tested for diffusion dialysis and the results will be discussed and compared to commercial membranes that are already on the markets.

## 2. Experimental section

### 2.1. Materials and reagents

Pyridine and 11-bromo-1-undecanol were commercially obtained from Sinorpharm Chemical Reagent Co. Ltd (China). Tetraethylorthosilane (TEOS) was obtained from domestic chemical company (China). sodium chloride (AR grade), iron chloride (AR grade), silver nitrate (AR grade), potassium chromate (AR grade), sodium sulfate (AR grade), hydrochloric acid (AR grade), potassium manganate (AR grade), and sodium carbonate (AR grade) were purchased from Shanghai-Sinopharm Chemical Reagent Co. Ltd (China) and used without further purification. Polyvinyl alcohol (PVA, 99%) was supplied by Shanghai Yuanli Chemical Co (Shanghai, China). The average degree of polymerization was $1750 \pm 50$ (corresponding a molecular weight of $77{,}000 \pm 2200$). Solvents such as dimethyl sulfoxide (DMSO), acetone and deionized water were also used as received.

### 2.2. Preparation of polyvinyl alcohol (PVA) solution

The solution of PVA (5 wt%) was prepared by boiling 95 g of DMSO in oil bath at 90 °C for a period of 30 min before addition of PVA. Then 5 g of PVA was added in boiled DMSO and the boiling time was prolonged for 8 h at the same temperature under vigorous magnetic stirring. Finally, homogeneous and transparent 5% PVA was obtained and PVA solution was kept in a proper flask for further use [32].

### 2.3. Preparation of anion exchange pyridinium salt

The anion exchange pyridinium salt was prepared by mixing pyridine with 11-bromo-1-undecanol in a bottom flask at room temperature under vigorous magnetic stirring and reflux for a period of 4 h. The obtained product was precipitated in acetone, filtered and then being dried in vacuum oven for 24 h. The obtained powdered product was kept in container for further $^1$H NMR characterization before use.