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Mixed matrix membrane performance enhancement using alkanolamine solution

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ABSTRACT

Mixed matrix membranes (MMMs) containing diethanolamine (DEA) and carbon molecular sieve (CMS) in polyethersulfone (PES) were synthesized and characterized to study the efficiency of CO_2 separation from CH_4. The membranes were fabricated by adding fixed amount of CMS and polymer into a solvent with DEA at different concentrations. These membranes were characterized for physicochemical properties by employing field emission scanning electron microscopy (FESEM), thermogravimetric analysis (TGA), and Fourier transform infrared spectroscopy (FTIR). The permeability and selectivity studies were carried out by using pure carbon dioxide and methane in a small laboratory test cell. The characterization results revealed that the structure of the membranes was dense and non-porous. It was also found that carbon molecular sieve was uniformly distributed in the polymer matrix. The addition of DEA significantly enhanced the performance of the investigated MMMs such that the CO_2 permeance and CO_2/CH_4 selectivity were enhanced up to 172.41% and 283.21% respectively at a pressure of 6 bar. A comparison with the performance of a few other membranes decisively establishes the superiority of the membranes prepared and tested in this study.

1. Introduction

Over the last two decades, membrane technology has found a widespread use for gas separation owing to some prominent advantages that this technology has to offer which include low energy consumption, less space requirement, simple process design, and ease of up-scaling & module construction [1,2]. Due to relatively better efficiency of the membrane technology, it is preferred over the other conventional methods of CO_2 removal such as absorption, adsorption, and cryogenic distillation [3–5]. The most common types of membranes tested for this purpose are polymeric membranes, inorganic membranes, mixed matrix membranes (MMMs) and facilitated transport membranes (FTMs) [6–8]. These membranes play an effective role in gas separation, especially for carbon dioxide removal.

Despite the aforementioned advantages, these membranes do have limitations. For example, chemical degradation and thermal instability of polymeric membranes [9,10], augmented cost, handling problems, and difficult processing of inorganic membranes [11], mechanical instability and loss of membrane solvent [12], inactivation of carrier, low diffusivity and defect formation in case of FTMs [13]. In order to overcome these limitations, further research work has been conducted and some advancement in membrane technology has been reviewed in the literature [14–16].

An example of such advancements is the improvement of separation performance of the membranes by incorporation of inorganic molecular sieves such as zeolite, silica, metal organic frame work (MOF), porous silica and CMS in polymer matrix. Such membranes are known as mixed matrix membranes (MMMs) [17–21]. The advantages of polymeric membranes and the superior separation performance of rigid molecular sieves to pass Robeson upper bound limits are integrated in MMMs [22,23]. A number of attempts at increasing the gas separation performance of MMMs have been reported over the past three decades. These reports showed good interaction of the filler with polymer matrix and consequently high performance was achieved. However, some other studies revealed low performance of the membranes which is associated to the complex process of fabricating MMMs due to

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weak contact of the fillers and poor filler distribution in the continuous polymer matrix phase. Furthermore, polymer properties, particle and pore size of filler and loading of the filler can affect the MMMs properties [6].

Facilitated transport membranes (FTMs) were applied since long to remove CO_2 from mixtures. Such membranes involve a carrier-mediated transport process in addition to a permeant physical dissolution and diffusion. The existence of a carrier which can react reversibly with the permeant provides high selectivity and usually also high permeability [24]. The gas transport mechanism of these membranes is reversible reaction between the specific gas molecules and the reactive carriers. There are two types of carriers used - fixed and mobile. Fixed carriers can be chemically or physically bound to the solid matrix, whereby the solute hops from one site to the other. Mobile carrier molecules have been incorporated in liquid membranes, which consist of a solid support of polymer matrix and a liquid phase containing the carrier molecules [25]. These membranes can attain high selectivity and permeability but are fragile in nature. Facilitated transport of carbon dioxide from CO_2/CH_4, CO_2/N_2 and CO_2/C_2H_6 mixtures using various carrier species such as monoethanolamine (MEA) [26,27], diethanolamine (DEA) [27–29], diisopropylamine (DIPA) [28], ethylenediamine (EDA) and $EDAH^+$ [30,31], diglycolamine (DGA) and triglycolamine [32], and N-methyl-diethanolamine (MDEA) [33] has been investigated. However, the applications of these membranes are often limited due to loss of solvent and carrier, temperature limitations, large membrane thickness, low permeability, limited solubility of the carrier in the liquid medium and low fluxes [13]. DEA is the most extensively used secondary amine for the removal of acid gases, due to favorable reaction kinetics, stability and rapid formation of carbamates while reacting with CO_2 [34]. It is also resistant to solvent degradation [35] and has less vapor pressure than primary alkanolamines [36]. A number of facilitated membranes consisting of secondary alkanolamines have been reported and evaluated for CO_2/CH_4 [37,38] and CO_2/N_2 [34] separation. Thus, DEA is emerged as a preferred choice to enhance the performance of gas separation membranes when applied for acid gas purification.

CMS is widely used for gas separation due to its porous property [39,40]. The incorporation of CMS lends a higher permeability to MMMs due to a high degree of porosity and fine pore size distribution. Moreover, the size of pore opening of CMS is of the same order as the size of gas molecules, thus allowing precise discrimination of certain gas species [41]. Vu et al. [21] investigated the gas separation performance of CMS and Matrimid® 5218 mixed matrix membrane. A 45% increase in CO_2/CH_4 selectivity was observed and it was found that CMS has better adhesion with the polymer matrix than zeolites. The high performance engineering thermoplastic PES was selected as the membrane polymer in this study. The repeating unit in the structure of PES possesses a certain degree of rigidity such that it has a glass transition temperature of 225 °C [42] and is thus a glassy polymer. Such distinct properties have made PES a distinguished membrane material for various applications [43].

As discussed above the MMMs still need improvements to make them attractive for industrial applications. An extensive literature review has revealed that this polymer and filler with alkanolamine has not yet been used to prepare MMM. In this study, different concentrations of DEA were added with fixed loading of CMS in PES matrix and tested for permeation of CO_2 and CH_4. Effects of DEA addition on permeance and ideal selectivity of CO_2 and CH_4 in the synthesized DEA-mixed matrix membranes were investigated. From the separation performance perspective, the DEA-mixed matrix membrane was found more efficient than the developed pure PES membrane. In these membranes CMS and DEA provide better transport of the gas. Due to synergetic effect of CMS and DEA with polymer, these membranes exhibited much better separation performance.

2. Theory and background

Gas transport through a mixed matrix membranes is a complex phenomenon. Several theoretical models have been used to predict the permeation properties of mixed matrix membranes as functions of the permeabilities of the continuous and dispersed phases. Petropoulos [44] and Shimekit et al. [45] present a comparative summary of various models. The classical model of Maxwell [46] for prediction of the permittivity of a dielectric has been successfully adapted to estimate the effective permeability of a membrane. The constitutive equations governing electrical potential and the flux through membranes are analogs and this justifies the application of Maxwell's results to transport in mixed matrix membranes. The equation (Maxwell – Wagner – Sillar model) for effective permeability of a mixed matrix membrane with a dilute dispersion of filler may be expressed as follows [47]:

$$P_{eff} = P_C \left[\frac{nP_d + (1-n)P_C - (1-n)\varphi_d(P_C - P_d)}{nP_d + (1-n)P_C + n\varphi_d(P_C - P_d)} \right] \quad (1)$$

here, P_{eff} is the effective permeability of a gas penetrant in a mixed matrix membrane with a volume fraction (φ_d) of dispersed phase (d) in a continuous matrix phase (C), P_C and P_d represent the gas penetrant permeabilities in the continuous and dispersed phases (CMS), respectively, and n is the shape factor of the dispersed (CMS) phase.

The mechanism of gas transport through CMS is the molecular sieving effect where molecules of smaller dimensions permeate preferentially in comparison with molecules of larger dimensions [48]. Both repulsive and attractive forces are involved in the interaction of gas molecules with the pore walls of CMS. Gas molecules are required to overcome an activation energy barrier originating from the repulsive forces in order to pass through the pore openings [49]. The large molecule (CH_4) faces stronger repulsive force than small gas molecule (CO_2) [50]. Hence, the size discrimination process enables very high selectivity in CMS.

The Dankwerts' Zwitterion reaction mechanism for DEA reaction with CO_2 has become a generally accepted mechanism facilitation of the transport process. Numerous studies have investigated the chemistry of CO_2–amine solutions due to its important industrial application for the removal of CO_2 from gas streams. The overall reaction between CO_2 and secondary amines is given as follows:

$$CO_2 + 2R_1R_2NH \leftrightarrow R_1R_2NH_2^+ + R_1R_2NCO_2^- \quad (2)$$

where R represents the functional groups (for MEA, $R_1 = -H$, $R_2 = -CH_2CH_2OH$; for DEA, $R_1 = R_2 = -CH_2CH_2OH$) [51–54].

In this study the investigated membrane combined the mechanism of solution–diffusion, molecular sieving and Dankwerts' Zwitterion reaction mechanism as shown in Fig. 1, and provided a better separation performance when compared to native polymeric membrane

3. Experimental methods

3.1. Materials

The PES (ULTRASON® E 6020P) was purchased from BASF® Germany; it has an average molecular weight of 50,000 g/mol. It was the main polymer for the fabrication of polymeric membranes due to number of favorable properties including thermal stability. The N-Methyl-2-Pyrrolidone (NMP), supplied by Merck® Germany, was used as a solvent for the preparation of dope solution due to its