Effect of Additives on Morphology and Permeability of Dendrimer Membrane for CO₂ Separation

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Abstract- *PAMAM- Dendrimers are the molecules which selectively separated CO₂ from a gaseous mixture. We have prepared PAMAM – Dendrimer and Polysulfone composite membranes by using various non- solvent additives. The membranes have been prepared by phase inversion technique using different non - solvent additives with a definite amount of PAMAM - Dendrimer and Polysulfone. SEM (Scanning Electron Microscope) pictures showed that Poly (ethylene glycol) (PEG-400) containing membranes are dense membranes and homogeneous in nature. We have studied the CO₂ permeation performances of the prepared membranes. All membranes showed general efficiency for CO₂ permeation wherever the membranes containing PEG as non-solvent additive are the best membrane for CO₂ permeation.*

Key Words: **PAMAM –dendrimer, selectivity, phase inversion, homogeneous, CO₂ permeation, dense membrane.**

1. INTRODUCTION

The membrane separation for removal of carbon dioxide from natural gas has advantages over the other conventional separation methods because of it's low capital cost, high-energy efficiency and it is environmental friendly. The commercially available polymeric membranes have both high permeabilities and selectivities. One of the advantages of a gaseous membrane separation process is it's simplicity; there is no need to regenerate an absorbent/adsorbent. In addition, membranes are simple to operate, compact and can be retrofitted easily etc.

A large numbers of researchers carried out their research studies to study the effect of various additives on membrane preparation. Lang et al; studied the roles of alkali metal counter-ions in the formation of PVDF/PFSA-M composite hollow fiber membranes [1]. Tager and his coworkers studied the effect of inorganic salt additives on the cellulose acetate membranes [2]. Han et al; studied the effect of additives on the performance and morphology of co Phthalazinone ether sulfone composite UF membrane [3]. Vilakati investigated the mechanical and thermal properties of polysulfone composite membranes modified with synthetic and natural polymer additives [4]. Ismail et al; studied the effect of additives concentration on the surface properties and performance of PVDF ultrafiltration membranes for refinery produced waste water treatment [5].

PAMAM - Dendrimers are a new class of artificial macromolecules which are synthetic, highly branched, monodisperse, globular and nanopolymeric in configurations. These PAMAM- Dendrimer macromolecules have definite molecular weight, shape and size, which make them excellent candidates for numerous industrial applications. PAMAM- Dendrimers are globular nanostructures that are precisely engineered to carry molecules encapsulated in their interior void spaces or attached to the surface. PAMAM- Dendrimers provide polyvalent interactions between surfaces and bulk materials which makes it suitable for various applications such as surface coatings etc. Because of it's control over size and surface makes PAMAM - Dendrimers one of the smartest or customizable commercially available nanotechnologies [6]. Due to their very well defined structures PAMAM- Dendrimers are the candidates for the purpose of membrane formation which facilitates the separation of CO₂ from a gaseous mixture [7]. PAMAM- Dendrimer based polymeric membranes have been developed for variety of industrial applications including reverse osmosis, ultra- filtration and gas separation processes because of their high permeability and selectivity. One promising means of lowering the cost of CO₂ separation is the development of high performance CO₂ separation membranes that allow CO₂ recovery via membrane separation. PAMAM-Dendrimer composite membrane comprising a gas selective layer is applicable for gas separation processes   [8-10].Thus, in continuation of our activities on membrane research, we have been pursuing research on preparation and characterization of PAMAM - Dendrimer composite membranes useful for CO₂ separation from a gaseous mixture . We have studied the effect of various non-solvent additives on membranes formation with an emphasis to study the morphology and performances of the membranes for CO₂ separation.

2. EXPERIMENTAL SECTION

2.1 Materials

Polysulfone (average molecular weight 22000) was obtained from Aldrich Chemicals were used as the main membrane material. N-Methyl-Pyrollidine (NMP ;> 99%) obtained from Rankem, India was added as a solvent. Commercial PAMAM-

Dendrimer (Zero generation) purchased from Sigma Aldrich Chemical Ltd was used as membrane material. The non solvent additives used in the preparation of membrane were Polyethylene Glycol (PEG-400), Ethanol, Isopropanol; Butanol etc were obtained from Sigma-Aldrich, Central Drug House (P) Ltd, Bombay-New Delhi. Water used was obtained from Millipore water system. The gas cylinders were purchased from M.S Gas centre, Jorhat.
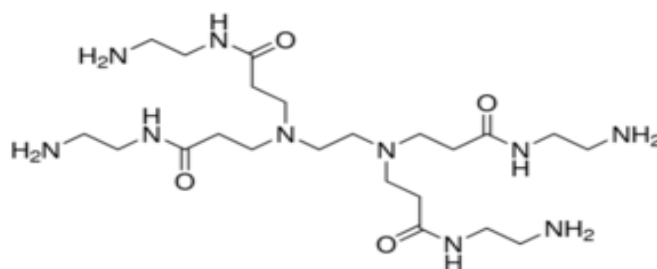

Chemical structure of PAMAM- Dendrimer (Generation 0)

2.2 The Synthesis of Polysulfone / Dendrimer Blend Casting Solution

Polysulfone were dissolved in NMP at room temperature (28 °C). A certain amount of PAMAM dendrimer (G-0) was added into the solution at ambient temperature, under rigorous stirring for 1 h. Then the temperature was increased to 45 °C. Additives with different compositions including 6 wt% PEG-400, 6 wt% Ethanol , 4 wt % Ethanol+ 2 wt % Isopropanol, 4 wt % Ethanol + 2 wt % Butanol, 4 wt% Ethanol + 1 wt% Isopropanol+ 1wt % Butanol were introduced into the solution. After stirring for six hours situpolycondensation was completed and the reaction solution was degassed for 12 h at room temperature. The casting solution above was used to investigate the thermodynamic properties.

2.3 Preparation of Membranes

The above prepared Polysulfone / Dendrimer Blend casting solutions were casted onto some cleaned glass plates at ambient temperature using a glass rod with a gap distance of 210 µm. Then, the glass plates were immersed immediately into deionized water using as coagulant for 24 hours. Then the nascent membranes were washed with deionized water for several times. Then the flat sheet membranes were dried at room temperature (28 °C).
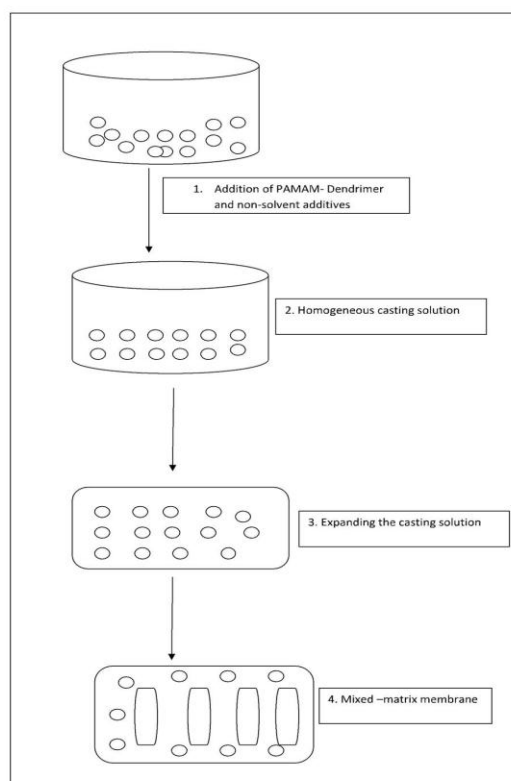
Fig - 1: Schematic diagram of membrane preparation procedure

2.4 Cloud point measurement

The cloud points were determined by means of the simple titration method. Binodal lines were obtained for non-solvent additive used in this study based on cloud point measurement keeping polysulfone, dendrimer and solvent/additive ratio constant at 23 wt%, 0.4 wt% and 76.6 wt % respectively. Polysulfone and PAMAM- Dendrimer are taken as the main polymer for casting solutions. Various compositions were prepared from the polymers and the coagulant. Distilled water was gradually added to a solution of Polysulfone – PAMAM- Dendrimer and solvent/non solvent additive mixture slowly until the solution became slightly turbid. During, the titration processes the casting solutions were well stirred and kept at a constant temperature. The composition at which turbidity occurred was called the Cloud point that represents the composition where the phase transition occurred. The cloud points were marked on the ternary phase diagram, including only the solvent (NMP), non solvent additives and the polymer (Polysulfone and Dendrimer).
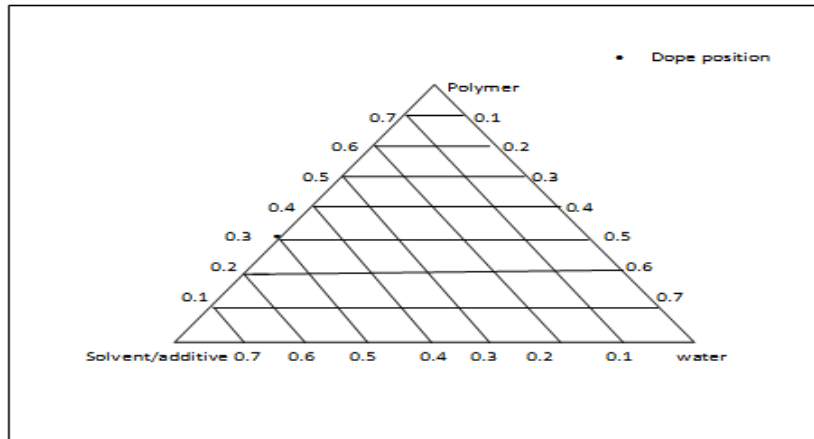

Fig- 2: Dope position in triangular coordinate

2.5 Gas Permeation Experiment

The pressure-normalized fluxes of the fabricated flat sheet membranes were measured for permeation of CO_2 at room temperature (28° C). Circular membrane discs with a 3 cm in diameter and an effective permeation area of 7.065 cm^2 was used for this study. The standard permeate volumetric flow rate at atmospheric conditions was measured by a flow meter. The experimental set – up for the permeation experiment is shown in Figure. 3. The permeability, through the membranes can be calculated by the following equation.

$$F = Q/A.\Delta P \qquad [1]$$

Where Q is the measured flow rate (at standard pressure and temperature), F is permeability of gaseous component, A is effective membrane area and ΔP is the Pressure difference across the membrane. The common unit of permeability is GPU (1 GPU= 10^{-6} cm^3 (STP)/cm^2 s cm Hg).
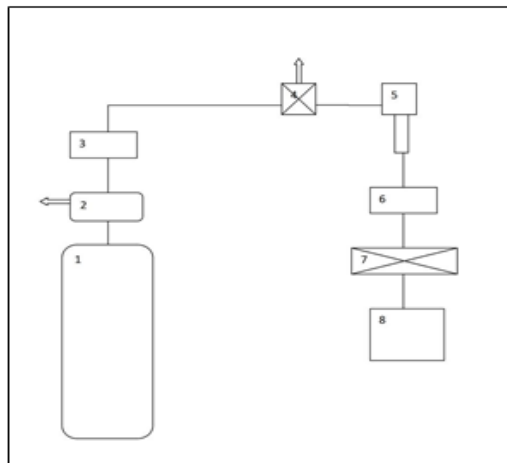

Fig- 3: Flow diagram for experimental set-up of gas permeation experiment

1. **C**O_2 Gas Cylinder 2. Gas regulator 3.Inlet flow -meter 4. Pressure regulator 5. Valve 6. Membrane module 7. Outlet flow - meter 8.Gas collector

       Gaseous pure CO_2 was passed through the membrane module. The flow –meters were used to measure the inlet and outlet flow rates. From the differences of inlet and outlet flow rates we calculated the permeated gas flow rates. Thus; we calculated the permeabilities of the gases passed through the membrane.

3. RESULTS AND DISCUSSIONS

3.1.Effect of the additives on the isothermal phase diagram

     Based on the cloud-point experiment, the equilibrium phase diagram of polymer-Solvent-water at 28 º C with and without additives was made and is shown in the Figure 4.

Figure 4 shows that addition of non solvent additives to the polymer solution brought the cloud point curves closer to the (Polymer)-(solvent/additive) axis, making the one-phase region narrower. That is, the presence of the non-solvent decreases the solvent power and thus polymer-polymer interactions increases. Therefore, when additives are added to the casting dope, less water is needed to precipitate the polymer [11]. The figure also indicates that addition of PEG-400 to the polymer-solvent system can bring the binodal line closer to the (polymer)-(solvent/non-solvent) axis as compared to polymer-solvent system with addition of other nonsolvent/additives like ethanol, ethanol- Isopropanol – Butanol , ethanol- Isopropanol and Ethanol- Butanol . Thus, on addition of PEG-400 as the additive gives a better dendrimer membrane for CO_2 separation. Similar observations were observed for Polymer-NMP system while using PEG-400, Polyvinylpyrrolidone (PVPK 15) and glycerol as additive [12].
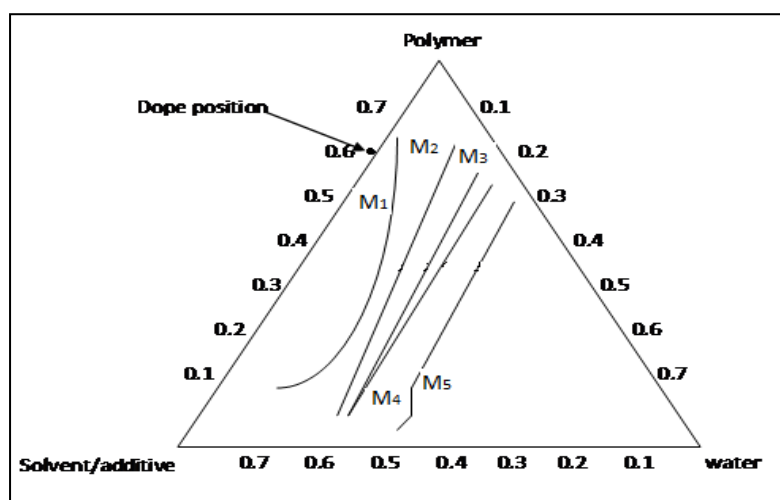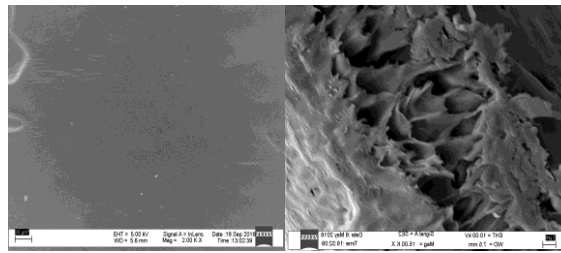

Fig-4: Effect of additives on isothermal phase diagram; M_1. PEG M_2. Ethanol, M_3. Ethanol, Isopropanol, M_4. Ethanol, Butanol, M_5. Ethanol, Isopropanol, Butanol.

3.2 Effect of additives on the morphology of membranes

     The SEM photographs of the membranes prepared by using different additives are shown in Figure 5. From the figure it is seen that the morphology of the membranes are different and depends on the additives. Addition of a suitable non-solvent additive into the casting solution shortens the precipitation path and that accelerates the coagulation process. As a result a thinner skin layer and a more uniform structure can be obtained. In our case, the membranes with PEG-400 as additive gives the thinnest skin layer as it is in the miscible region. Other membranes with different nonsolvent additives as also give the thinner layer in the order. Thus addition of nonsolvent additives can alter the membrane morphology. Again the thinnest skin results from the casting dope whose composition is nearer to the binodal line leading to the highest CO_2 permeation properties. The membranes prepared without additive has the finger like structure with pinhole and but the membranes prepared by using ethanol nodular sub layer at the surface of the membranes this type of pinhole was absent. The membranes prepared by using PEG-400 have a sponge like structure and no pinholes found in this membrane. Thus this membrane is efficient for CO_2 separation. Similar observations were made for some other membranes prepared by using glycerol as additive which has sponge like structure and has the highest selectivity for CO_2 The permeation of CO_2 gas occurs through the membranes matrix of the thinnest skin layer gives the highest flux. Thus selectivity and flux can be altered by proper adjustment of the skin layer thickness and the sublayer morphology which can be done by proper choice of additive.

It is seen from the Figure 5, that the membrane containing PEG-400 as additives has the most uniform morphology and suitable for CO_2 separation. Again; the membrane using Ethanol, Isopropanol and Butanol as additive has the least uniform morphology and is not suitable for CO_2 separation.
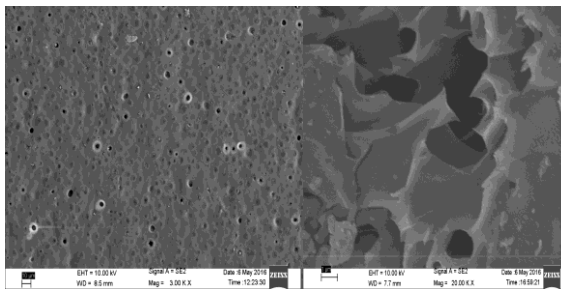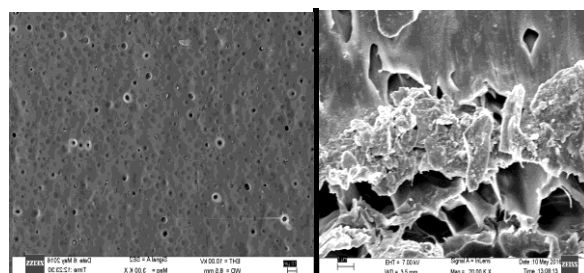

Front view and Side view of the membrane M_1
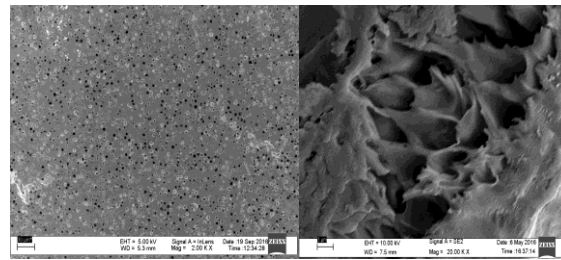
Front view and Side view of the membrane M_2
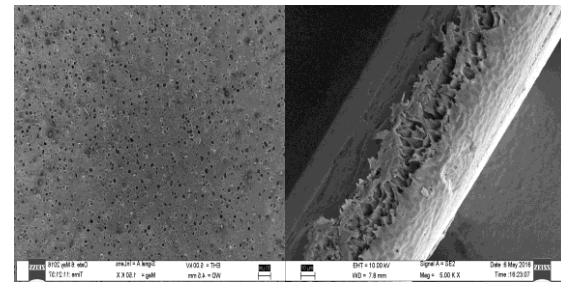
Front view and Side view of the membrane M_3

Front view and Side view of the membrane M_4

Front view and Side view of the membrane M_5

Fig- 5: SEM photographs of Membranes prepared with different additives; M_1. PEG M_2. Ethanol; M_3. Ethanol, Isopropanol M_4. Ethanol, Butanol, M_5. Ethanol, Isopropanol, Butanol.

3.3 Membrane formation mechanism

After immersion of casting solution into the coagulation bath, the uppermost region can form an integral skin because of demixing and in this way the region below the top skin layer is crystallised. Thus diffusion of no solvent from the coaugulant bath into the casting solution occurs and liquid-liquid demixing phase separation takes place. This diffusion depends on molar volume of the coagulant with small molar volume favours rapid diffusion into the casting solvent .We used water as coagulant which diffuse easily into the cast film and but due to the non compatibility with polysulfone and PAMAM-Dendrimer, water cannot diffuse easily into the casting solution through the membrane skin. Thus it forms membrane by leaving NMP mainly. The mechanism is similar to the mechanism of dense membrane suitable for gas separation.
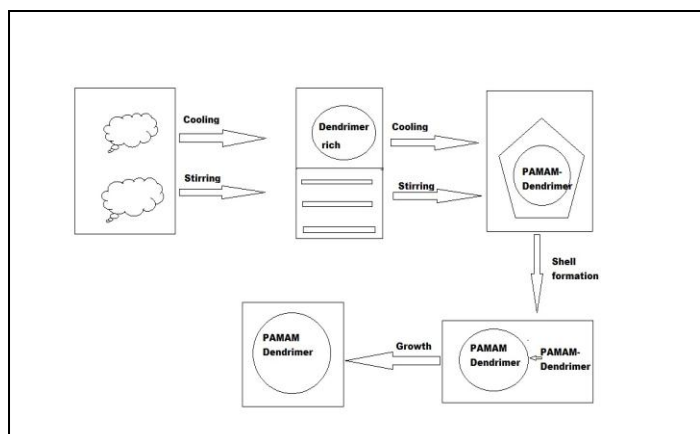

Fig- 6: Schematic diagram of membrane formation mechanism

3.4 Effect of additives on gas Permeabilities of Membranes

Figure 7 shows the effects of different additives on membranes for permeation of carbon dioxide at a pressure up to 50 cm/Hg .As shown in the Figure 7, the addition of PEG as additive gives the highest CO_2 permeability factor. The permeability of CO_2 varies with different non- solvent additives .This can be attributed to instaneous demixing induced by the addition of non-solvent additives [13]. The membrane prepared from dope containing PEG- 400 is more permeable than the membranes containing other additives such as Ethanol, Isopropanol and Butanol and their mixture. This can be attributed to the pore forming property of PEG [14]. On the other hand, the membrane containing Ethanol, Isopropanol and Butanol as additives shows the lowest permeability. Similar type of observations was also reported elsewhere for gas separation by membrane prepared by using organic solvent and polymer as nonsolvent additives [13].
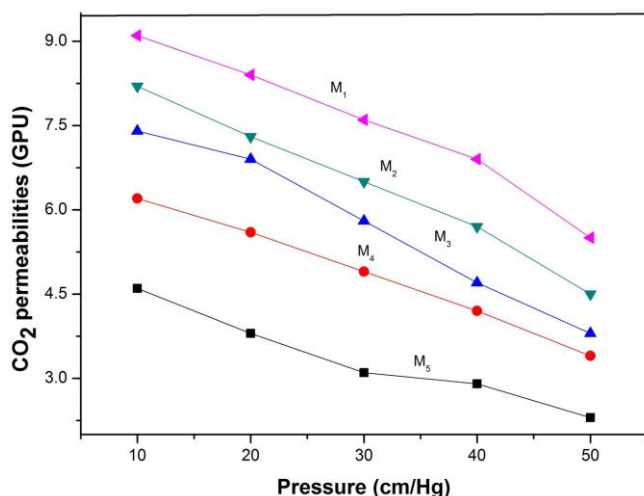

Fig- 7: Effect of feed gas pressure on CO_2 Permeabilities of membranes prepared with various additives; Operating conditions: 28 ºC Temperature. Feed gas pressure: 10-50 (cm/ Hg). M_1 : PEG, M_2: Ethanol , M_3: Ethanol, Isopropanol, M_4: Ethanol, Butanol, M_5: Ethanol, Isopropanol, Butanol.

The high permeabilities of PAMAM – Dendrimer composite membranes are attributed to the facilitated transport mechanism of PAMAM- Dendrimer molecules incorporated into the membranes. According to the facilitated transport mechanism of PAMAM- Dendrimer molecules CO_2 was transformed as small and mobile ion HCO_3^- ion. Thus it enhances the transportation of CO_2 through the PAMAM- Dendrimer composite membranes.

4. CONCLUSIONS

Asymmetric membranes were prepared by the phase inversion technique, using Polysulfone and Dendrimer as the membrane material and PEG, Ethanol, Isopropanol, Butanol as nonsolvent additives. The addition of nonsolvent additives into polymer solutions significantly alters the membranes morphology and membranes separation performance for CO_2 separation. Change in membrane morphology with the addition of different additives in the casting solutions are indicated by SEM photographs. It can be concluded from SEM results that the membrane containing PEG as additive possess the minimum pore size and shows that the greatest permeability factor. The membrane containing PEG as additive shows the highest permeability at a feed gas pressure of about 50 cm/Hg. Thus, the types of non-solvent additives has been proven to be one of the most influential parameters in membrane fabrication and needs careful attention if a better performing membrane is to be fabricated.

ACKNOWLEDGEMENTS

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