Razi University

Faculty of chemistry
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M.Sc. Thesis

Title of the Thesis
Preparation and characterization of polymeric membranes for ethylene/nitrogen separation

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October ٢٠٠٩

Abstract:

This paper deals with the preparation and characterization of some polymeric membranes to study the efficiency of gas separation performance. Membrane performance was evaluated using pure gases (N_2 and C_2H_4) at different feed pressures. This work contains two parts. The aim of the first part was to improve gas separation performance of (pyromellitic dianhydride-co-٤, ٤'-oxy dianiline (PMDA/ODA)) polyimide membranes by means of different additive agent such as Polyvinylidene fluoride (PVDF) and polyethersulfone (PES). The ideal selectivity of ١٠٠٪ (ethylene permeation only) was achieved at ١ bar feed pressure using PMDA/ODA polyimide membranes with addition of ١ wt % PVDF. Addition of PES did not have any important influence on ideal selectivity of the prepared membranes. By adding PES, there was an evidence of approximately spherical droplets which have been dispersed throughout the polyimide membrane matrix. Part two of the paper was to prepare blend membranes of PES-based. PES- (PMDA/ODA) polyamic acid (PAA) blend membranes were prepared by using blends of different compositions of PES (٢٥ wt %) and PAA (١٥ wt %) solutions in NMP. The composition of casting solutions of PES-PAA solutions has a main influence on the ideal selectivity of blended membrane. The ideal selectivity of ٢,٩ for ethylene was achieved at ٣ bars feed pressure using blend membranes with ٠,٥ wt % PAA solution in their casting solutions. PES- PMDA/ODA polyimide membranes were also prepared from blend casting solutions by thermal imidation. Immiscible blend membranes were achieved at different compositions of the casting solutions. The blend membranes have huge amount of gas permeance with poor selectivity. IR spectroscopy and Scanning Electron Microscopy (SEM) images were employed to characterize the membranes.

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Chapter One

Overview of membrane science and technology

١-١ Introduction

In recent years, membranes and membrane separation techniques have grown from a simple laboratory tool to an industrial process with considerable technical and commercial impact. Today, membranes are used on a large scale to produce potable water from the sea by reverse osmosis, to clean industrial effluents and recover valuable constituents by electrodialysis, to fractionate macromolecular solutions in the food and drug industry by ultra filtration, to remove urea and other toxins from the blood stream by dialysis in an artificial kidney, and to release drugs such as scopolamin, nitroglycerin, etc. at a predetermined rate in medical treatment. Although membrane processes may be very different in their mode of operation, in the structures used as separating barriers, and in the driving forces used for the transport of the different chemical components, they have several features in common which make them attractive as a separation tool. In many cases, membrane processes are faster, more efficient and more economical than conventional separation techniques. With membranes, the separation is usually performed at ambient temperature, thus allowing temperature-sensitive solutions to be treated without the constituents being damaged or chemically altered.

This is important in the food and drug industry and in biotechnology where temperature-sensitive products have to be processed. Membranes can also be “tailor-made” so that their properties can be adjusted to a specific separation task.

Membrane science and technology is interdisciplinary, involving polymer chemists to develop new membrane structures; physical chemists and mathematicians to describe the transport properties of different membranes using mathematical models to predict their separation characteristics; and chemical engineers to design separation processes for large scale industrial utilization. The most important element in a membrane process, however, is the membrane itself. To gain an understanding of the significance of the various structures used in different separation processes a brief discussion of the basic properties and functions of membranes, and the driving forces and fluxes involved is essential [١].

١-٢ Definition of a membrane

A precise and complete definition of a membrane which covers all its aspects is rather difficult, even when the discussion is limited to synthetic structures as in this outline. In the most general sense, a synthetic membrane is a barrier which separates two phases and restricts the transport of various chemical species in a rather specific manner. A membrane can be homogeneous or heterogeneous, symmetric or asymmetric in structure; it may be solid or liquid; it may be neutral, may carry positive or negative charges, or may be bipolar. Its thickness may vary between less than ١٠٠ nm to more than a centimeter. The electrical resistance may vary from several mega ohms to a fraction of an ohm, mass transport through a membrane may be caused by convection or by diffusion of individual molecules, induced by an electric field, or a concentration, pressure or temperature gradient.

The term “membrane”, therefore, includes a great variety of materials and structures, and a membrane can often be better described in terms of what it does rather than what it is. Some materials, though not meant to be membranes, show typical membrane properties, and in fact are membranes, e.g., protective coatings, or packaging materials. All materials functioning as membranes have one characteristic property in common: they restrict the passage of various chemical species in a very specific manner [١].

In essence a membrane is nothing more than a discrete, thin interface that moderates the permeation of chemical species in contact with it. This interface may be molecularly homogeneous, that is, completely uniform in composition and structure, or it may be chemically or physically heterogeneous, for example, containing holes or pores of finite dimensions or consisting of some form of layered structure. A normal filter meets this definition of a membrane, but, by convention, the term filter is usually limited to structures that separate particulate suspensions larger than ١ to ١٠ μm. The principal types of membrane are shown schematically in Figure ١-١. For relative information see [٢].

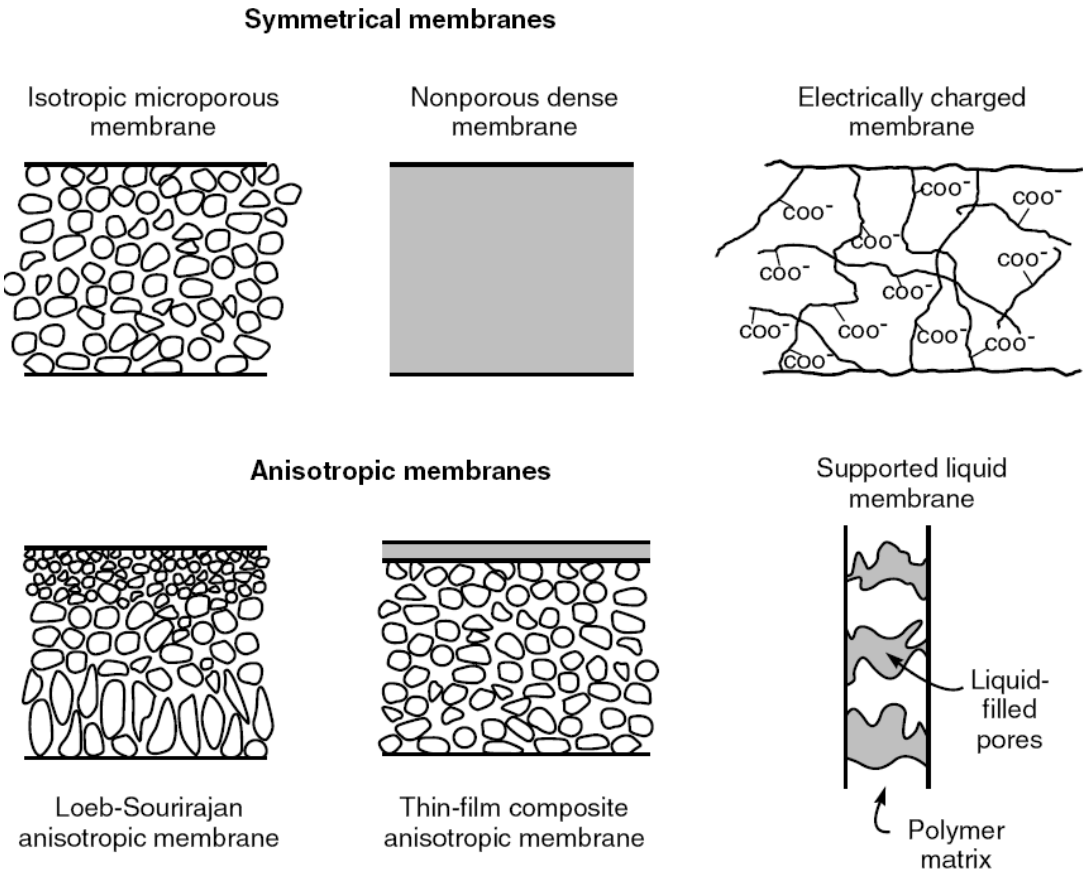

Figure١-١ Schematic diagrams of the principal types of membrane [٢]

Chapter Two

Gas separation with membranes

٢-١ Introduction

The separation of gas mixtures with membranes has emerged from being a laboratory curiosity to becoming a rapidly growing, commercially viable alternative to traditional methods of gas separation within the last two decades. Membrane gas separation has become one of the most significant new unit operations to emerge in the chemical industry in the last ٢٥ years [٣]. As a result, gas separation by membrane process has acquired great significance in the industrial application in terms of economical considerations, as gases occupy a central position in the chemical feed stock industry

Organic polymers are the dominating materials for gas separation membranes. Many polymers exhibit sufficient gas selectivity and they can be easily processed into membranes. Palladium alloys are the only inorganic materials which are currently used for gas separation (ultra-pure hydrogen generation) on a commercial scale. However, during the last decade inorganic materials have been developed with exciting unmatched selectivity for certain gas mixtures and some of the inorganic membranes described in the scientific literature seem to be on the brink of commercialization. Table ٢-١ shows relevant membrane materials for gas separation [٣].

Tab ٢-١ Materials for gas separating membranes

Organic polymers	***Inorganic materials***
Polysulfone, polyethersulfone	**Carbon molecular sieves**
Cellulose acetate	**Nanoporous carbon**
Polyimide, polyetherimide	**Zeolites**
Polycarbonate (brominated)	**Ultramicroporous amorphous silicia**
Polyphenyleneoxide	**Palladium alloys**
Polymethylpentene	**Mixed conducting perovskites**
Polydimethylsiloxane	**-**
Polyvinyltrimethylsilane	**-**

۲-۲ Types of membranes

Membranes for the separation of gas mixtures are of two very different kinds: one a microporous membrane, the other nonporous.

۲-۲-۱ Microporous membranes

Microporous membranes were the first to be studied and the basic law governing their selectivity was discovered by Graham. When pore size of a microporous membrane is small compared to the mean-free-path of the gas molecules, permeate will be enriched in the gas of the lower molecular weight. Since molecular weight ratios of most gases are not very large and since the selectivity is proportional to the square root of this ratio, not only practical but theoretical enrichments achievable by this method necessarily will be small. In order to have an efficient separation of a gas mixture, many separation stages are required. On the other hand, since this method of separation is based strictly on mass ratios and not chemical differences, it is the only membrane based method capable of separating isotopes of a given compound [۳].

۲-۲-۲ Nonporous membranes

The other membrane-based gas separation method utilizes non-porous membranes. In permeating through the membrane, the gases are separated due to differences in their diffusivity and solubility in the membrane matrix (normally an organic polymer). Molecular size will play a role in such separations but so will the chemical nature of the gas. Thus, conceptually very efficient separations should be possible this way. As polymer science developed, many polymers were tested for gas permeabilities and indeed some with very good selectivities were found [۳].

۲-۳ Theoretical background

The average pore diameter in a membrane is difficult to measure directly and must often be inferred from the size of the molecules that permeate the membrane or by some other indirect technique. With this caveat in mind membranes can be organized into the some general groups shown in Figure ۱-۱.

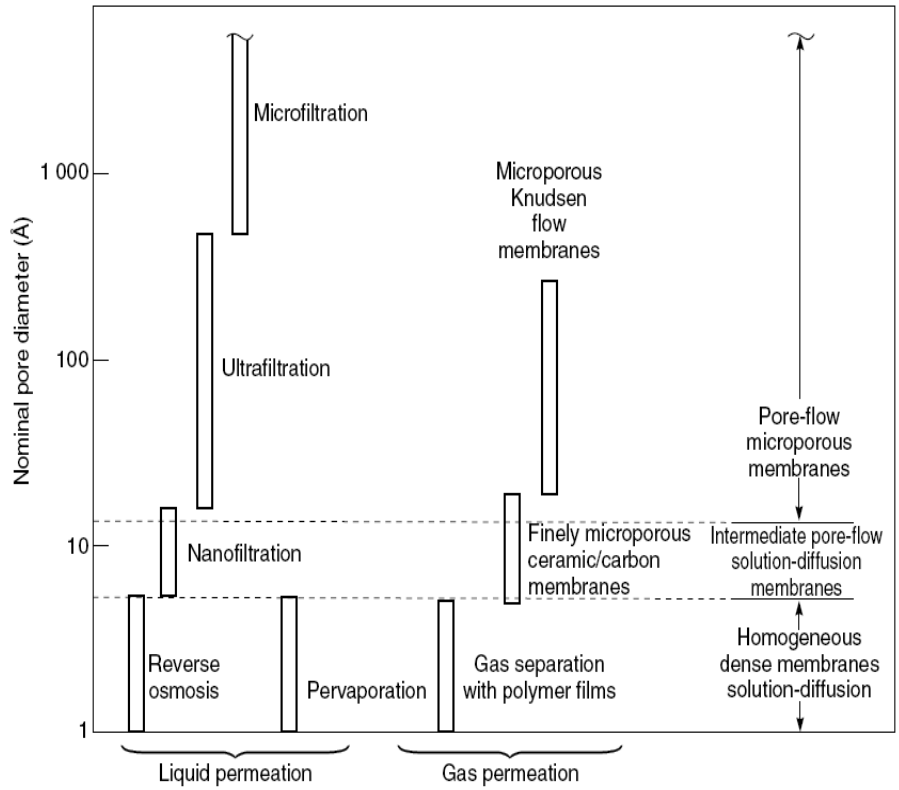

Figure ٢-١ Schematic representation of the nominal pore size and best theoretical model for the principal membrane separation processes [٢]

Both porous and dense membranes can be used as selective gas separation barriers; Figure ٢-١ illustrates the mechanism of gas permeation. Three types of porous membranes, differing in pore size, are shown. If the pores are relatively large from ٠,١ to ١٠ μm, gases permeate the membrane by convective flow, and no separation occurs. If the pores are smaller than ٠,١ μm, then the pore diameter is the same size as or smaller than the mean free path of the gas molecules. Diffusion through such pores is governed by Knudsen diffusion, and the transport rate of any gas is inversely proportional to the square root of its molecular weight. This relationship is called Graham's law of diffusion. Finally, if the membrane pores are extremely small, of the order ٥ – ٢٠A°, then gases are separated by molecular sieving. Transport through this type of membrane is complex and includes both diffusion in the gas phase and diffusion of adsorbed species on the surface of the pores (surface diffusion). These very small-pore membranes have not been used on a large scale, but ceramic and ultramicroporous glass membranes with extraordinarily high selectivities for similar molecules have been prepared in the laboratory.