ABSTRACT

ABSORPTION OF CO_2 THROUGH HOLLOW FIBER MEMBRANES USING AQUEOUS SOLUTIONS OF VARIOUS ABSORBENTS

by
Praveen Babu Kosaraju

Absorption behavior of CO_2 was studied in different hollow fiber membrane modules fabricated using Celgard (polypropylene) and poly(4-methylpentene-1) microporous hollow fibers. Pure water, aqueous solutions of poly(amidoamine) (PAMAM) dendrimer of generation zero and monoethanolamine (MEA) were used as the absorbent; the absorbent solution flowed through the fiber bore, the gas mixture of CO_2 and N_2 flowed countercurrently on the shell side. The system consisted of absorption in one module and stripping with Helium in another module of the same fibers. The absorption characteristics of the dendrimer solution and the MEA solution were studied in the modules built of Celgard fibers and poly(4-methylpentene-1) fibers respectively. The overall CO_2 mass transfer coefficients were calculated for the above-mentioned cases and compared. Experiments were carried out for a long period of time to study the stability of the system and hence the wettability of the membranes by the absorbents. The permeation of the absorbents through the pores of the fiber from the tube side to the shell side of the module was also studied especially in the case of MEA.

From the experimental observations, it was concluded that the pores in the Celgard membrane were not wetted at all by the aqueous dendrimer solution; the MEA was found to permeate through the pores of the poly(4-methylpentene-1) fiber. MEA present in the pores while permeating may have reduced the membrane resistance slightly and hence, increased the absorption rate.

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Dedicated to my parents

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A_T	mass-transfer area based on surface area of gas-liquid contact (cm^2)
C_1	solubility ratio of CO_2/N_2O
C_{gin}	concentration of the absorbed gas species at the gas stream inlet (mol/cm^3)
C_{gout}	concentration of the absorbed gas species at the gas stream outlet (mol/cm^3)
C_{ig}	concentration of species *i* in the gas phase at the gas-liquid interface (mol/cm^3)
C_{il}	concentration of species *i* in the liquid phase at the gas-liquid interface (mol/cm^3)
C_{lin}	concentration of free CO_2 in liquid inlet (mol/cm^3)
C_{lout}	concentration of free CO_2 in liquid outlet (mol/cm^3)
C^t_{lin}	concentration of total CO_2 in liquid inlet (mol/cm^3)
C^t_{lout}	concentration of total CO_2 in liquid outlet (mol/cm^3)
ΔC_{lm}	logarithmic mean concentration difference of CO_2 (mol/cm^3)
d_i	fiber internal diameter (cm)
H	Henry's law constant
H_{N_2O}	Henry's law constant for N_2O in water
K_{Olm}	overall mass-transfer coefficient (cm/s)
l	effective length of the module (cm)
n	number of fibers in the module

LIST OF SYMBOLS
(Continued)

ΔP_{cr}	breakthrough pressure (dyne/cm^2, atm.)
P	pressure or partial pressure (atm.)
r_p	pore radius (cm)
T	room temperature (°C)
V_g	feed gas flow rate (cm^3/min)
V_l	absorbent liquid flow rate (cm^3/min)

Greek

γ_C	critical surface tension (dyne/cm)
γ_{LV}	surface tension at the liquid-vapor interface (dyne/cm)
γ_{SL}	surface tension at the solid-liquid interface (dyne/cm)
γ_{wo}	surface tension of the absorbent liquid exposed to the gas mixture (dyne/cm)
θ_c	contact angle

Subscripts

B	bulk
g	gas
i	species
l	liquid
m	membrane

CHAPTER 1

INTRODUCTION

1.1 Background

Separation and purification of gas mixtures with energy efficiency and selectivity is vital to a broad array of industries and technologies. Separation of different gas species in a mixture is usually achieved by either chemical or physical means. Such approaches include gas absorption into a solvent, pressure swing adsorption, cryogenic separation, distillation, membrane-based separation etc. Due to the advantages of gas separation membranes, they are now applied in a wide range of processes including the production of nitrogen from air, hydrogen recovery from refinery, petrochemical and ammonia-purge streams, CO_2 removal from natural-gas streams and other mixtures with hydrocarbons and dehydration of compressed air (Karoor and Sirkar, 1993).

Gas mixtures are usually dispersed and contacted with liquids in conventional gas absorption processes employing several types of devices like packed tower, spray tower, venturi scrubber or bubble column. Dispersion in these contacting devices has many drawbacks. Membrane-based contacting devices could overcome these shortcomings by preventing gas dispersion in the contacting phase (Sirkar, 1992; Yongtaek et al., 2001). Major advantages of membrane-based gas absorption include independent variations of the gas and liquid flow rates without flooding, loading, weeping, foaming, etc. Membrane-based processes are easy to scale up because of their modularity, have low maintenance and labor costs associated with their operation and have low energy requirements (Sirkar, 1992).

Different absorbents and membranes have being studied for a long time for better separation and purification processes. Qi and Cussler (1985 a, b) studied the absorption of a number of gases using various solvents and aqueous solutions in a hydrophobic microporous hollow fiber device where the membrane pores were gas filled. Ogundiran et al. (1988, 1989) in their experiments with absorption of SO_2 using microporous hydrophobic hollow fibers found this technique to be an extremely promising alternative to conventional scrubbers used for flue gas desulfurization. Karoor and Sirkar (1993) have studied gas absorption in microporous hollow fiber membrane modules and the processes were simulated using a numerical model for species transport.

1.2 Membrane-based Gas Absorption and Stripping

In membrane-based gas absorption and stripping, gas flows on one side of the membrane and the absorbent or stripping liquid will be flowing on the other side and both are separated by an immobilized gas/liquid interface. The pores can be either filled with liquid or gas depending on the mode of operation. If the pores are filled with liquid, it is called the wetted mode; if the pores are filled with gas, it is called the non-wetted mode of operation. When an aqueous solution is used as the absorbent, we can operate hydrophilic membranes in wetted mode only, whereas hydrophobic membranes can be operated in both wetted and non-wetted modes.

To ensure nondispersive gas absorption with microporous hydrophobic or hydrophilic membranes, the pressure of the phase not in the membrane pores must not exceed the pressure of the phase in the membrane pores by a critical amount ΔP_{cr}. This maximum allowable value of differential pressure is identified as the breakthrough pressure.

If the microporous membrane could be modeled as a collection of parallel cylindrical pores of radius r_p, then the breakthrough pressure is related to other relevant variables by the Young-Laplace equation

$$\Delta p_{cr} = \frac{2\gamma_{wo}\cos\theta_c}{r_p} \tag{1.1}$$

where γ_{wo} is the surface tension of the absorbent liquid exposed to the gas mixture, θ_c is the contact angle and r_p is the pore radius.

"Consider a hydrophobic membrane with non-wetted mode of operation shown in Figure 1.1. An aqueous solution that does not wet the membrane flows on one side of the membrane and a gas mixture flows on the other side at a pressure less than that of the aqueous phase. As long as the aqueous solution pressure is less than the breakthrough pressure, ΔP_{cr}, the aqueous solution will not penetrate the pores. Unless the gas phase pressure is higher than that of the aqueous phase, the gas will not bubble into the aqueous solution. Thus over the excess aqueous phase pressure range of 0 to ΔP_{cr}, the gas/liquid interface is immobilized at the pore mouth of the hydrophobic membrane on the solution side. Through such an interface, one or more gas species may be absorbed into the aqueous solution." (Sirkar, 1992)

Sirkar (1992) has reviewed non-dispersive gas absorption with the gas phase at a higher pressure by considering the wetting of the hydrophobic membrane via an exchange process and incorporating an aqueous solution in the membrane pores. The solute partial pressure and the concentration profiles in gas absorption through a gas/liquid interface immobilized at the pore mouth of a microporous hydrophobic membrane with absorbent filled pores are shown in Figure 1.1.

"Gas/liquid contacting can also be carried out using a microporous hydrophilic membrane, which is spontaneously wetted by the aqueous absorbing liquid. The direction of phase pressure differential however is different; the gas phase pressure has to be higher than the liquid phase pressure to immobilize the gas/liquid phase interface at the pore mouths on the gas side of the membrane." (Sirkar, 1992)

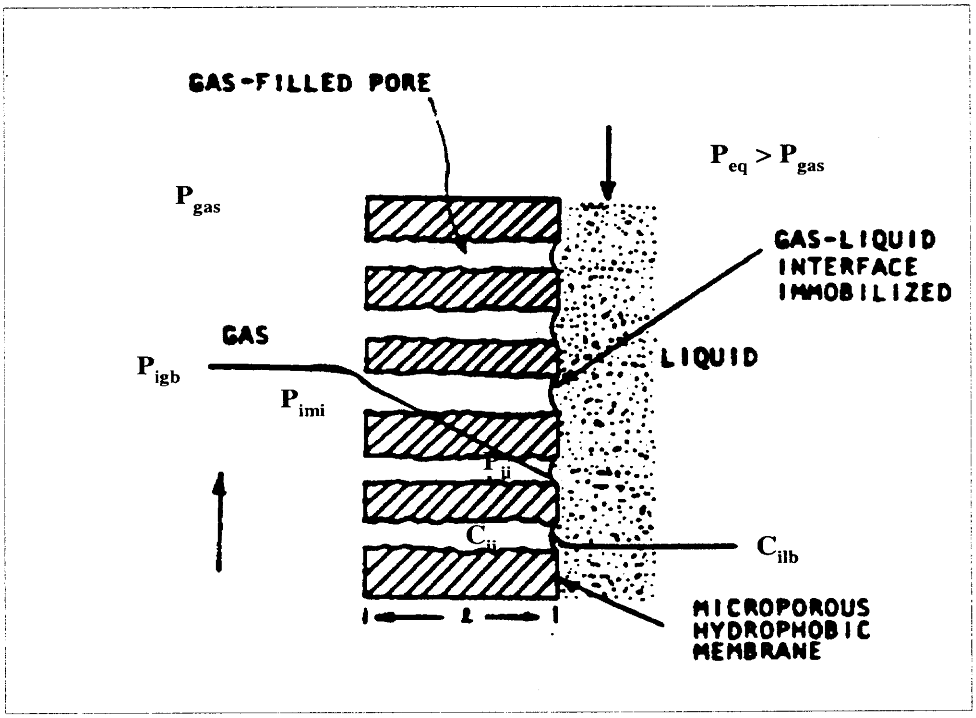

Figure 1.1 Solute partial pressure and concentration profiles in gas absorption through a gas/liquid interface immobilized at the pore mouth of a microporous hydrophobic membrane with gas-filled pores (Sirkar, 1992).

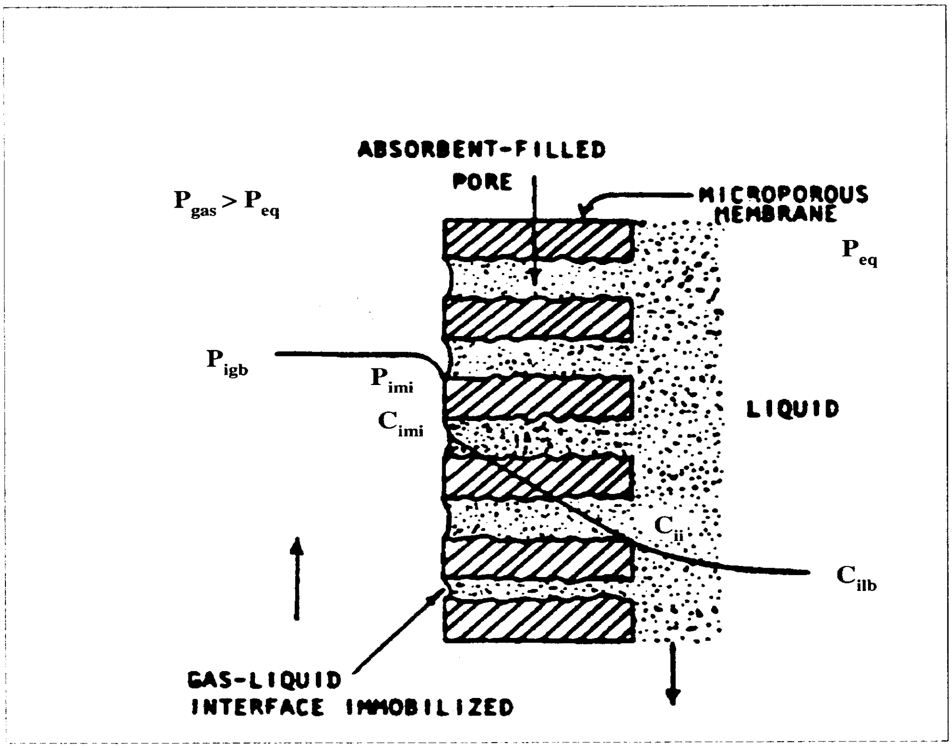

Figure 1.2 Solute partial pressure and concentration profiles in gas absorption through a gas/liquid interface immobilized at the pore mouth of a microporous hydrophobic membrane with absorbent-filled pores (Sirkar, 1992).

Karoor and Sirkar (1993) have conducted experiments for the removal of CO_2 using microporous hydrophobic polypropylene hollow fibers in both wetted mode and non-wetted modes of operation. They reported that by filling the pores with the absorbent liquid, the membrane-phase resistance is increased as the liquid offers additional resistance to the transport. This behavior highlights the fact that the process is a liquid-phase-controlled process. Hence, it would not be advantageous to operate under wetted-mode conditions for this particular system. Therefore, one has to ensure that the excess pressure of the liquid phase over the gas phase does not exceed the ΔP_{cr} value for the membrane material, pore size and gas/liquid system. From the above inferences, one can say that wetting plays the major role in the membrane-based gas absorption, and the influence the wetting are the membrane material, pore size and the surface tension of the absorbent solution.

Gas absorption can also be carried out in the asymmetric membranes whose pore size on the inside surface will be different from the outside surface. These membranes consist of two layers, each one made of a different material and has a different pore size. The skin coated on the surface of the one membrane layer, alters the membrane properties such as pore size and the critical surface tension of the membrane and hence, cahnging the wetting behavior of the membrane and the permeation of the absorbent through the membrane.

1.3 Wetting by Aqueous Solutions

The specific surface free energies of liquids are less than 100 ergs per sq.cm. at ordinary temperatures and that of hard solids are about 5000 to 500 ergs per sq.cm. Soft organic solids like solid organic polymers have much lower specific surface free energies, generally under 100 ergs per sq.cm. "Because of the comparatively low specific surface free energies of organic and most inorganic liquids, one would expect them to spread freely on solids of high surface energy, since that would result in a large decrease in the surface free energy of the system. However since the surface free energies of such liquids are comparable to those of low-energy solids, among these liquids should be found those exhibiting nonspreading on low-energy solids" (Zisman, 1964).

The causes for and effects of the wetting of low-energy solids by the aqueous solutions are discussed here. The major changes in the surface properties of solids occurr with the adsorption of a monomolecular layer on solids. Therefore, prior to 1960's, it was assumed that an adsorbed monolayer of an organic polar compound could radically change the wetting properties of solid surfaces. The theories earlier to 1960's about the wetting ability of surface-active agents in aqueous systems either state or imply that spreading results because the wetting agent becomes selectively adsorbed on the surface so as to orient the hydrophilic group toward the aqueous solution. But the studies conducted by Zisman (1964) on adsorption at solid-air and solid-liquid interfaces made it increasingly improbable that the major mechanism of wetting is the result of the ability of the nonpolar group of the wetting agent to adsorb by its hydrocarbon "tail" on the low-energy surfaces and so convert it into high-energy surface.

"A more reasonable assumption is that spreading of aqueous solutions on low-energy surfaces is caused by the lowering of the surface tension of water. If the solute molecules do adsorb at the solid-liquid interface, it is one of the results of wetting-not the cause. Hence, changes in surface tension at the solid-liquid interface, $\gamma_{SL,}$ must play a minor role in the presence of solutions of wetting agents." (Zisman W.A., 1964). Therefore, Zisman (1964) assumed that the ability of the aqueous solution to spread on such low-energy surface is determined by the value of the critical surface tension, γ_C, of the solid to be wetted and the amount of the wetting agent, which must be dissolved in water to depress the surface tension of water below γ_C.

These ideas were verified by Zisman (1964) in experiments on two low-energy solids, polyethylene ($\gamma_C \approx 31$ dynes per cm.) and polytetrafluoroethylene ($\gamma_C \approx 18$ dynes per cm.), using a variety of well-defined aqueous solutions. Pure water ($\gamma_{LV} = 71.9$ dynes per cm. at 25°C.) will not spread on either of these two surfaces. Fischer and Gans (1946) have pointed out that conventional surface-active agents do not lower the surface of tension of water at 25°C below between 26 and 27 dynes per cm. It follows from the definition of the critical surface tension that whenever any wetting agent lowers the liquid surface tension below 31 dynes per cm., the solution will spread on the surface of smooth clean polyethylene. However, aqueous solutions containing conventional wetting agent should not spread on polytetrafluoethylene, since wetting agent capable of depressing the surface tension below 18 dynes per cm would be needed.

Due to their hydrophobic-hydrophilic structures, each of the most effective wetting agents adsorbs to form a thin film on the free surface of the aqueous solution. At sufficiently high solute concentrations, this film will make the aqueous liquid appear to be a hydrocarbon liquid whose surface is comprised of the oriented, packed, hydrophobic groups characteristic of the organic structure of the wetting agent. The experiments conducted by Zisman (1964) led him to conclude that bringing the low-energy surface of polytetrafluoroethylene (or polyethylene) into contact with this film-coated water did not change the orientation or packing of the film adsorbed at the water-air interface.

From these considerations, one can predict that γ_{SL} will decrease as adsorption of the wetting agent increases. At high solute concentrations, γ_{SL} will become small because the interface will be between an organic low-energy solid and a hydrocarbon-like liquid, in other words, the much greater adhesion of the polar groups to the water and the much lower adhesion of the hydrocarbon groups to the low-energy solid surface will have caused the interface determining spreading and wetting to become the hydrocarbon-like outer surface of the film of adsorbed wetting agent. Hence, γ_{SL} will decrease with increased solute concentration and will become nearly constant at high concentrations as the adsorbed film approaches closest packing. Thus, the value of γ_C will vary with the nature of the wetting agent only in so far as there are differences in the nature and packing of the hydrocarbon groups of the wetting agent in the adsorbed state at the water-air interface. One would expect γ_C to be least for n-alkane long-chain derivatives; it will be greater on each surface for branched hydrocarbon derivatives; and it will be least for aromatic polar compounds.

1.4 Factors that Influence Gas Absorption Processes

Other than the factors that influence wetting of the membrane like pore size, membrane material and the surface tension of the absorbent solution, the other important aspects that influence gas absorption processes are loss of the absorbent and the corrosion effects due to the absorbents. Partial pressure difference being the driving force for the permeation of the absorbent through the pores of the membrane, loss of absorbent from the absorbent liquid depends on the vapor pressure of the absorbent, size of the absorbent molecule and the membrane pore size. High vapor pressure of the absorbent, larger membrane pore size and low molecular dimensions of the absorbent leads to a higher loss of the absorbent.

1.5 Carbon Dioxide Removal

Separation of CO_2 from gas mixtures is vital for a wide range of applications. Removal of carbon dioxide from gas streams is of importance both in terms of its impact on environmental and process economics. Most sources of carbon dioxide emissions are identified as energy generators where carbon dioxide is currently emitted at relatively high concentrations, around 10-15%. Similarly, other industrial process streams contain relatively high concentrations of carbon dioxide. Carbon dioxide removal is also desired in processes such as synthesis gas production, upgrading of natural gas, landfill gas recovery, coal liquefaction, production of hydrogen and enhanced oil recovery (Quinn and Laciak, 1997). Natural gas and biogas contain high concentrations of carbon dioxide, where issues of corrosion and regulatory constraints play a major role in a determined effort to reduce carbon dioxide from these gas streams and sequester it.

Some of the processes currently commercialized to remove carbon dioxide from gas streams are (Kohl and Riesenfeld, 1979):

- Absorption with volatile carriers such as ethanolamines (mono-and di-) and ethylene diamines(EDA)
- Pressure swing adsorption processes
- Membrane-based processes.

Among these processes, membrane-based processes offer unique advantages. Karoor and Sirkar (1993) extensively explored separation of CO_2 from N_2 with either pure water or an aqueous amine solution. They carried out comprehensive absorption experiments on gas separation including pure CO_2 and its mixture with nitrogen using a microporous hydrophobic hollow-fiber-based module in a parallel flow configuration. They also proposed a theoretical model to describe a system with an absorbent of pure water resulting in a partial differential equation; they have solved the equation with appropriate boundary conditions numerically and compared the results with the experimental data. Teramoto et al. (1996) showed that the permeation rates of CO_2 could be simulated by a theory of facilitated transport through a supported liquid membrane of aqueous amine solution. The experimental data could be successfully predicted by their theoretical approximation method. Al-sofar et al. (1997) conducted a separation of CO_2 using porous and non-porous hollow fiber membrane contactors with an aqueous diethanolamine solution as an absorbent. Even if good CO_2 removal efficiencies were obtained for both membranes, the lower permeation rate was achieved in the non-porous membrane. However, they proposed that the improved CO_2 selectivity in the non-porous membrane might compensate for the relatively low permeation rate.

1.6 Significance of Amines in Carbon Dioxide Separation

In general, amines as carriers perform better than carbonate/bicarbonate solutions for carbon dioxide separation. Among various amines, sterically hindered ones have higher capacities for CO_2 than unhindered primary and secondary amines (Bosch et al., 1989).

In systems where amines are used as carriers, the reactions can occur with primary, secondary or tertiary amine. A primary amine reacts with carbon dioxide according to

$$CO_2 + 2RNH_2 \Leftrightarrow RHNCOO^- + RNH_3^+ \tag{1.2}$$

The secondary amines also react with CO_2; the reaction can be described satisfactorily with the base-catalysis reaction mechanism

$$CO_2 + 2R_2NH \Leftrightarrow R_2NCOO^- + R_2NH_2^+ \tag{1.3}$$

Although the tertiary amine is not supposed to react directly with CO_2 like a primary or a secondary amine because they lack the proton needed in the de-protonation step, tertiary amines show considerable reactivity toward CO_2; further water is essential for this reaction. The reaction of CO_2 with tertiary amines can be described satisfactorily with the base-catalysis reaction mechanism (Little et al., 1990; Versteeg and van Swaaij, 1988).

$$CO_2 + R_3N + H_2O \Leftrightarrow HCO_3^- + R_3NH^+ \tag{1.4}$$

Most of these amines are volatile and are considered generally toxic. If the amine functional group could be stabilized in a form where it is not volatile, it can be expected that such a carrier would perform on par with a solution containing volatile amines without the associated problems.

1.7 Significance of Dendrimers in Carbon Dioxide Separation

Dendrimers are a novel class of polymers having some unusual properties. They essentially form the fourth major class of known macromolecular architectures. The traditional macromolecular architectures have been linear, cross-linked and branched. The term dendrimer comes from dendron (the Greek word for tree), which refers to a general polymer architecture. The basic structural elements of a dendrimer are (Dvornic and Tomalia, 1995):

- a central molecular core
- terminal surface groups, which may be chemically reactive or inert
- interior branch junctures having various branching functionalities or multiplicities, and
- connectors, divalent segments that covalently connect neighboring branching structures and provide internal molecular armature that holds together the entire dendritic molecular structure.

A major class of dendrimers which has been studied in a wide range of applications is Starburst® poly(amidoamine) (PAMAM) dendrimer. Depending on the interior core initiator, whether ammonia or ethylene diamine (EDA), 3 or 4 dendrons are contained in the dendrimer.

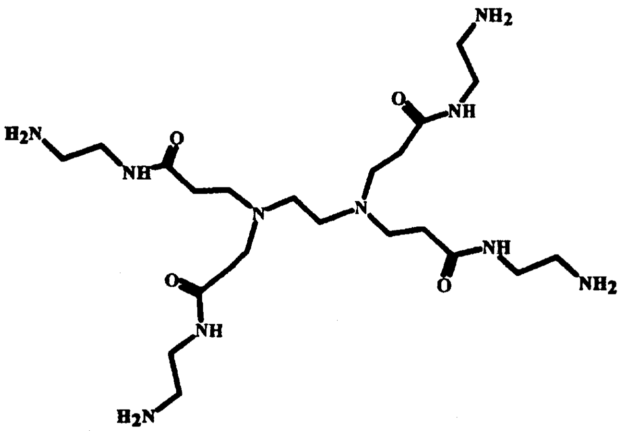

Figure 1.3 Schematic of the structure of EDA core PAMAM dendrimer of generation 0.

This also influences the spatial distribution of the dendrons. It is possible to modify the surface groups of PAMAM dendrimers to obtain polymers with unique properties. An interesting aspect of this surface modification of dendrimers through the amidation reaction is that a mixed-surface dendrimer (a dendrimer that contains two types of functional groups) can also be prepared.

Different dendrimers have been synthesized with about 30 different initiator core compounds and 100 different surface functional groups. As diverse as the dendrimers are, their applications are equally diverse. Their main applications are found in biomedical, pharmaceutical and industrial areas. Table 1.1 lists a few important applications involving dendrimers.

In this thesis, Starburst® polyamidoamine (PAMAM) dendrimers of generation 0 with ethylenediamine (EDA) core were studied for carbon dioxide separation. The study was focused on generation zero dendrimer because of its very suitable characteristics for the application of CO_2 separation. The structure of PAMAM dendrimer of generation zero with EDA core is shown in Figure 1.3.

Table 1.1 Current Research and Applications in Dendrimers

Application	Reference
Biomedical	
CKMB immunoassay	Singh et al., 1994
Pharmaceutical	
Controlled release of aspirin	Tomalia et al., 1994
Industrial	
Asymmetric catalysis	Bolm et al., 1996
Reactions with proteins	Singh, 1998
Homogeneous catalysis	Knapen et al., 1994
Electrokinetic chromatography	Dubin et al., 1992; Tanaka et al., 1995, 1997
Photoresponsive dendrimers	Junge and Mcgrath, 1997
Immobilized liquid membrane	Kovvali et al., 2000; Kovvali and Sirkar, 2001

The number of functional groups in a particular dendrimer molecule doubles with each generation. Generation zero PAMAM dendrimer with EDA core, the smallest of this class of dendrimers, has four amine functional groups. It has a molecular weight of 518 and density of 1.162 grams/cm^3. The molar concentration of primary amines is 9.1 M, and that for tertiary amines is 4.6 M. It is supposedly nonvolatile and is available in a 20% methanol solution, from which methanol could be removed by vacuum to yield a pure dendrimer liquid. PAMAM dendrimers are considered nontoxic up to generation 5 (Roberts et al., 1996). PAMAM dendrimers have a very high density of primary amine functional groups on their surface.

Carbon dioxide absorption has been studied in the context of microporous polypropylene hollow fibers, which are said to get wetted with monoethanalamine-containing aqueous solutions. Do PAMAM solutions wet these fibers? If they do not and their absorption characteristics are good, then we have an excellent solution for CO_2/H_2S absorption. Correspondingly, there are hydrophobic microporous fibers (poly(4-methylpentene-1)) which have a dense skin with a maximum pore size of 6 Å. Such skin will prevent the loss of amines substantially. Therefore, MEA solutions may be used with PMP fibers. The question is: will such a skin reduce the CO_2 absorption rates significantly? This study proposes to answer such questions.

CHAPTER 2

EXPERIMENTAL

2.1 Approach

To study the absorber-stripper behavior for CO_2 absorption, experiments were carried out with different hollow fiber modules fabricated with either Celgard X-10 polypropylene or poly(4-methylpentene-1) hollow fibers. Deionized water, an aqueous solution of dendrimer, and an aqueous solution of monoethanolamine were used separately as the absorbent. A gas mixture of 5% CO_2 in N_2 (balance) was used as the feed gas and helium (zero) was used as the sweep gas. In all experiments, the feed gas was passed through the shell side and the absorbent was passed countercurrently through the tube side. Solutions containing different concentrations of absorbents were prepared and their surface tensions were measured using an Interfacial Tensiometer to provide a background on membrane wettability and the effect of surface tension, if any.

2.2 Hollow Fiber Modules Used in the Study

2.2.1 Hollow Fiber Module Fabrication and Testing

One set of two modules for CO_2-absorption and CO_2-stripping was fabricated from hollow fiber membranes supplied by Celgard (Charlotte, North Carolina); the other set of two modules having the same absorber/stripper area ratio was prepared using the poly(4-methylpentene-1) hollow fiber membranes supplied by DIC Inc. (Tokyo, Japan). In the case of Celgard , fibers were taken from a roll; in the case of poly(4-methylpentene-1), fibers were directly taken from the bundle. The fibers were cut to a length little longer (by 1/4″) than that required. Polytetrafluroethylene(PTFE) tubing was used as the shell for the module. The tubing was fitted with 1/4″ male run tees at both ends. The required number of fibers was matted on a vinyl sheet laid on a table. Deionized water was sprayed on these hydrophobic fibers for ease of handling. The fibers laid down were bundled and one end was tied with a string. This end was pulled through the bore of the tubing filled with water.

A leak-free tube sheet was prepared at the two ends of the tubing.The tube sheet held the bundle of fibers in place and prevented the shell side and tube side from mixing. A two layer potting was done to prepare each tube sheet for a module. A two-component RTV 118 translucent silicone rubber adhesive sealant (General Electric Co., Waterford, NY) was applied as the first layer due to its viscous nature. After curing for one day, epoxy (C-4: resin; D: activator; weight ratio:4/1; Beacon Chemicals, Mt.Vernon, NY) was applied as the second layer through the nearest shell side outlet using a glass dropper. Epoxy was used as the second layer because its sealing properties with PTFE are better than those of silicone rubber adhesive which had very good bonding with the fiber. In retrospect, one layer of potting adheres to the fibers; a thin layer in turn binds to the inside of the tubing. Both ends of the module were potted in this way. The effective module length would be the length of the PTFE tubing less double the potting thickness (to account for both sides of the potting). Specifications of the modules are provided in Tables 2.1 and 2.2.

Before using these modules, some preliminary tests were carried out. To test for any leakage, the shell side of the module was filled with deionized water. Water pressure was maintained at 15-25 psig (103.42-172.37 kPag) for about 1-2 hours. If no water leaked through the potting, the module was considered leak-free. Pure air was passed

Table 2.1 Specifications of Poly (4-methylpentene-1) Hollow Fiber Modules

Module no.	Fiber o.d., µm	Fiber i.d., µm	Shell diam, cm	Length of module, cm	No. of fibers	Fiber wall porosity	Packing fraction	Area of gas-liquid contact*, cm^2
Absorber-1	260	180	0.48	17.1	80	0.3	0.234	77.3
Stripper-1	260	180	0.76	17.6	160	0.3	0.187	159.2

* Based on fiber internal diameter (i.d.)

Table 2.2 Specifications of Celgard X-10 Polypropylene Hollow Fiber Modules

Module no.	Fiber o.d., µm	Fiber i.d., µm	Shell diam, cm	Length of module, cm	No. of fibers	Fiber wall porosity	Packing fraction	Area of gas-liquid contact*, cm^2
Absorber-2	300	240	0.48	17.1	40	0.3	0.156	51.5
Stripper-2	300	240	0.48	17.0	80	0.3	0.312	102.0

* Based on fiber internal diameter (i.d.).

through the tube and shell side for a couple of hours to completely dry these hydrophobic fibers.

2.3 Experimental Setup

2.3.1 Materials, Chemicals and Equipment

The materials, equipment and chemicals used for the experiments are listed below:

- Celgard X-10 polypropylene hollow fibers (Charlotte, NC); poly(4-methylpentene-1) hollow fibers (DIC Ltd., Tokyo, Japan)
- Multiple Flow Controller (Model 8209, Matheson, E.Rutherford, NJ)
- Mass Flow Transducer (Model 8102-1452 FM, Matheson, E.Rutherford, NJ)
- Mass Flow Transducer (Model 8102-1451 FC, Matheson, E.Rutherford, NJ)
- ORION pH/ISE meter (Model 710A, Orion Research, Belle Mead, NJ)
- CO_2 electrode (Model 95-02, Orion Research, Belle Mead, NJ)
- Gas Chromatograph (GC, Hewlett Packard Model 5890 series II)
- Integrator (Hewlett Packard Model 3396 series II)
- Gas Chromatograph (GC, Hewlett Packard Model 6890 series)
- Integrator (Hewlett Packard Model 6890 series)
- Head Space Sampler (Hewlett Packard Model 7694 Headspace Sampler)
- Interfacial Tensiometer (Model K8, KRUSS, Hamburg, Germany)
- Micro pump (Model No.7144-04, Cole Parmer Instrument Co., IL)
- Bubble Flow Meter (Varian, Sugarland, TX)
- Pressure Gages (Model 63-5631, Matheson, E.Rutherford, NJ)
- Helium Zero (Matheson, Rutherford, NJ)

- 5% CO_2 gas mixture (Nitrogen Balance), Certified Standard (Matheson, Rutherford, NJ)
- Monoethanolamine (Aldrich, Milwaukee, WI)
- Ethylenediamine (Acros, Miami, FL)
- PAMAM Dendrimer of generation 0 having an ethylenediamine core (Dendritech, Midland, MI)

2.3.2 Experimental Procedure

PAMAM (polyamidoamine) dendrimer of generation zero in methanol, obtained from Dendritech, Inc., was recovered from methanol by subjecting the solution to vacuum for several days; the resulting pure dendrimer solution was stored in a desiccator till used. 21.66 vol % of aqueous solution of dendrimer was prepared. A gas mixture of 5% CO_2 in N_2 and a cylinder of pure Helium(zero) were obtained from Matheson (E.Rutherford, NJ).

The experimental setup is shown in Figure 2.1. Polyethylene tubing having 1/8″ or 1/4″ diameter was used for connections. Both feed and sweep gases were humidified by two humidifiers connected in series to ensure complete humidification of the gas mixtures. The bypass for the humidifiers was provided using two-way valves in order to maintain continuous gas flow even while refilling the water in the humidifiers.

The gas flow rates were controlled by mass flow transducers (Matheson, E.Rutherford, NJ); absorbent flow rate was controlled by the Micro pump (Cole Parmer, Vernon Hills, IL). Inlet and outlet pressures of the absorbent solutions were monitored by pressure gages (Matheson, E.Rutherford, NJ).

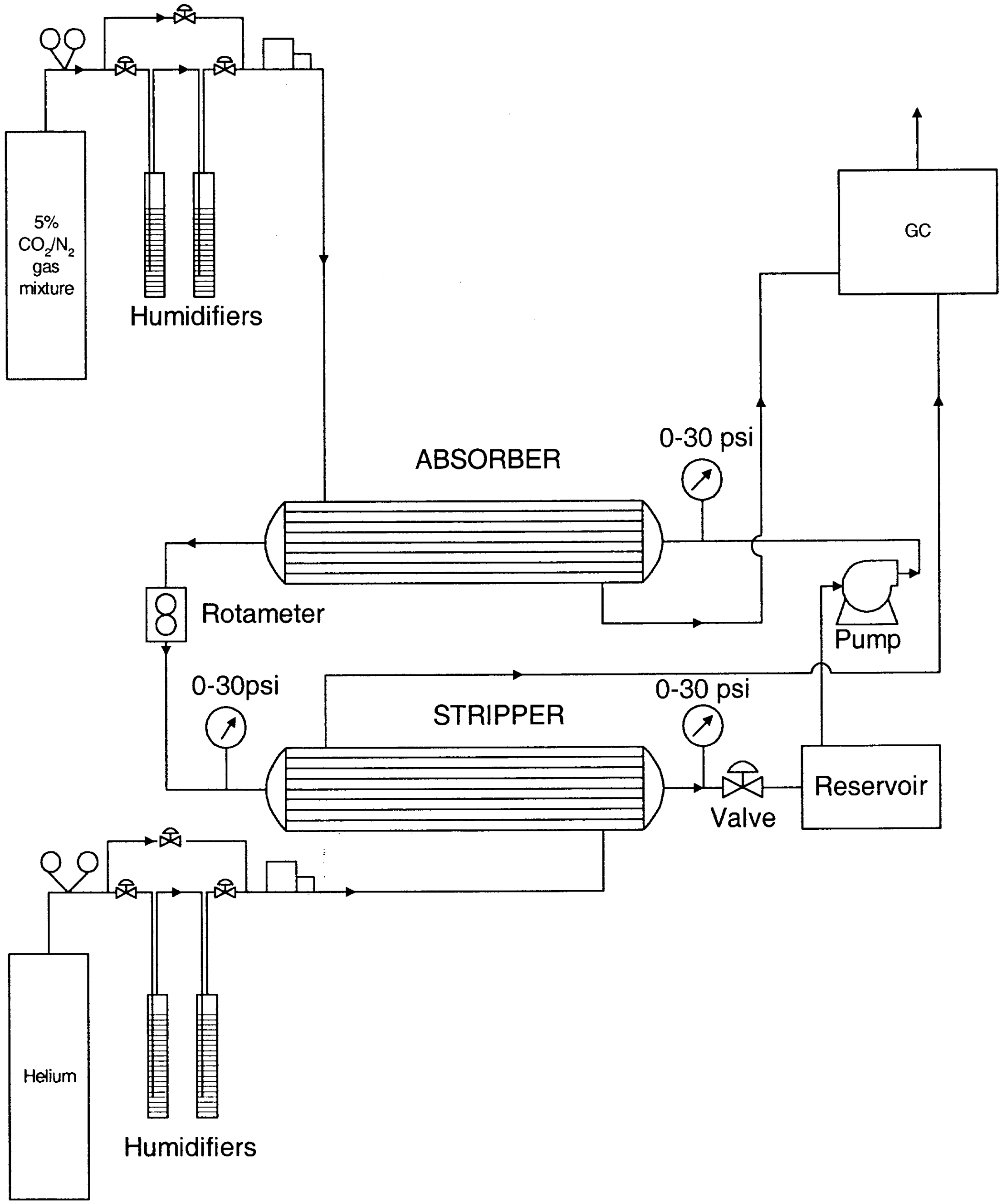

Figure 2.1 Schematic diagram of the experimental setup.

A 50 cm^3 reservoir was mounted before the pump and in-between the absorber and the stripper. The rotameter was calibrated for the aqueous solutions used in order to maintain the desired constant flow rate throughout the duration of an experiment. The lines were connected in such a way that a sample of the feed gas as well as the treated retentate gas could be sent to the gas chromatograph (GC) for analysis.

The experiments were started by first passing the absorbent liquid through the tube side of the modules followed by passing the feed and sweep gases countercurrently on the shell side. The feed and sweep gas flow rates were held constant at 8.74 cm^3/min and 61.34 cm^3/min respectively. The absorbent liquid was also allowed to flow at a constant rate of 6.8 cm^3/min for runs in all systems. Runs for each system were continued for a long time (50-55 days) by maintaining constant flow rates throughout the period; the extent of CO_2 absorption was frequently analysed. Later, the absorbent liquid flow rate was changed to other values and held constant till steady state was reached.

The absorber-stripper behavior in the Celgard fiber modules for the case of a 21.66 vol % of aqueous solution of dendrimer as the absorbent was studied for 55 days. To compare these results with that of pure water as the absorbent, the experiment was continued using the same flow rates by passing deionized water as the absorbent after washing the modules with water to remove and recover the dendrimer from the Celgard fiber-based modules. Runs were continued with an aqueous solution of monoethanolamine (MEA) as the absorbent to study the wettability of Celgard fibers by MEA.

Additional studies were continued for more than 70 days in the PMP fiber-based modules fabricated using the same absorber/stripper area ratio as that of the Celgard fiber-based modules by using an aqueous solution of monoethanolamine as absorbent. The experimental run was started with 11.67 vol % of MEA solution (equivalent to that of the dendrimer solution used) and the permeation of MEA from tube side to the shell side was monitored periodically by analysing the absorbent samples collected from the reservoir. After 65 days, pure MEA was added to the reservoir to bring the absorbent concentration to the level of the original value and the treated retentate gas was analysed for different absorbent flow rates.

2.3.3 Analytical Measurements

A Hewlett-Packard 5890 series II (Hewlett Packard, Wilmington, DE) gas chromatograph (GC) was used to determine the composition of the gas streams. The GC was calibrated for the required CO_2 concentration range. The column in the GC was Porapak Q 80/100, 6 feet long, 0.085″ ID and 1/8″ OD. The liquid-phase concentrations were analyzed by a CO_2 electrode (Model 95-02, Orion Research). When MEA was used as the absorbent, the loss or permeation of the absorbent through the pores of the fibers from the tube side to the shell side of the module was monitored by analysing the liquid samples collected from the reservoir using another GC (HP 6890 series). The column in the GC was HP-1, 30 m long, 0.53 mm diameter and 3 μm thickness. A headspace sampler (HP 7694 Headspace Sampler) was used to inject the samples. The GC was calibrated for the concentration range of 2.5 to 12.5 vol % of MEA.

2.3.4 Surface Tension Measurements

An aqueous solution of 30 cm^3 containing 40 vol % of dendrimer was prepared from 13.94 grams of the pure dendrimer. Solutions of 30, 20, 15, 10 and 5% dendrimer were also prepared by diluting the 40, 30, 20, 15, 10% solutions respectively. Aqueous solutions containing 5, 10, 15, 20, 30 and 40 vol % of MEA and EDA were also prepared. The surface tensions of the prepared solutions were measured by a Interfacial Tensiometer (Model K8, KRUSS, Hamburg, Germany). For the measurement procedure, the operational manual for the device was consulted.

2.4 Calculation of Overall CO_2 Mass Transfer Coefficient

Experimentally observed concentration changes from the feed to the outlet of the module in the gas phase was used to determine the logarithmic mean concentration difference-based overall mass transfer coefficient, using the following equation

$$K_{OLM} = \frac{V_l(C^t_{lout} - C^t_{lin})}{60A_T(\Delta C)_{lm}} \tag{2.1}$$

Here V_l is the liquid flow rate, A_T is the mass transfer area based on the surface area of gas-liquid contact, C^t_{lin} and C^t_{lout} are the total CO_2 concentrations at the liquid inlet and outlet respectively.

The quantity $(\Delta C)_{lm}$, the logarithmic mean concentration difference of gas species, is given by

$$(\Delta C)_{lm} = \frac{(HC_{gin} - C_{lout}) - (HC_{gout} - C_{lin})}{\ln\left(\dfrac{HC_{gin} - C_{lout}}{HC_{gout} - C_{lin}}\right)} \tag{2.2}$$

here C_{gin} and C_{gout} are the CO_2 concentrations at the gas inlet and outlet, respectively. C_{lin} and C_{lout} are the free CO_2 concentrations at the liquid inlet and outlet respectively, and they are assumed to be zero in the bulk of the liquid.

H is Henry's law constant which is the ratio of the interfacial concentration of absorbed species i in the liquid divided by that in the gas

$$C_{il} = HC_{ig} \tag{2.3}$$

The calculation of *H* value is specific to the absorbent solutions used and is given below.

2.4.1 Calculation of Henry's Law Constant for the Aqueous Solution of MEA - CO_2 System

The N_2O analogy (the ratio of the solubilites of CO_2 and N_2O remains constant for various solutions) was used to calculate the solubility of CO_2 in an aqueous solution of MEA. The ratio of the solubilities of CO_2 and N_2O is constant for aqueous solutions MEA (Versteeg and Swaaij, 1988):

$$\text{solubility of } CO_2 = C_1 * \text{ solubility of } N_2O \tag{2.4}$$

where C_1 is the constant and is equal to 1.36 at 298 K.

The solubility of N_2O in an aqueous MEA solution is a function of amine concentration and at 298 K, it is given by the following equation:

$$\text{Solubility of } N_2O = 0.598 + 0.007*10^{-3}[\text{amine}] - 0.024*10^{-6}[\text{amine}]^2 + 0.015*10^{-9}[\text{amine}]^3 - 0.003*10^{-12}[\text{amine}]^4 \tag{2.5}$$

where [amine] is the amine concentration in mol/m^3.

An aqueous solution of 11.67 vol % of MEA was used in the experiments. Therefore moles of MEA that will be present in 1000 cm^3 of 11.67 vol % of MEA solution = 116.7*density/molecular weight = 116.7*1.012/61 = 1.936

Each MEA molecule has one primary amine.

So, moles of primary amine present in 1000 cm^3 of 11.67 vol% solution = 1.936 Mol

$\therefore$ Concentration of primary amine = 1936 $gmol/m^3$

By substituting the value of amine concentration in equation (2.5) we have

$$\text{Solubility of } N_2O = 0.588 = H_{N_2O}$$

$$\therefore \text{Solubility of } CO_2\,(H) = C_1 * \text{ solubility of } N_2O\,(H_{N_2O})$$

$$= 1.36*0.588 = 0.800 \text{ at } 298\text{ K} \qquad (2.6)$$

2.4.2 Calculation of Henry's Law Constant for the Aqueous Solution of Dendrimer - CO_2 System

The same N_2O analogy used to calculate the solubility of CO_2 in an aqueous solution of MEA was used to calculate the solubility of CO_2 in an aqueous solution of dendrimer. Since the solubility data for N_2O in an aqueous dendrimer solution was not available in the literature, the same correlation that was used for MEA was used to calculate the solubility of N_2O.

The solubility of N_2O in an aqueous dendrimer solution is a function of primary amine concentration and at 298 K, it is assumed to be given by the following equation:

$$\text{Solubility of } N_2O = 0.598 + 0.007*10^{-3}[\text{primary amine}] - 0.024*10^{-6}[\text{primary amine}]^2 + 0.015*10^{-9}[\text{primary amine}]^3 - 0.003*10^{-12}[\text{primary amine}]^4 \qquad (2.7)$$

A 21.66 vol % of dendrimer was used in the experiment.

Moles of dendrimer that will be presented in 1000 cm^3 of 21.66 vol % of dendrimer solution = 216.6*density/molecular weight

= 216.6*1.162/518 = 0.4858

Each dendrimer molecule has four primary amines.

So, moles of primary amine presented in 1000 cm^3 of 21.66 vol % solution = 0.4858*4 = 1.943

$\therefore$ Concentration of primary amine = 1943 $gmol/m^3$

By substituting the value of amine concentration in equation (2.7), one gets

Solubility of N_2O = 0.588

$\therefore$ Solubility of CO_2 (H) = C_1* solubility of N_2O

$$= 1.36 * 0.588 = 0.800 \text{ at } 298 \text{ K} \tag{2.8}$$

CHAPTER 3

RESULTS AND DISCUSSION

3.1 Dendrimer Based Gas Absorption of CO_2 in Celgard Fibers

Amine functional groups in a form where they are not volatile and can act as good carriers for CO_2 absorption are useful since they will not be lost by volatilization. Hence an aqueous solution of dendrimer was used for the studies. The absorber-stripper behavior for CO_2 absorption was studied for an extended period of 55 days in Celgard hollow fiber modules having a constant flow rate of an aqueous solution of dendrimer. The absorption of CO_2 was found to be essentially constant throughout the experimental period. The CO_2 concentration at the feed outlet and the CO_2 mass transfer coefficient are plotted against the time and are shown in the Figure 3.1. The scattering of the data in the plot are most likely due to the temperature variation in the laboratory. It was also observed that the absorption of CO_2 at the feed outlet in the initial period (before reaching the steady state) was very high and is shown in the Figure 3.2. Obviously, the stripping arrangement was insufficient to maintain a very high level of CO_2 removal during the steady state. It leads to the conclusion that the aqueous solution of dendrimer can be used successfully for the removal of low and high concentrations of CO_2 from gas mixtures by using better-designed modules and stripping conditions.

The pressures in the tube side of the modules are shown in Table 3.1. At the end of the experimental period, a small increase in pressure drop in the tube side was observed at the inlets of both absorber and stripper. It was found that the increase in the pressures was due to the deposition of miscellaneous material at the entrance of the hollow fibers. Moreover, the pressure drop was found to be constant throughout the

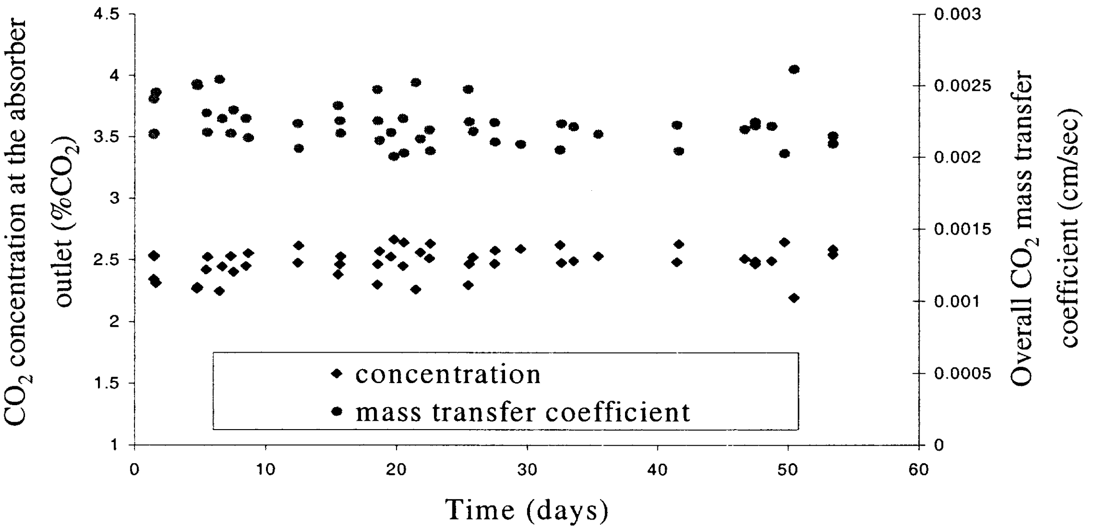

Figure 3.1 Absorber-Stripper behavior for CO_2 absorption in aqueous dendrimer solution carried out in Celgard hollow fiber modules.

experimental period. The experimental results clearly indicate that the aqueous solution of the dendrimer does not wet the pores of the Celgard fibers and there was also no loss of the dendrimer because of its vanishingly low vapor pressure, if any. The CO_2 mass transfer coefficient when pure water was used as the absorbent liquid, was also calculated for the same experimental conditions and compared in Table 3.2. Naturally, the CO_2 mass transfer coefficient with pure water was lower than that with the dendrimer solution.

3.2 MEA Based Gas Absorption of CO_2 in PMP Fibers

The absorption of CO_2 in PMP fibers by the 11.76 % aqueous MEA solution was studied for a period of more than 80 days using constant as well as different flow rates of the absorbent liquid. The CO_2 was absorbed steadily for 55 days. The concentration of MEA in the reservoir was found to be decreasing with time during the experiment. From this observation, it was concluded that MEA was permeating through the pores of the membrane from the tube side to the shell side. The absorption of CO_2 remained constant for a long time even though the concentration of the absorbent in the liquid was getting reduced.

This observed phenomenon leads to the conclusion that the membrane resistance was possibly reduced due to the presence of the MEA in the pores. MEA present in the pores while permeating from the tube side to the shell side is acting as a carrier for CO_2, and thus reducing the membrane resistance. Alternately, one could argue that the membrane resistance was controlling and there was excess of MEA present in the solution. The CO_2 concentration at the feed outlet and the mass transfer coefficients are plotted against time and are shown in Figure 3.3. The pressures in the tube side of the modules are shown in Table 3.1. After 55 days, a gradual increase in the CO_2 concentration in the feed out was observed. These observed results are explainable. The CO_2 absorption started decreasing, when the amine concentration in the reservoir reached a certain level at which the decrease in the membrane resistance could not counter the effect of the decrease in the amine concentration. Alternately, at the prevailing membrane resistance, the decrease of amine concentration became rate-controlling. The CO_2 in the feed out had gone up to 3.9 vol%.

Table 3.1 Pressures in the Tube Side of the Modules for an Absorbent Flow Rate of 6.8 cm^3/min

Type of fibers used in the modules	Absorbent liquid	Absorber		Stripper	
		Inlet pressure, psig	Outlet pressure, psig	Inlet pressure, psig	Outlet pressure, psig
Celgard*	21.66 vol % dendrimer	6	1.4	11	6
PMP**	11.67 vol % MEA	21	1.1	31	21

* Celgard X-10 polypropylene hollow fibers

** Poly (4-methylpentene-1) hollow fibers

MEA was added to the reservoir to bring the concentration up to the original concentration and the CO_2 absorption was observed to come back to the original level. Experiments were also conducted with different flow rates of the absorbent liquid and the results are presented in Table 3.3. A very little decrease in the CO_2 absorption was observed with the decrease in the absorbent flow rate leading to a possible conclusion that the membrane resistance is controlling the mass transfer.

Table 3.2 Comparison of Overall CO_2 Mass Transfer Coefficients

Module no.	Type of fibers used in the modules	Absorbent liquid	CO_2 in feed out, vol %	Overall CO_2 mass transfer coefficient, cm/sec
Absorber-1	Celgard*	21.66 vol % dendrimer	2.55	0.002148
Absorber-1	Celgard*	Water	3.75	0.000915
Absorber-2	PMP**	11.67 vol % MEA	3.33	0.000957
Absorber-2	PMP**	Water	3.54	0.000799

* Celgard X-10 polypropylene hollow fibers
** Poly (4-methylpentene-1) hollow fibers

Table 3.3 Absorption of CO_2 in a PMP Module for Different Flow Rates of 11.67 vol% MEA Solution

Absorbent liquid flow rate, cc/min	CO_2 in feed out, vol %	Overall CO_2 mass transfer coefficient, cm/sec
6.8	3.33	0.000957
5.06	3.438	0.000656
3.16	3.496	0.000399
1.89	3.469	0.000234

3.3 Comparison of Surface Tensions of Aqueous Solutions of Various Absorbents

Since the surface tension of the absorbent liquid influences the wetting, the surface tensions of aqueous solutions of different absorbents were measured. The measured surface tensions for different volume fractions of aqueous solutions of Dendrimer, MEA and EDA were plotted against volume fractions and compared in the Figure 3.4. A small difference in behavior at the low volume fractions was observed in case of dendrimer when compared to that of the MEA and EDA. For aqueous solutions of dendrimer, the surface tension did not decrease so rapidly at low volume fractions as it did for other aqueous solutions. It was also observed that 21.66 vol% of dendrimer solution has a much higher surface tension than the 11.67 vol% of aqueous solution of MEA.

It appears for the measurements that by themselves, none of these solutions will approach the critical surface tension for polypropylene (γ_C = 29 dynes per cm. (Brandrup and Immergut, 1989)). These solutions ought not to wet the pores of Celgard fibers. However, volatilization of MEA etc. and their subsequent sorption on polypropylene surface may alters the γ_{SL} values substantially.

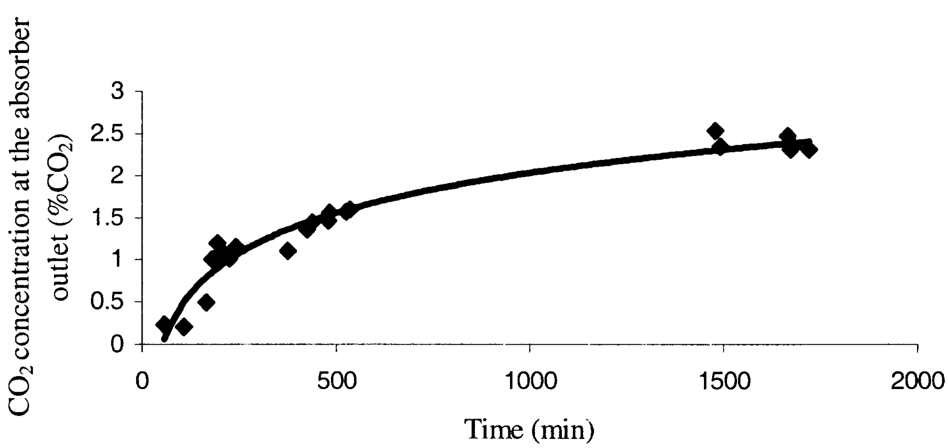

Figure 3.2 Absorber-Stripper behavior for CO_2 absorption in aqueous dendrimer solution carried out in Celgard hollow fiber modules.

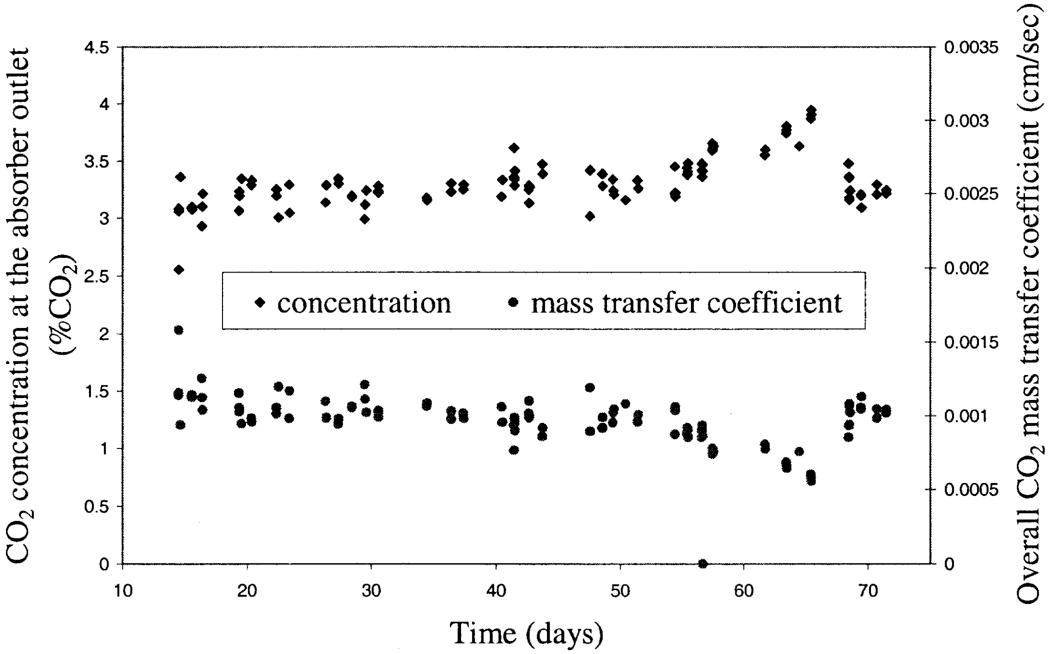

Figure 3.3 Absorber-Strippper behavior for CO_2 absorption in aqueous MEA solution carried out in PMP hollow fiber modules.

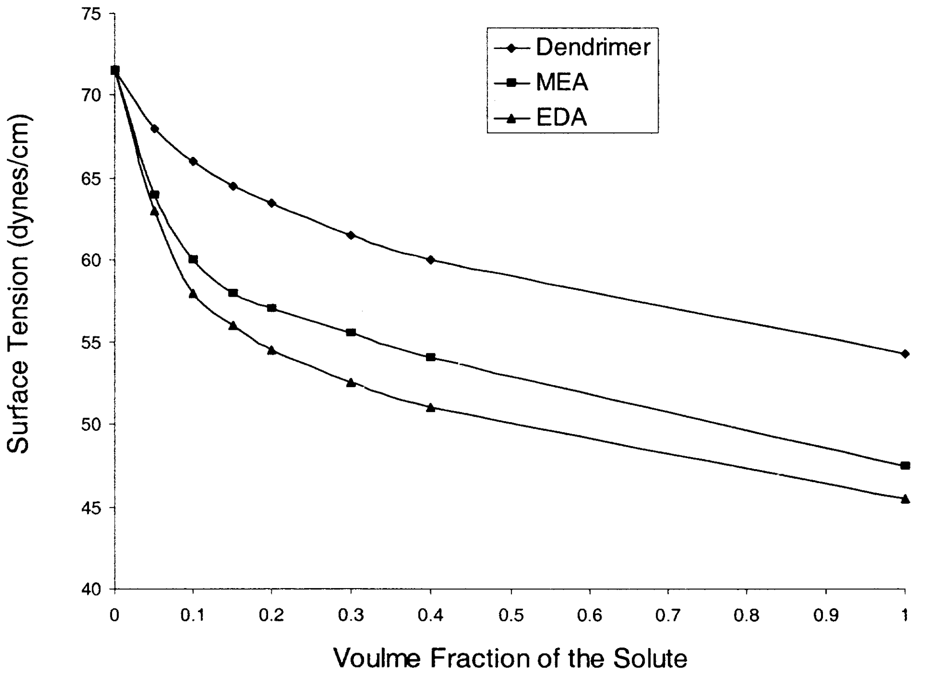

Figure 3.4 Comparison of surface tensions of aqueous solutions of Dendrimer, MEA and EDA.

CHAPTER 4

CONCLUDING REMARKS

Absorption of CO_2 through the Celgard fiber-based membrane module was studied using an aqueous solution of dendrimer flowing through the fiber bore as the absorbent. Since the extent of absorption was constant throughout the experimental period, it was concluded that the pores in the Celgard membrane was not wetted at all by the aqueous dendrimer solution and the absorption of CO_2 by the aqueous solution of dendrimer was found to be promising.

Absorption studies of CO_2 was also carried out by an aqueous MEA solution in an asymmetric membrane (PMP) which has a skin on the outside of the fiber. From the observations, it was concluded that MEA is permeating through the pores of the membrane. Though the loss of the solute is disadvantageous in terms of the operating costs, the permeation of solute may have helped in increasing the absorption by decreasing the membrane resistance.

Mass transfer coefficients in the case of an aqueous solution of dendrimer in the Celgard fiber-based module was found to be higher than that of the aqueous MEA solution as the absorbent in the PMP fiber-based module for the same absorbent flow rates.

At the same time, the absorbent solution was regenerated in the stripper for the above mentioned two cases and the absorber-stripper behavior was also studied and was found to be steady.

APPENDIX

The calculation of the logarithmic mean concentration difference-based overall mass transfer coefficients were shown here.

Values of the experimental conditions and the parameters:

Absorbent liquid flow rate, $V_l = 6.8$ cc/min

Feed gas flow rate, $V_g = 8.74$ cc/min

Area of gas-liquid contact, $A_T = \pi * d_i * n * l = 3.14 * 240*10^{-4}*40*17.1 = 51.5$ cm^2

Henry's law constant, H = 0.8 moles of CO_2 in liquid / moles of CO_2 in gas at 298 K (From section 2.4.2)

Calculation of concentrations:

Pressure, P = 1 atm.

Temperature, T = 273+25 = 298 K

R= $0.082*10^3$ cm^3 atm. / mol K

Consider one cm^3 of 5 vol % of the feed gas mixture. It will have 0.05 cm^3 of CO_2.

Volume, V = 0.05 cm^3

No of moles, $n = PV/RT = 1*0.05/0.082*10^3*298 = 2.0461*10^{-6}$ mol

$\therefore$ Concentration of CO_2 in the feed inlet, $C_{gin} = 2.0461*10^{-6}$ mol/cm^3

Similarly,

Concentration of CO_2 in the feed outlet, $C_{gout} = 2.55$ vol % = $1.0435*10^{-6}$ mol/cm^3

Material balance:

Basis: one minute of the operation

Moles of CO_2 coming in to the absorber = Moles of CO_2 going out from the absorber

$$C_{gin} * V_g + C^t_{lin} * V_l = C_{gout} * V_g + C^t_{lout} * V_l$$

$$\therefore C^t_{lout} - C^t_{lin} = \frac{V_g * (C_{gin} - C_{gout})}{V_l} = \frac{8.74 * (2.0461 * 10^{-6} - 1.0435 * 10^{-6})}{6.8} = 1.2886 * 10^{-6} mol/cm^3$$

Calculation of mass transfer coefficients:

The quantity $(\Delta C)_{lm}$, the logarithmic mean concentration difference of gas species is given by

$$(\Delta C)_{lm} = \frac{(HC_{gin} - C_{lout}) - (HC_{gout} - C_{lin})}{\ln\left(\frac{HC_{gin} - C_{lout}}{HC_{gout} - C_{lin}}\right)}$$

$$= \frac{(0.8 * 2.0461 * 10^{-6} - 0) - (0.8 * 1.0435 * 10^{-6} - 0)}{\ln\left(\frac{0.8 * 2.0461 * 10^{-6} - 0}{0.8 * 1.0435 * 10^{-6} - 0}\right)} = 1.191 * 10^{-6} mol/cm^3$$

Logarithmic mean concentration difference-based overall mass transfer coefficient is given by

$$K_{OLM} = \frac{V_l (C^t_{lout} - C^t_{lin})}{60 A_T (\Delta C)_{lm}} = \frac{6.8 * (1.2886 * 10^{-6})}{60 * 51.5 * 1.191 * 10^{-6}} = 2.38 * 10^{-3} cm/\mathrm{sec}$$

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