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Recovery of $[\text{CO}_2]_{\text{T}}$ from Aqueous Bicarbonate using a Gas Permeable Membrane

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14. ABSTRACT Celgard 2400 gas permeable membranes were in contact with a model sodium bicarbonate solution on a closed system at elevated water pressures. When gaseous carbon dioxide was removed from the water by diffusion through the membrane, the bicarbonate disproportionated to carbon dioxide and carbonate. The carbon dioxide permeance rate and effect of ionic strength on disproportionation is reported.					
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RECOVERY OF $[\text{CO}_2]_{\text{T}}$ FROM AQUEOUS BICARBONATE USING A GAS PERMEABLE MEMBRANE

1.0 BACKGROUND

The U.S. Navy has expressed interest in producing synthetic fuel from renewable sources in the field in order to avoid the risks inherent in procuring fuel from foreign sources and/or maintaining long supply lines. The procurement and transportation risk can be reduced by producing synthetic fuel (JP-5) from hydrogen and carbon generated near the point of fuel use. The Navy has proposed moving to a common fuel JP-5, throughout its operations [1]. If the Navy does move to a single fuel this would simplify any future shipboard production of fuel. The sea based production of synthetic fuel would increase the Navy's operational flexibility and time on station.

Technologies currently exist to synthesize hydrocarbon fuel on land, given sufficient primary energy resources such as coal. However, these technologies are not practical for sea-based generation. The approach presented uses gas permeable membranes for sequestering $[\text{CO}_2]_{\text{T}}$ from seawater. This carbon feedstock could then be catalytically reacted with hydrogen to form oil. Excess nuclear power on ships can initially be used to electrolyze seawater for hydrogen production. This synthetic fuel production process would provide an alternative energy source to fossil fuels that would be directly intended to benefit the U.S. Navy. In 2004 the US Navy's fuel cost was in excess of \$1.6 billion. Because this fuel is intended for use by the U. S. Navy and because the Navy nuclear ship-bound electricity is involved in its creation, a necessary constraint is that this process must be performed aboard ships at sea.

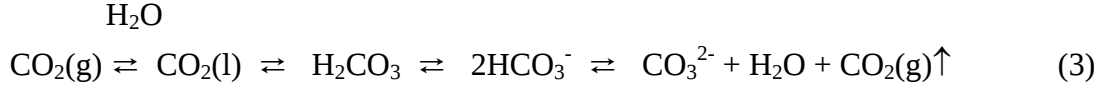
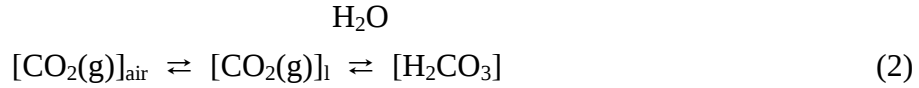
2.0 INTRODUCTION

The ocean could be an important resource with regard to its total carbon dioxide content. If carbon can be economically extracted from the ocean, then marine engineering schemes could be proposed to utilize this carbon as a potential chemical feedstock in processes such as catalytic polymerization with a source of hydrogen. The ocean pH below the well mixed layer of the top 100 meters is relatively constant. The most important buffer system maintaining this pH is the carbonate/bicarbonate system. The total carbon dioxide concentration $[\text{CO}_2]_{\text{T}}$, as shown in equation 1 is the sum of the concentration of dissolved gaseous CO_2 , bicarbonate, and carbonate.

$$\Sigma [\text{CO}_2]_{\text{T}} = [\text{CO}_2(\text{g})] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}] \quad (1)$$

At a typical ocean pH of 7.8, $[\text{CO}_2]_{\text{T}}$ is about 2000 $\mu\text{moles/kg}$ near the surface, and 2400 $\mu\text{moles/kg}$ at all depths below 300 meters [2,3]. This equates to approximately 100 mg/L of $[\text{CO}_2]_{\text{T}}$. The concentration of $[\text{CO}_2]_{\text{T}}$ in air is 370 ppm (v/v) and this is 0.7 mg/L (w/v). Comparing these two concentrations on a (w/v) basis, it is readily apparent that CO_2 in seawater is about 140 times greater than air [4]. At this pH the $[\text{CO}_2(\text{g})]$ in equation (1) is about 2 to 3% of the total. The concentration of dissolved carbonate is about 1% of the total and the remainder is dissolved bicarbonate. Dissolved $[\text{CO}_2(\text{g})]$ is actually hydrated with one mole of water in the

form known as carbonic acid as shown in equation 2. The dissolved bicarbonate and carbonate are in equilibrium with this dissolved carbonic acid species as shown in equation 3.



The carbonic acid species is in equilibrium with the gas phase above the water as carbon dioxide, and so any reduction of carbon dioxide partial pressure in the gas phase will cause the equilibria of the entire system to shift to the left (equation 3) [5]. Kinetically, this is a very slow and not well understood process in such a complex system as seawater [6]. For example, it would take about 2.8 hours to completely remove all the ionic species in one liter of seawater by applying a vacuum of 15 mm of Hg to the seawater spread in a thin film (such as in a rotary evaporator) [5]. From an ocean engineering point of view, this rate of carbon recovery aboard a very large vessel would be entirely too slow to obtain useful amounts of carbon on the order of 10 kg/sec. Even a bulk process such as vacuum degassing of the 2 to 3% of carbon dioxide gas would yield only 0.1 kg/sec of carbon dioxide under the maximum pumping rates available for a very large vessel.

To increase the rate and yield of carbon dioxide recovery from the sea, Hardy et al. investigated the use of a simple strong cation exchange resin system [7]. Johnson et al. showed that when the pH of seawater is decreased to 6 or less, the entire carbonate/bicarbonate equilibrium is shifted to the left so that total CO_2 exists only in the dissolved gas form (equation 3) [8]. The ion exchange system successfully acidified seawater below pH 6 and subsequently the spent ion exchange resin was regenerated using water instead of a strong acid. The volume of water per unit weight of resin required to regenerate the resin was much larger than the volume of carbon dioxide recovered, and so this approach was deemed impractical. Thus as one further avenue of exploration to increase carbon yield from the sea, gas permeable membranes are being investigated. It is well known that these membranes work on the principle of dissolved gases such as carbon dioxide diffusing across the membrane through the pores as a function of differential partial gas pressures. Therefore it has been assumed for gas/liquid systems that only the dissolved carbon dioxide gas is removed while the bound carbon dioxide in the ionic form of bicarbonate and carbonate is not involved [9]. The rate and yield of carbon dioxide for a given separation is dependent on several parameters which include the degasification matrix, membrane material and geometry, temperature, and pressure [10].

Gas permeable membranes are available commercially for the removal or addition of gases to liquids. Most of these applications are near atmospheric pressure and include water purification, blood oxygenation and artificial lung devices [11-14]. However some are operated at higher pressures such as beverage carbonation [15,16]. Because of the potential to operate gas permeable membranes underwater for recovery of carbon, this work was performed at pressures normally seen at about 300 meters (500 psi or 4 MPa). Further, in order to simplify the initial results a model system was adopted. The model consisted of either deionized or typical potable fresh water of known carbon dioxide content. The carbon content of the water was increased by

the addition of sodium bicarbonate to concentrations near ten times that seen in typical seawater. In these studies, the bicarbonate disproportionates to carbon dioxide and carbonate, when gaseous carbon dioxide is removed from the water by diffusion through gas permeable membranes at elevated bulk water pressures (500 psi). The rate of disproportionation and the effect ionic strength has on disproportionation is discussed.

3.0 EXPERIMENTAL

Reagent grade sodium bicarbonate was added to deionized water at a concentration of 1 gram per liter with the total CO₂ concentration approximately 12700 µmoles/kg by coulometry. The pH of the water/bicarbonate solution measured 8.56, and all pH measurements were conducted with a standardized Fisher combination glass electrode. A microporous polypropylene membrane commercially designated as 2400 Microporous Membrane with a 37% porosity, 0.117 x 0.042 µm pore size, 25 µm thickness, 24 seconds gurley, and 1300 kg/cm² tensile strength was used in the studies, and it was obtained from Celgard (Charlotte, NC). The membrane is known to preferentially permeate CO₂ gas and not water at low pressures [17]. The membranes were never reused throughout the experiments. Figure 1 is a schematic of the high pressure membrane extractor.

A Monel pressure cylinder held approximately 150 cm³ of water and the membrane filter holder approximately 45 cm³. A stainless steel frit was used to support the membranes (Phenomenex, 2.54 cm diameter, 1.5 mm thickness) and stainless steel fittings held the frit and membranes in place. In Figure 1, the water/bicarbonate solution was pumped into the top of the high pressure cylinder and pressurized using the stainless steel syringe liquid pump from Teledyne ISCO, Inc (Lincoln, NE 68504). The water/bicarbonate solution was pressurized and maintained at 500 psi in the cylinder and membrane holder. The pressurized solution was in constant contact with the membrane. A stir bar was used in the Monel cylinder and membrane filter holder to increase mass transfer. In each experiment, the water/bicarbonate solution was in contact with 7 layers of membrane at 500 psi for 5 hours. Seven layers of membrane were used to minimize water permeation in the system at 500 psi. After each experiment, the water/bicarbonate solution was depressurized and the amount of total CO₂ extracted from the solution in the pressure cylinder was measured by a UIC Coulometric system (UIC Inc, Joliet, IL 60436) [8] or by strong acid titration [18,19]. All solutions for the coulometer were of reagent grade and purchased from UIC Inc. The lower values from the coulometer represent the µmoles/kg of CO₂ gas released from the water/bicarbonate solution under pressure (after contact with membrane) compared to the water/bicarbonate solution not subjected to pressure time regimes (inlet sample). Each solution was measured in duplicate by the coulometer. For the potentiometric titrations, the entire 150 mL of the water/bicarbonate solution sample was collected and titrated with 0.2 M HCl. The titration endpoint for the pressurized solution in contact with the membranes was compared to the endpoint obtained for the same solution that was never in contact with the membranes and was at atmospheric pressure and temperature.

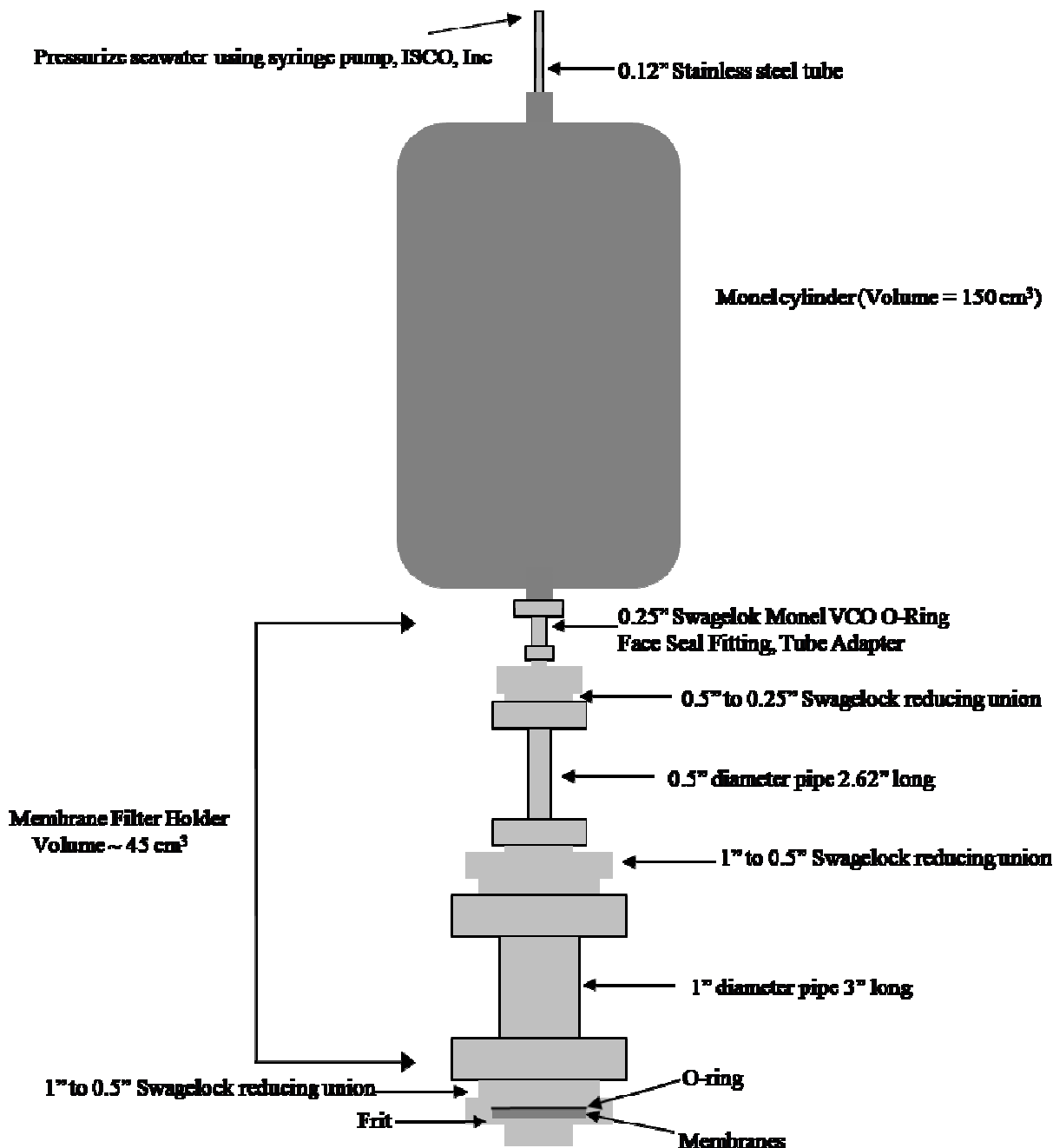
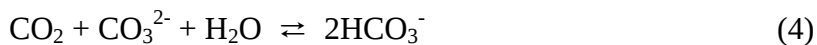


Figure 1. Membrane Extractor

4.0 RESULTS

A great deal of research has focused on using simple concentrated water/bicarbonate solutions in Facilitated Transport Membrane (FTM) systems. In these systems, bicarbonate-carbonate acts as carrier species that reversibly react with CO₂ as shown in equations 3 and 4 to increase CO₂ gas selectivity and flux in CO₂ separation applications [10,20-23].



In the present work the sequestering of bound CO_2 in ionic form from these solutions by gas permeable membranes is being discussed.

During typical experimental runs using this simple water/bicarbonate system, the gas permeable membranes were clearly reducing the $[\text{CO}_2]_{\text{T}}$ by a much greater percentage than the fraction of simple gaseous carbon dioxide. The reduction of about 10% under these experimental conditions is significant as it would represent an increase of about an order of magnitude in recovery rates. The yield for a very large shipboard constrained system could be as high as 1 kg/sec. During the time of the experiment, the bicarbonate is re-equilibrating to gaseous carbon dioxide, which is being removed from the system by diffusion through the membrane. Thus an aliquot of aqueous sodium bicarbonate after exposure to the membrane will show a reduction in $[\text{CO}_2]_{\text{T}}$ by coulometry as shown in Table 1.

Table 1. CO_2 Results

	Conditions	$\mu\text{mols/kg CO}_2$	% Loss
0.01 M NaHCO_3 in tap water	Inlet sample	12700	11
	After contact with membrane	11300	
0.01 M NaHCO_3 in deionized water	Inlet sample	12650	8.3
	After contact with membrane	11600	
0.01 M NaHCO_3 in deionized water and NaCl	Inlet sample	12500	11
	After contact with membrane	11100	
Sample	Conditions	Endpoint mL	% Loss
0.01 M NaHCO_3 /0.5 M NaCl in tap water	Inlet sample	11.75	0
	After contact with membrane	11.75	

Figure 2 is a schematic diagram showing the equilibrium equations that describe the gas permeable membrane process for the model sodium bicarbonate solution. As the bicarbonate dissolves in water the bicarbonate ion becomes a strong conjugate base ($\text{pK}_a=10.3$). This causes the bicarbonate ion to accept a proton from water resulting in the formation of undissociated carbonic acid as shown in equation (a), Figure 2. It is the decomposition of this undissociated carbonic acid at the membrane surface which initiates a change to the bulk liquid. As the CO_2 ($\text{pK}_a=1.4$) passes through the membrane the bulk liquid experiences an increase in pH (loss of an acidic species) as shown in equation (b) of Figure 2. In order to compensate for this, the remaining carbonic acid begins to dissociate, contributing a proton and a bicarbonate ion, equation (c) Figure 2. Bicarbonate ions disproportionate ($\text{pK}_a=10.3$) according to equation (d) of Figure 2, this time resulting in the loss of an acidic species through the membrane (CO_2) and the formation of the strong base carbonate ion ($\text{pK}_a=3.7$). The ratio of carbonate to bicarbonate limits the pH change. Carbonate is the stronger base and so bicarbonate concentrations decrease as illustrated in equations (c) and (d). The process occurring in equations (a) and (b) is essentially physical in nature and initiates a second process that is represented by moving from

equation (a) to (c) and finally (c) to (d) which is essentially chemical in nature. In addition to these two aqueous phase buffer anions, we must also consider the phase transfer of CO_2 . It is reasonable to expect a well designed buffer system which works in equilibrium with all three species to begin to replace removed CO_2 as a new equilibrium is approached, equation (d). Time is now a factor to consider in that the dissolution and hydration of CO_2 , equations (a and b), is relatively slow compared to concentration changes in the anions, equations (c and d) [5]. This shift appears to be independent of solution ionic strength as shown in Table 1 where 29.5 grams per liter of sodium chloride is added to the system in order to take the next step towards simulating a real seawater system. This ionic strength independence will be discussed in detail in a subsequent account on the effect of gas permeable membranes on seawater systems.

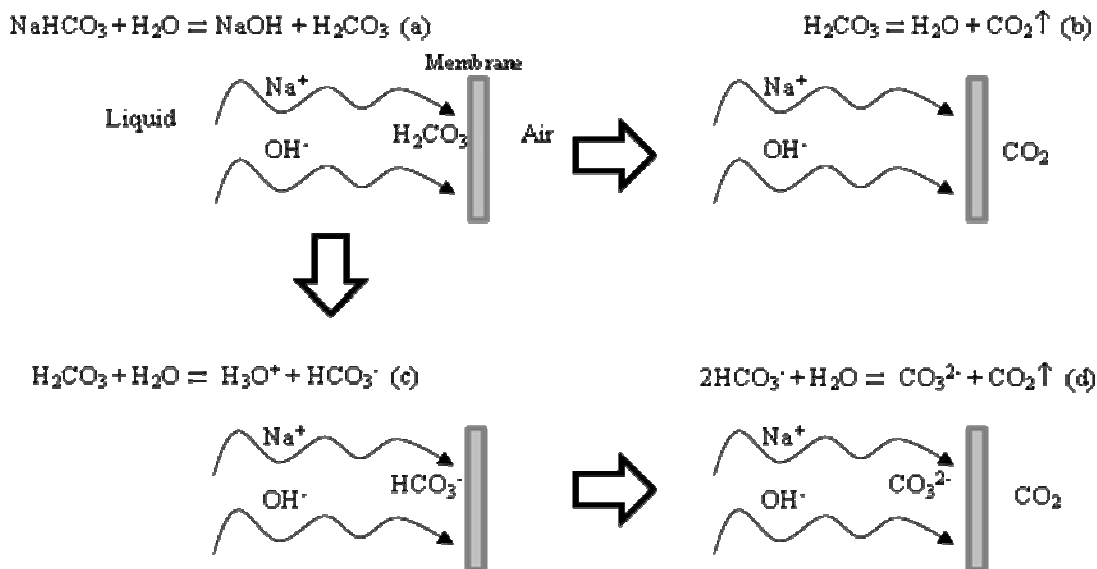
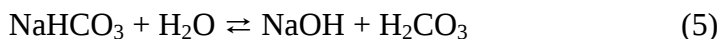


Figure 2. Schematic Diagram of Gas Permeable Membrane Process. The equations discussed in the text are placed either to the left or right (or directly over the membrane) to show the loss of CO_2 from the bulk liquid (on the left of the membrane) into air (on the right of the membrane). The actual effects of the CO_2 loss on the species remaining in the bulk liquid are shown.

All of the data have been determined by standard coulometric titrations. Acid titrations using potentiometry were also employed and as noted in Table 1, no reduction in $[\text{CO}_2]_{\text{T}}$ was seen. The explanation is in how equilibrium is shifted by the addition of the acid protons. In deionized water the bicarbonate species forms a basic solution as show in the following equations (5 and 6).



Titration with acid only titrates the hydroxide ion of which is unchanged by any loss of CO_2 . Thus when the solution is titrated with HCl it appears that no change in pH has been produced,

even though some of the bicarbonate has been removed through re-equilibration to gaseous carbon dioxide and subsequent transfer to the gas phase on the air side of the membrane, as illustrated in Figure 2.

Since the reduction in carbon dioxide has been measured, the rate of CO₂ permeability across the membrane for this system may be determined by Fick's law shown in equation 7:

$$F = n/At \quad (7)$$

where F is the CO₂ flux, n is the moles of CO₂, A is the membrane area and thickness, and t is the time [5]. Table 2 gives the CO₂ permeability for this system as 4.0×10^{-7} mL/sec cm² cm Hg. In the context of typical microporous membrane systems, the membrane permeability in gas-liquid systems has been shown to be on the order of two to five times slower than gas-gas systems (Table 2). This difference has been attributed to liquid infiltration into the membrane pores along with slower gas diffusion in a liquid medium [12-14,24]. However, since CO₂ is in the ionic form as carbonate and bicarbonate in this gas-liquid membrane system, the degree of flux across the membrane will also be dependent on the rate of CO₂ disproportionation in the system and the relatively much more rapid ion mobility to the membrane surface. Disproportionation occurs at the surface of the membrane and contributes to increasing CO₂ flux across the membrane as the removed CO₂ is continually being replenished as carbonic acid, carbonate and bicarbonate re-equilibrate. In typical gas-liquid systems CO₂ gas diffusion is slow. The addition of carrier species described in FTM systems enhances ion diffusion mobility to increase the flux of CO₂ across the membrane. Thus ion mobility will contribute to increasing CO₂ flux in this gas-liquid membrane system.

From Table 2 we can see that the rates of permeance of CO₂ is generally much higher than that of oxygen whether in a gas-gas or gas-liquid system. Regardless of membrane material and treatment, the range of oxygen permeabilities for oxygen in a gas-liquid system is from about 1 to 140×10^{-7} and for carbon dioxide about 840 to 3200×10^{-7} for literature values. These values are about 100 times higher than those of the present work. This is likely attributed to the fact that the bulk water pressures of our system were significantly higher. Previous work was done from atmospheric to about 100 psi, whereas this work was performed at 500 psi bulk pressure. This higher pressure causes a significant permeance of water into the membrane which effectively lowers the rate of gas permeance. We intend to report our work with this model system at lower pressures more consistent with previous literature. This has the salient effect of greater experimental ease and possibly higher gas permeance rates.

Table 2. Gas Permeability in Membrane Configurations

Material	System	Rate Gas permeance mL/sec cm ² cm Hg	System	Rate Gas permeance mL/sec cm ² cm Hg	Ref
KPF 280E	gas-gas	1.3×10^{-2} CO ₂ gas	gas-liquid	3.2×10^{-4} CO ₂ gas	13
KPF 280E	gas-gas	1.6×10^{-2} O ₂ gas	gas-liquid	1.4×10^{-5} O ₂ gas	13
Mitsubishi MHF 200L	-	-	gas-liquid	8.4×10^{-5} CO ₂ gas	12
Mitsubishi MHF 200L	-	-	gas-liquid	7.9×10^{-6} O ₂ gas	13
Celgard X30-240	gas-gas	1.5×10^{-2} CO ₂ gas	-	-	12
Celgard X30-240	gas-gas	1.7×10^{-2} O ₂ gas	-	-	12
Celgard X30-240	gas-gas	1.6×10^{-2} CO ₂ gas	-	-	14
Celgard X30-240	gas-gas	1.8×10^{-2} O ₂ gas	-	-	14
Celgard 2400	-	-	gas-liquid	2.83×10^{-6} - 4.0×10^{-7} CO ₂ gas	Present work
Silicone Rubber	gas-gas	3.90×10^{-6} O ₂ gas	gas-liquid	1.81×10^{-6} O ₂ gas	24
Silicone-coated Millipore filter	gas-gas	2.51×10^{-2} O ₂ gas	gas-liquid	1.35×10^{-7} O ₂ gas	24
Olefin paper	gas-gas	7.60×10^{-2} O ₂ gas	gas-liquid	1.97×10^{-7} O ₂ gas	24
Silicone-coated olefin paper	gas-gas	6.46×10^{-2} O ₂ gas	gas-liquid	1.95×10^{-6} O ₂ gas	24
Porous polysulfone membrane	gas-gas	9.16×10^{-2} O ₂ gas	gas-liquid	2.97×10^{-6} O ₂ gas	24

5.0 CONCLUSIONS

A simple model system of aqueous sodium bicarbonate has been used to investigate the rate of permeance of carbon dioxide (primarily through bicarbonate disproportionation) at relatively high pressures using a typical gas permeable membrane supported on a porous stainless steel frit. The results indicate that bicarbonate does appear to equilibrate (through disproportionation) and that carbon dioxide permeance rates may be high enough to warrant further use of gas permeable membranes in open ocean systems. The disadvantage of operating gas permeable membranes at pressures above 100 psi is decreased permeance rates. Operating at lower pressure should make future investigations easier experimentally.

6.0 ACKNOWLEDGMENTS

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