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LETTER

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Foam Films as Thin Liquid Gas Separation Membranes

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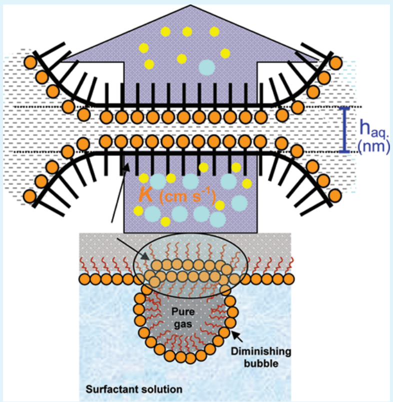
ABSTRACT: In this letter, we testify the feasibility of using freestanding foam films as a thin liquid gas separation membrane. Diminishing bubble method was used as a tool to measure the permeability of pure gases like argon, nitrogen, and oxygen in addition to atmospheric air. All components of the foam film including the nature of the tail (fluorocarbon vs hydrocarbon), charge on the headgroup (anionic, cationic, and nonionic) and the thickness of the water core (Newton black film vs Common black film) were systematically varied to understand the permeation phenomena of pure gases. Overall results indicate that the permeability values for different gases are in accordance with magnitude of their molecular diameter. A smaller gaseous molecule permeates faster than the larger ones, indicating a new realm of application for foam films as size selective separation membranes.



KEYWORDS: foam film, permeability, thin liquid membrane, diminishing bubble, gas separation

Recently, the quest for developing ultrathin, dense, and cost-effective gas/vapor separation membrane is keep escalating despite the fact that the membrane-based gas separation is a subject of investigation for over a century.[1] Invention of polymer-based membranes for gas separation has significantly revolutionized various industrial processes within the last three decades.[2] In the concept of membrane science, a separation membrane behaves as a thin barrier between two phases through which differential transport can occur. There are several driving forces that facilitate the nonequilibrium transport process across the membrane that include pressure gradient, concentration gradient, electrical potential gradient, and temperature gradient.[3,4] Typically, for gas separation, polymer based membranes act as a semipermeable gate to the permeating gases through which certain gas molecules move faster than other molecules in the gas mixture. The gas flux is driven by either concentration or pressure gradient across the membrane. Permeability and selectivity are two characteristic parameters that determine membranes suitability for gas separation applications.[5] Having high permeability and high selectivity is always desirable; however, often as the membranes permeability increases, the selectivity decreases and vice versa. There are various mechanisms proposed for gas permeation across a polymeric membrane that includes surface diffusion, capillary condensation, and molecular size selective permeation.[6]

Foam films contain two identical monolayers of surfactant molecules that are adsorbed at the gas/liquid interface and are separated by a thin aqueous core with a thickness h_{aq} as it is shown in Figure.1. The interaction between the two surfaces of the film can be precisely tuned and films with different thickness can be obtained as equilibrium structures. There are two states of the foam films designated as common black film (CBF) with h_{aq} > 100 nm or Newton black film (NBF) h_{aq} < 100 nm,[7] which are practically two thin layers of surfactant molecules. The film thickness is one of the most important and very well characterized properties of the films. It is usually measured using different interferometric techniques.[7]

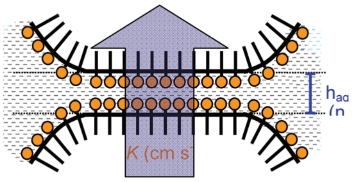


Figure 1. Schematic representation of a freestanding foam film where the arrow indicates the direction of the gas permeation and h_{aq} indicates the thickness of the aqueous core between two adsorbed surfactant monolayers that stabilize the film.

The permeability of a foam film was first demonstrated by Blank and McBain and later studied in more details by Princen, and Mason over half a century ago.[8−11] In the 1980s, a group of Bulgarian scientists (Krastev and co-workers) systematically exemplified the permeability of CBF and NBF using mainly the anionic surfactant sodium dodecyl sulfate (SDS) as a stabilizing agent.[12−14] Afterward, a number of researchers have published their results on the permeability of foam films that are stabilized with different types of surfactants at various thermodynamic conditions.[15,16] For instance, the effect of hydrophobic chain length on air permeability was studied by Krustev et al.[17] The difference in the film permeability of hydrocarbon chain vs perfluorocarbon chain was reported by Ramanathan et al.[18] The influence of charge on the headgroup of the surfactant molecules such as negatively charged SDS, positively charged alkyltrimethlammonium halides and nonionic polyoxyethylene and sugar-based

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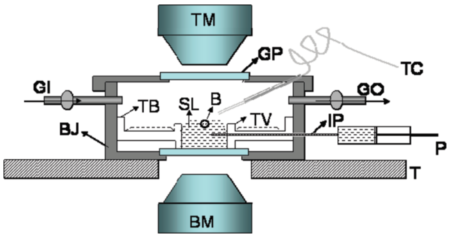

Figure 2. Experimental cell specially designed for single gas permeability measurements. TM and BM are top and bottom microscopes, respectively. (GP) Plane parallel glass plate, (GI) gas inlet, (GO) gas outlet, (BJ) air-tight brass jacket, (TC) temperature controller, (TB) Teflon body, (TV) Teflon vessel, (IP) injection port, (B) diminishing bubble, (SL) surfactant solution, (P) piston.

surfactants on the film permeability have been well investigated.[7,19−21] Effects of concentration of surfactants, ionic strength, temperature, applied pressure, and curvature of the film are some of other rigorously studied parameters. Müller and Krustev[22] have convincingly demonstrated that the permeability of a freestanding foam film can be used as a sensitive tool to evaluate some minute changes that occur within the film architecture such as the change in the surfactant packing density as a function of distance between two adsorbed monolayers.

Ironically, thus far, most of the permeability experiments in freestanding foam films are done with atmospheric air as a permeating gas with some rare exceptions.[23] In this letter, we intend to testify the permeability of foam films to different single gases. We have chosen oxygen, nitrogen and argon as single gases and compared the permeability of the films to air measured previously at the same conditions. A systematic variation of every component of foam films (headgroup, tail, and film thickness) enabled us to testify the possibility of using thin liquid films as thin liquid gas separation membranes.

There are various methods that have been used to measure the permeability of air through foam films. In this work, we have used the well-established and a straightforward method known as the "diminishing bubble" method.[12] Basically, in the diminishing bubble method, a small freely floating bubble is formed at the air/solution interface. At the contact between the bubble and the surface a foam film is formed. Because of the higher pressure in the bubble, it diminishes spontaneously, releasing the gas through the foam film. In a typical experiment, the bubble is observed from the top and from the bottom simultaneously. The radius of the bubble, R_b and the radius of the film formed on the top of the bubble, r, are measured as a function of time, *t*.

Measurements on permeability of films to single gases requires that the bubbles are filled only with the studied gas and additionally the measuring chamber has to be saturated to the same gas and isolated from the external environment. It should be leak proofed for the external air. We have designed an extension of the standard chamber used for the "diminishing bubble" method[7,12] (see Figure 2). It fulfills the necessary requirements for measuring the permeability of pure/single gases. The measuring cell, made up of Teflon (diameter of 1 cm), was threaded into an airtight brass jacket. The small radius of the vessel allows the formation of a convex surface. The brass jacket has three holes, two on the top (inlet and outlet) for the continuous flow of the single gas during the measurements and a third one for the syringe used for the formation of the bubble. The permeability experiments are very sensitive to the temperature and its changes. The whole experimental chamber is placed on a thermostatic table of the microscope. The temperature is measured close to the floating bubble in the gas phase over it and controlled with a precision of ±0.05 °C. Additionally, the temperature in the laboratory was also kept constant with a precision of ±0.5 °C.

Before starting the experiment the test solution was purged with the single gas to remove the dissolved gases. The solution was injected into the measuring cell through the injection port. Before filling the surfactant solution the cell was circulated with the single gas saturated on water vapors for one hour. During that time a small portion of the single gas was taken by a syringe used for bubble formation which was kept in the gas injection port (IP). The gas circulation continues during the whole measurement and assures that no contamination of air from the surrounding will enter in the chamber. (Even though we used single well-defined and pure gases one has to consider that all experiments were performed with gases which are saturated to water vapors. This is due to the lack of stability of the foam films in completely dry atmosphere. On the other hand the films are formed from water based solutions. We assume that the water vapors do not influence the permeability of the other gases because the water molecules are larger and heavier thus slower and their contribution to the permeability process is negligible. One also has to consider that the concentration of water molecules in the used gas mixtures was always the same as all experiments were performed at constant temperature.) The gas which is taken in the syringe is used to form the bubbles. A tiny floating bubble with radius R_b of 100 μm is formed under the surface of the investigated solution. The bubble floats to the surface and at the contact a foam film with radius *r* is formed on top of the bubble. Because of the curvature of the solution the bubble is fixed in its center. It is observed from the bottom in reflected light by using an inverse microscope. The film formed on top of the bubble is observed simultaneously with a second microscope in transmitted light from the top. Both microscopes are coaxial, which allows simultaneous observation of the radius of the bubble and the radius of the film.

Owing to the capillary pressure, $P_C = 2\sigma/R_b$ which varies between 700 and 1000 Pa in the case of our experiments the gas pressure in the bubble $P = P_{at} + P_C$ is higher than the atmospheric pressure, $P_{at.}$ Therefore the gas in the bubble permeates continuously from the bubble to the atmosphere through the foam film. The overpressure changes during the experiment because the bubble shrinks. This change in the pressure is much lower compared to the disjoining pressure in the film and cannot change its thickness during the experiment. The overpressure creates a difference in the concentration of the gas inside and outside the bubble ΔC_g[12]

$$\Delta C_g = \frac{P_C}{RT} = (2\sigma/R_b)(1/RT) \qquad (1)$$

Here, σ (mN/m) is the surface tension at the interface gas/solution measured separately, *R* is the universal gas constant, and *T* is the temperature.

As a consequence of the concentration difference the bubble shrinks and R_b (radius of the bubble) and *r* (radius of the film) decrease with time. Since the gas is treated as an ideal, the number of moles of the gas in the bubble $\Delta N(t)$ as a function of the time *t* is

$$N(t) = \left(P_{at} + \frac{2\sigma}{R_b}\right)\frac{4}{3}\pi R_b^3/RT \qquad (2)$$

here, P_{at} is the atmospheric pressure.

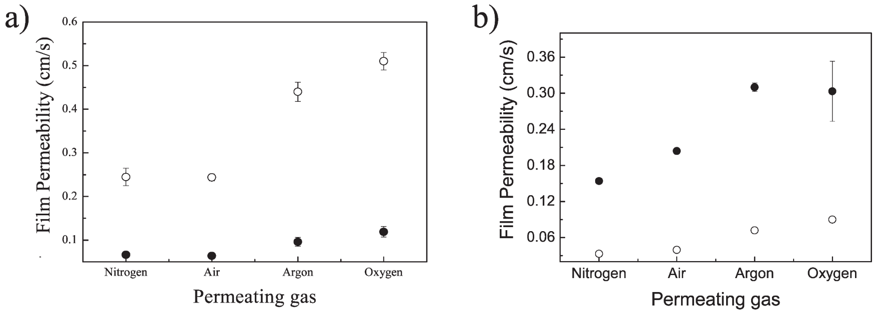

Figure 3. Permeability of different gases through anionic surfactant stabilized foam films. (a) Fluorinated PFOS surfactant stabilized foam films, (b) SDS surfactant stabilized foam films: ○ NBF; ● CBF.

This equation is valid only for spherical bubbles. All experiments in the present study were performed with bubbles with a radius of less than 100 μm. This assures that the bubbles in our experimental geometry are not deformed by the gravity and they are spherical.[13] Small deviation of the spherical shape can be caused by the formation of the foam films on the top of the bubble, but it causes an error of less than 3% by the calculation of the volume of the bubble.[24]

A measure of the gas permeability of a membrane such as a foam film is the permeability coefficient K (cm/s) defined by[9,11]

$$\frac{dN}{dt} = -KS\Delta C_g \qquad (3)$$

Here, dN is the number of moles of gas that permeate through the film for certain time interval dt, and S is the area of the film. The permeability coefficient, K, is calculated from the following relation obtained by substitution of eqs 1 and 2 in eq 3[12]

$$K = \left[(P_{at}/2\sigma)(R_0^4 - R_t^4) + \frac{8}{9}(R_0^3 - R_t^3)\right]\left(\int_0^{-t} r^2 dt\right)^{-1} \qquad (4)$$

here, R_0 is the initial radius of the bubble at time 0, and R_t is the final radius of the bubble at time t. The both radii R_b and r are measured in 1 min intervals or often if the permeability process is fast. The integral in the denominator of eq 4 is numerically evaluated using the calculation procedure described in ref 24. The permeability coefficient is usually calculated for successive 20 min intervals from the time dependencies of R_b and r. The precision of the method is ±0.002 cm/s. All presented K values are arithmetical means of more than 10 single experimental values. The sample standard deviation is shown as error bars on the graphs.

Anionic fluoro carbon surfactant—highly purified tetraethyl ammonium salt of perfluoro octane sulfonate (PFOS) with a chemical formula $(CF_3\,(CF_2)_7\,SO_3)^-[N\,(C_2H_5)_4]^+$, was obtained from Institut für Dünnschichttechnologie and Mikrosensorik e.V, (Teltow, Germany). Complementary anionic hydrocarbon surfactant, sodium dodecyl sulfate was purchased from Henkel (>99.5%purity) and later purified by the method described in ref 25 Cationic dodecyl trimethyl ammonium bromide (DoTAB) was purchased from Aldrich (99% purity) and used without any further purification; Nonionic dodecyl heptaoxyethylene glycol ($C_{12}E_7$) was purchased from Fluka (>98% purity) and used without any further purification; Another nonionic surfactant n-dodecyl-β-Maltoside (β-$C_{12}G_2$) was purchased from Glycon biochemicals, (Luckenwalde, Germany) (>99.5% purity) and used as received.

Foam films stabilized by any of these surfactants form thick films with a thickness over 100 nm because of the strong electrostatic repulsion between two surfaces of the films[7,18,21,26,27] The film thickness was precisely tuned in the present work by adding different amount of salt to the film forming solutions. The following salts were used to screen the electrostatic interactions between the film surfaces, (i) sodium chloride (NaCl) purchased from Merck, Germany and roasted at 600 °C for 5 h to remove the traces of highly surface-active contaminations; (ii) potassium bromide (KBr) purchased from Merck; (iii) ammonium chloride (NH_4Cl) purchased from Sigma, both KBr and NH_4Cl were used as received. The purity of the used gases (Oxygen, O_2; Nitrogen, N_2; and Argon, Ar) was better than 99.998%. The exact salt concentrations necessary for formation of either CBF or NBF with well-defined thickness were obtained in earlier works.[7,18,20,21,26,27]

The permeability coefficient K of CBF and NBF stabilized with PFOS for nitrogen, argon and oxygen are shown in Figure 3a. For all gases, the thinner NBFs permeate faster than the thicker CBFs. Because of the small K values of the CBF it is hard to differentiate between N_2 and O_2 but the NBF show that N_2 is much less permeable compared to O_2. The K values for nitrogen are similar to those of air, whereas the K values for argon and oxygen are higher.

On the basis of Figure 3a one can conclude that the fluorocarbon presented in the hydrophobic chain of the surfactant molecule influences the permeability and enhances the transport of oxygen through the film. Before arriving at such a conclusion one should know how these gases permeate through other films without any fluorocarbon. So, the permeability of foam films stabilized by surfactants containing no fluorocarbon but only hydrocarbon in their hydrophobic part to the above-mentioned gases were measured. Different films were chosen with different ionic and nonionic surfactants to avoid the charge effects. The surfactant concentration is always two times of their respective critical micelle concentration (cmc) and the salt concentrations are chosen accordingly to form CBF or NBF.

Figure 3b shows the permeability of foam films stabilized by anionic surfactant SDS to different gases. The notable point here is that the thicker CBF permeates faster than the much thinner NBF. Such a result for air permeability has already been shown by Krustev et al.,[17,18] later it was reasoned by Krustev and Müller.[22] According to their arguments the film interaction free energy (Δg^f) is very negative in the foam films stabilized with SDS, which enhances the adsorption of surfactant ions and respectively decreases the permeability. Our results shown on Figure 3b show that not only the air but also all other gases permeate slower through the thinner NBF prepared from SDS. This is a unique property for this particular surfactant (SDS). However, the permeability trend for different gases is similar to the one for the fluorinated surfactant stabilized foam films, that is, oxygen permeates faster than nitrogen.

The foam films stabilized with the cationic DoTAB also demonstrate a similar permeability trend as in the case of the other two anionic surfactants (see Figure 4) concerning the differences between the gases. Surprisingly, no difference in the *K* values for CBF and NBF was observed even though the film thickness[7,17] is very different.

Figure 5a shows a weak trend for different gases in the foam films stabilized by the nonionic surfactant $C_{12}E_7$. The permeability of the NBF is bigger than that of the CBF. Figure 5b shows the permeability behavior of the foam films stabilized with β-$C_{12}G_2$, another nonionic surfactant. As it is shown in ref,[21,28,29] the surfactant monolayers which form these films are tightly packed and the β-$C_{12}G_2$ surfactants are more rigid than the complementary $C_{12}E_7$. Moreover, the slightly elevated pressure present in the diminishing bubble is sufficient to surpass the weak electrostatic repulsive forces in β-$C_{12}G_2$.[21] Therefore, regardless of the salt concentration, only NBF is formed on top of a diminishing bubble of β-$C_{12}G_2$.

From these results it appears that for all the foam films, irrespective of the nature of the tail or nature of the headgroup, the trend of the permeability of different gases remains the same which can be written as follows

$$N_2 \approx \text{air} < \text{Ar} \approx O_2$$

Permeability and selectivity are determined by various levels of physical as well as chemical structure. Furthermore, in the case of foam films, a gas separation model incorporating the concept of fixed micropores is worth of consideration. Such pores or holes can be formed in the foam films as defects in the density of the surfactant layers which form the film. Such idea has already been discussed by Exerowa and Kashchiev,[7] and experimentally proved by Krastev et al.[12,17,24] Permeability is usually taken as the product of two constituent parameters, diffusivity and solubility. Less polar, more permanent gases exhibit low molecular weights, symmetry and weak interactions. Solubility plays only a minor role in the separation of permanent gases. Instead, permeability is largely determined by the relative diffusivities of the gases. Diffusivity in turn is a function of the size and shape of the molecules of the permeate gas and of the size and shape of the membrane micropores. This discussion presupposes that the pore size and shape are similar in all foam films taken here for the discussion.

In Figure 6, the permeability of NBFs of different surfactants is compared for oxygen and nitrogen. In all cases the oxygen permeability is higher than the respective nitrogen permeability. As the molecular weight and polarity of the permeant increase, so do their condensability and the probability of specific interactions with polar groups on the foam films.

The Table 1 shows the solubility, diffusivity and van der Waals and kinetic diameter data of the used gases. The diffusion coefficients for oxygen and nitrogen are the same, so the difference in permeability arises from the size of the gas molecules. It is not easy to measure the exact radius of the gas molecules.

One of the methods to measure this is to take the components in the van der Waals equation state for real gases, where *a* is the measure of the attractive force between molecules and *b* is the finite volume of the molecules to their general incompressibility; *p* is the absolute pressure of the gas; *V* is the volume; *n* is the amount of substance.

$$\left(P + \frac{n^2 a}{v^2}\right)(v - nb) = nRT \qquad (5)$$

From the table, it is clear that the size of the oxygen molecule is nearly the same as the size of the argon which results in the same level of permeability for these gases. Whereas air is a mixture of

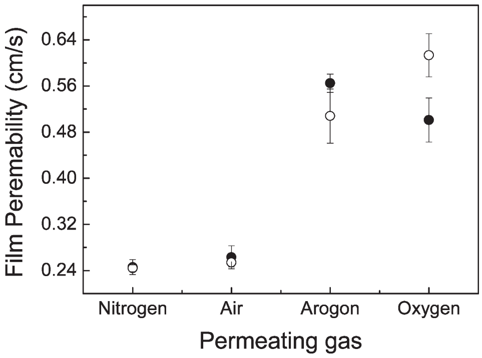

Figure 4. Permeability of different gases through DoTAB-stabilized foam films:○ NBF; ● CBF.

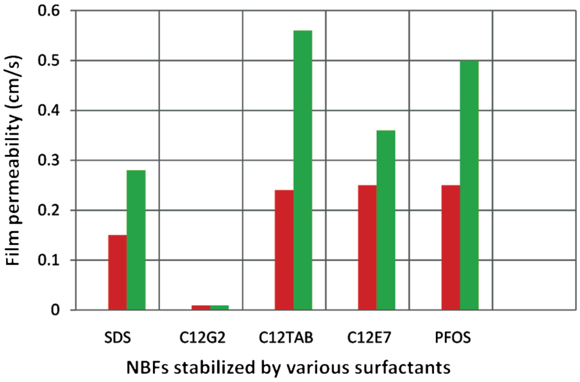

Figure 6. Permeability of O_2 and N_2 through different surfactant-stabilized foam films. red, nitrogen ; green, oxygen.

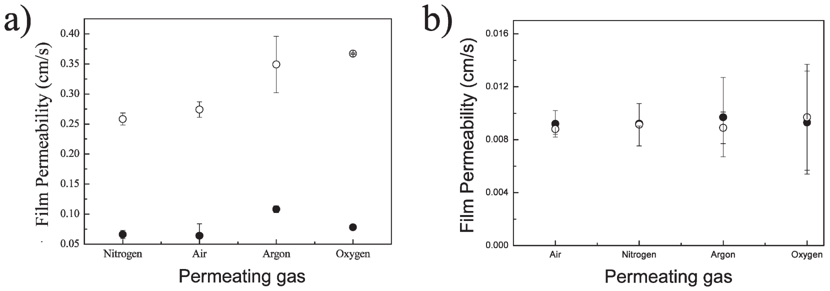

Figure 5. Permeability of different gases through nonionic surfactant stabilized foam films. (a) $C_{12}E_7$ surfactant-stabilized foam films; (b) β-$C_{12}G_2$ surfactant stabilized foam films. ○ NBF, ● CBF.

Table 1. Solubility Coefficients, Diffusion Coefficients, Van Der Waals Constants and Kinetic Diameters for Pure Gases

gas	solubility in water[30] $\times 10^{-5}$ (mol/cm^3)	diffusion coefficient[31] $\times 10^{-5}$ (cm^2/s)	van der Waals constant[2] a (L^{2}Atm/(mole^2))	van der Waals constant b (L/mol)	kinetic diameter[32] (Å)
nitrogen	1.19	2.34	1.390	0.03913	3.76
argon	2.52	2.01	1.345	0.0321	3.46
oxygen	2.29	2.33	1.360	0.03183	3.41

different gases among them the quantity of nitrogen is more than seventy percent which turns the air permeability to the level of nitrogen permeability. The size exclusive gas separation effect that we have observed with the freestanding foam films remains to be a common gas separation mechanism in inorganic (zeolite, sol−gel derived silica, etc.) and organic (polymeric) membranes and porous materials.[2,3,5,6] For instance, in polymeric membranes, it is shown that the gas diffusion coefficients scale with measures of molecular size, such as kinetic diameter or critical volume; the larger the molecule, then the lower the diffusion coefficient. The mobility selectivity for large and small gas molecules are shown to be a strong dependent on the nature of the polymer chain (glassy or rubbery).[33,34]

To summarize the results, we found that the magnitude of permeability of a freestanding foam film for different gases depends on the size of the permeating gas molecule. Nitrogen, which is larger in size, permeates slower; the air that consists of >70%nitrogen permeates the same level as nitrogen. Oxygen and argon have the nearly same molecular size, which is smaller than that of nitrogen. So, oxygen and argon permeate much faster than the air and nitrogen. This trend remains the same irrespective of the nature of the hydrophobic or hydrophilic part. These first-hand results that we presented in this letter are in favor of using freestanding foam films as a size selective gas separation membrane. That said, there still remain a number of fundamentally interesting questions that needs to be answered with more rigorous experiments and modeling. A follow-up research to the results presented in this letter is to measure the permeability behavior of freestanding foam films for mixture of gases and vapors, investigate the permeability behavior of a wide range of gases at the Knudsen diffusion regime, where the permeation rate of a gas molecule should be inversely proportional to the square root of its molecular weight.

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