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Study on the permeability of ethanol in polyamide membranes.

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Hablo en italiano con los embajadores; en francés, con las mujeres; en alemán con los soldados; en inglés con los caballos y en español con Dios.

Su Sacra Cesárea Católica Real Majestad
Carlos I de España y V Emperador
del Sacro Imperio Romano Germánico.

Las personas tranquilas y silenciosas son las que tienen las mentes más fuertes y ruidosas.

Stephen W. Hawking.

Cuando conozca a Dios, le voy a hacer dos preguntes: ¿Por qué la relatividad? Y, ¿Por qué la turbulencia? Realmente creo que Él tiene la respuesta para la primera.

Werner Heisenberg.

Le agradezco la ayuda y el apoyo prestados a toda mi familia y amigos.

Le doy las gracias al Dr. Llorens por haber sido un excelente tutor y por haberme permitido hacer con el este trabajo.

También darle las gracias en especial a la Dra. Chamarro por el apoyo prestado en estos años.

Quiero dedicarles este trabajo a mi familia y amigos. A los que fueron, son y serán.

CONTENTS

SUMMARY

This work consists of the study of the permeability of ethanol in different modified reverse osmosis and direct osmosis polyamide membranes, all of them working in direct osmosis. In this way, the behavior of these membranes in different mixtures of water and ethanol is studied using a mixture of glycerin with water as the osmotic solution. The membranes analyzed are commercial membranes that have been modified with the intention of reducing the thickness of the layer of the support, thus reducing one of the biggest problems of the membranes, the polarization of the concentration that occurs in the support.

In recent years, direct osmosis has been specially investigated, demonstrating advantages over reverse osmosis, which has been widely studied and developed. Membrane processes have wide applications today, so that in these years they have been optimized. Specifically, reverse osmosis processes are used for desalination of sea water so that it can be made drinkable. It is also used for energy production, which in recent years has made it efficient and profitable, making it a new type of renewable energy. Osmosis research is advancing, like other branches of science and engineering, at ever faster steps, sighting a promising future. It is presented as an option or alternative to end the problems of shortage of drinking water and the problems derived from fossil fuels such as pollution and climate change and avoiding the problems of many renewable energies since they are intermittent production. The important points of the history of membrane science and the applications of osmosis will be explained.

Keywords: Forward osmosis, Membrane Science, Thin-Film Composite, Reverse Osmosis, Direct Osmosis, Pressure-Retarded Osmosis.

RESUMEN

Este trabajo consiste en el estudio de la permeabilidad del etanol en distintas membranas de poliamida de ósmosis inversa modificadas y ósmosis directa, trabajando todas ellas en ósmosis directa. De esta manera se estudia el comportamiento de estas membranas en distintas mezclas de agua y etanol utilizando como solución osmótica una mezcla de glicerina con agua. Las membranas analizadas son membranas comerciales que se han modificado con la intención de disminuir el grosor de la capa del soporte reduciendo así uno de los mayores problemas de las membranas, la polarización de la concentración que se da en el soporte.

En los últimos años la osmosis directa ha sido especialmente investigada demostrando ventajas respecto la osmosis inversa que es la que ha sido ampliamente estudiada y desarrollada. Los procesos de membranas tienen amplias aplicaciones hoy en día, de manera que en estos años se han optimizado. En concreto, los procesos de ósmosis inversa se utilizan para la desalación de agua marina de manera que se pueda hacer potable. También se utiliza para la producción de energía, que en estos últimos años se ha conseguido que sea eficiente y rentable de manera que es un nuevo tipo energía renovable. La investigación en ósmosis avanza, como otras ramas de la ciencia e ingeniería, a pasos cada vez más rápidos avistando un futuro prometedor. Se presenta como una opción o alternativa para acabar con los problemas de desabastecimiento de agua potable y los problemas derivados de los combustibles fósiles como la contaminación y cambio climático y evitando los problemas de muchas energías renovables ya que son de producción intermitente. Se explicará los puntos importantes de la historia de la ciencia de membranas y las aplicaciones de la ósmosis.

Palabras clave: Ósmosis directa, Ciencia de Membranas, Thin-Film Composite, Ósmosis Inversa, Ósmosis Retardada por Presión.

1. INTRODUCTION

In recent decades, particularly since the 70s, the business technology industrial membrane separation has increased to over 2 billion per year in the United States. The market for this technology is highly fragmented, but the main industrial processes used today are: pervaporation, gas separation, microfiltration, ultrafiltration, and osmosis, both reverse and forward. It is this last process that will be discussed in depth. There is another process that is used especially for biomedical processes, dialysis. Among its applications we have haemodialysis, which is a renal replacement therapy in order to partially perform the function of the kidneys, and blood oxygenators that are intended to replace the lungs, being artificial lungs. Only these two biomedical applications already have a market of $ $2 \cdot 10^9$ each year.

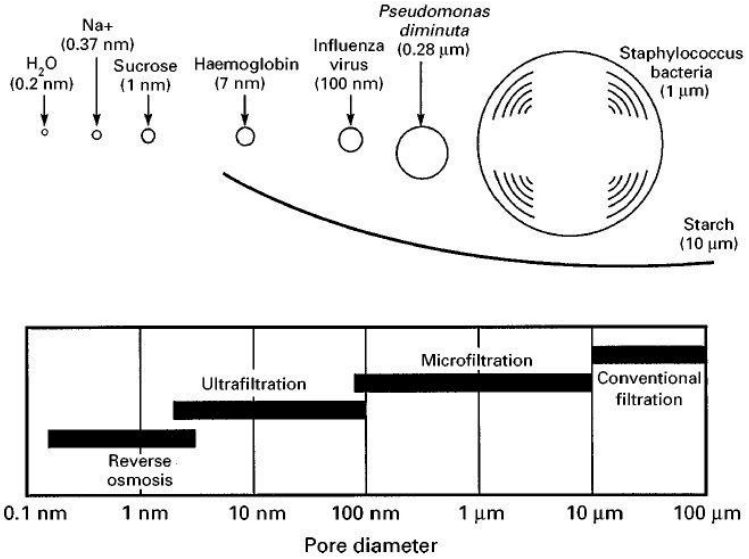

Figure 1. Comparative scheme of the pore size of the different membrane separation processes. *(Ghasem D. Najafpour et al, 2007).*

Today, various applications of membrane separation processes are being developed such as coupled and facilitated transport, membrane contactors and membrane reactors. Although similar membranes and module designs are used in the different processes, the way in which the separation process is carried out and its applications are very different.

1.1. **A BRIEF HISTORY OF MEMBRANE SEPARATION**

For more than 150 years, thermodynamics have tried to conceptually design an ideal semi-permeable membrane that would be capable of separating two species with minimal theoretical work. But until the early 1900s no attempts were made for practical separation. In this decade, Bechhold devised a technique to develop nitrocellulose membranes with a graduated pore size. Subsequently, there were other scientists such as Zsigmondy, Bachmann, Elford and Ferry who used these techniques to design membranes that were used to separate different laboratory solutions through dialysis and microfiltration processes.

By the 1930s, microporous membranes were already being produced commercially on a small scale. Virtually the same time the first ion exchange membranes were designed. The development of electrodialysis was due to the work of Meyer, Teorell and Seivers for the conceptualization of their own theory of ion transport.

Once arrival the decade of the 60 already had developed the elements of modern science of membranes, but at that time were only used in some small and specialized industries, but especially in laboratories for studying techniques. Therefore, the membrane industry and its economy were not significant at the time. It is estimated that sales failed to exceed 10 million US dollars. This was quite logical since the membranes then had serious difficulties that had not yet been solved: the process was excessively slow, very expensive and also very unselective, which made its widespread use very difficult. Since then, each of the aforementioned problems have been partially solved, thus leading to an increase of several hundred times the sales of membrane separation equipment. Currently, there is a well-established membrane industry with great growth prospects and several tens of millions of square meters of membranes are produced each year.

In the late 60s and early 70s, it managed to solve one of the biggest problems of membranes thanks to the development of very thin membranes, called ultrathin membranes, which have no imperfections. These new types of membranes are isotropic structures that

consist of a microporous substrate that provides the mechanical resistance to these membranes and a very thin selective surface film that is supported on the substrate. Said substrate is considerably thicker than the film. Thus, thanks to the thin selective surface film is achieved that such membranes have high flows.

The development of ultrathin membranes was a breakthrough for membrane science. The technique designed by Loeb and Sourirajan in the early 1960s revolutionized membrane separation processes. The first useful ultrathin membranes were cellulose acetate reverse osmosis membranes that these two scientists developed at the University of California, Los Angeles. The flow of the first reverse osmosis membrane developed by them achieved a flow 10 times higher than any membrane developed so far, due to this the membranes pass to the industrial sector, since it made reverse osmosis a potentially profitable and practical process for desalination of water.

This new developed technique, which was renamed the Loeb-Sourirajan technique, consisted of a solution containing approximately 20% of a polymer that is projected as a thin film on a non-woven fabric web and then precipitated by immersion in a bath of water. Water quickly precipitates the top surface of the cast film, thereby forming the selective layer. This layer then descends through the ingress of water into the underlying polymer solution, which precipitates much more slowly, thereby forming a more porous substructure. The thickness of the selective layer is generally less than 0.2 μm. Figure 2 shows a scanning electron microscope of a porous substructure and the selective layer of the Loeb-Sourirajan membrane.

Seeing the new developments of Loeb and Sourirajan, the US Department of the Interior decided to invest millions of dollars in research through the Office of Saline Water (OSW), which led to the commercialization of reverse osmosis. In addition, this government support was an important support for the development of microfiltration and ultrafiltration.

While the science of membranes was making its way in the industrial sector, the first medical applications were also being developed in parallel, one of the most important was the artificial kidney, it should be understood as an artificial kidney to hemodialysis machines that perform the function renal. As a curious fact to explain that the first artificial kidney was developed in 1945 in the Netherlands by Willem Johan Kolff, considered the father of artificial organs and one of the best doctors of the 20th century. But it wasn't until the breakthrough made by Loeb and Sourirajan approximately 20 years after the technology was perfected and

artificial kidneys came to be used on a large scale to save lives. In the United States at least 800,000 people live thanks to artificial kidneys, in Spain there are more than 60,000 patients, while open-heart surgeries number more than a million in the United States and this type of surgery can be performed thanks to the development of membrane blood oxygenator. Another important medical application is controlled drug delivery systems.

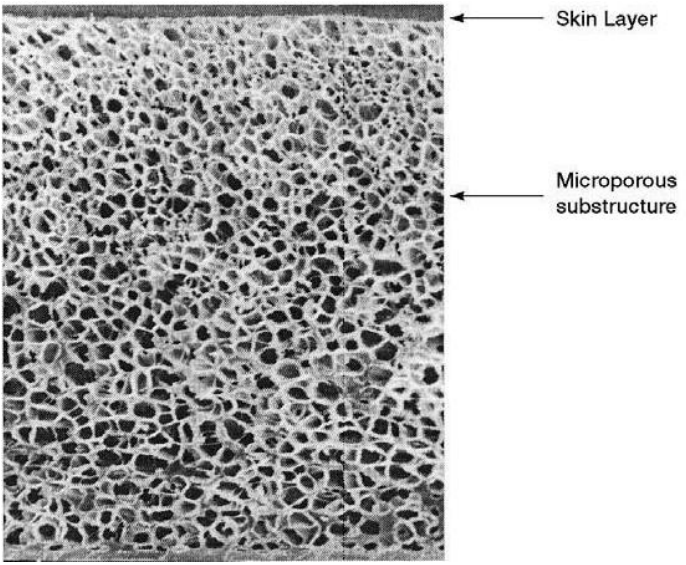

Figure 2. Scanning electron micrograph of the cross-section of a Loeb-Sourirajan reverse osmosis membrane. *(R. W. Baker et al, 2000).*

As can be seen, the twenty years between the 1960s and 1980s represented a before and after in membrane science, a true revolution. In those years, the Loeb-Sourirajan technique was improved so that various companies managed to design selective layers with a thickness of 0.1 μm and even less.

Shortly thereafter, once initiated 1980s, the problem of packing a large membrane area in a low cost module was solved. The modules that were designed at that time were plate-and-frame or tubular structure units like conventional heat exchangers. These first designs are still used today in some processes, such as ultrafiltration. In this type of process, the ability to clean fouling deposits from the membrane surface is very important. Despite the considerable advance that these designs entailed, they currently have a high cost compared to other

processes, so they are used, as mentioned before, in some processes. Today, hollow-fine-fibre, capillary and spiral-wound modules are more common.

One of the main limitations that continue to extend to this day is the low selectivity of the membrane processes. There is no general solution to this problem, but considerable progress has been made since the 1950s.

1.2. **OSMOSIS PROCESSES**

Osmosis is a physical phenomenon that consists of the net movement of solvent molecules through a selectively permeable membrane driven by a difference in osmotic pressure across the membrane. A correct selectively permeable membrane allows the passage of solvent molecules through the membrane itself but rejects the passage of solute molecules or ions. As all physical process, osmosis has a driving force, which in this case is the osmotic pressure (π).

Since the early days of humanity, osmosis processes have been used, even without knowing how it works. For example, humans in the first crops realized that if food was added salt, this served to dry them out and therefore achieve greater long-term preservation and this occurs because most bacteria, fungi and Other potentially pathogenic organisms become dehydrated, through the osmosis processes that take place in the cells, causing their death or inactivation until the minimum vital conditions for the organism are restored.

As previously implied, osmosis is a process that occurs also at the cellular level not only in man-made industries and technologies, but is a basic life process in biological systems. This is because cell membranes are semipermeable, so they are permeable to nonpolar or hydrophobic molecules such as lipids, and also to small molecules such as those present in cellular respiration: O_2 and CO_2; while they are impervious to large, polar molecules such as ions, proteins, and polysaccharides. Permeability not only depends on the size of the solute molecule, which is important, but also depends on charge, chemistry, and solubility.

Therefore, osmosis is the main process by which the cell is able to transport water from the inside to the outside and vice versa. Depending on how the medium is in the cell, it can maintain its turgor pressure. So there are different types of medium that apply to both cells and osmosis processes. The first would be the hypertonic one that occurs when the medium has a concentration of solute and therefore, is the solution to which the solvent goes; the second

would be the isotonic medium that occurs when the concentration of solute is the same in both parts of the membrane (or inside and outside the cell) so that the solvent flows in both directions; and finally, the hypotonic method, which is one that has a lower concentration than that of our solution (or inside the cell). An illustrative example applied to cells, particularly red blood cells, is shown in Figure 3.

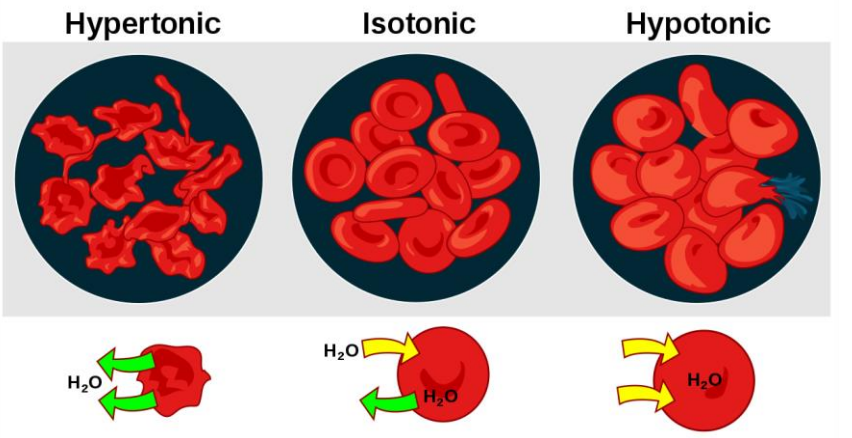

Figure 3. Effect of the osmosis process on red blood cells, extrapolated to any type of cell. *(15/03/2020, Wikipedia.org, Wikimedia Common Public Domain).*

There have been different explanations to try to describe the osmosis process that over time have been shown to be false, so that it is finally understood through the concept of chemical potential. So, on the side where pure water (or any other pure solvent) is where there is a greater chemical potential, so water (or another solvent) behaves differently if it is pure or in solution with some solute. By means of the virial theorem it is shown how the attraction between different molecules, water and solute (or in general solvent and solute), reduces the pressure so that the pressure exerted by the molecules of water (or other solvent) on each other is less than the pressure exerted on each other when it is pure water (or pure solvent). Therefore, pure water (or another pure solvent) passes through the membrane towards the solution with solute until the pressure reaches equilibrium.

It is important to correctly describe what osmotic pressure (π) is. Today it is defined as the minimum pressure that must be exerted on a solution to prevent the internal flow of its pure solvent through the semipermeable membrane. Another way to define the osmotic pressure would be the measure of the tendency of a solution to take pure solvent by osmosis.

1.2.1. Classification of osmosis processes

Osmosis has previously been defined as the transport of water from a region with a higher chemical potential to a region with a lower chemical potential, the two regions being separated by a semipermeable membrane. The driving force is the osmotic pressure (π) that depends directly on the concentration of solutes in the solution, so that the semipermeable membrane passes the solvent through it but retains or rejects the solute.

Thus, the forward osmosis (FO) uses the differential osmotic pressure (Δπ) through the membrane while reverse osmosis (RO) uses hydraulic pressure as the driving force. The forward osmosis process result in the feed solution is concentrated, while the draw solution is diluted. In addition, there is a third osmotic process called pressure-retarded osmosis (PRO), which is an intermediate between FO and RO. In PRO, hydraulic pressure is applied in the opposite direction to the osmotic pressure gradient, that is, in the same direction as in RO. While the net solvent flow is maintained in the direction of the extraction solution, as it happens in the FO. To simplify it in scientific notation: ΔP in FO is zero; in the RO it is always true that $\Delta P > \Delta\pi$; while in PRO $\Delta\pi > \Delta P$, thus giving an intermediate flow between FO and RO.

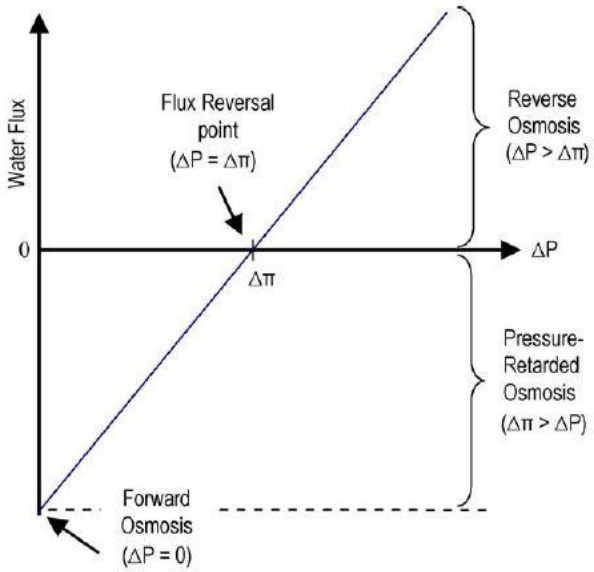

Figure 4. Direction and magnitude of water flux depending on the type of osmosis. *(Tzahi Y. Cath et al, 2006).*

Therefore, we can conclude that there are three different types of osmosis processes depending on what is the driving force:

- Forward osmosis (FO): the driving force is the gradient of the osmotic pressure ($\Delta\pi$) between the two solutions, feed and draw, separated by the semipermeable membrane. The feed solution has a lower osmotic pressure than the draw solution, therefore this will cause that from the feed solution there will be pure solvent that will go to the draw solution, thus giving rise to the concentration of the feed solution and to the dilution of the draw solution. The draw solution can then be recovered by other separation processes such as distillation, low temperature evaporation or even the reverse process, reverse osmosis.
- Reverse Osmosis (RO): in this type of osmosis the driving force is not the osmotic pressure gradient ($\Delta\pi$), it is the hydraulic pressure gradient (ΔP). So that it overcomes the osmotic pressure and causes the solvent to go in the opposite direction than in forward osmosis. Therefore, unlike FO, in this one requires the

energy expenditure for the use of pumps to exert the necessary pressure to overcome the osmotic pressure.

- Pressure-Retarded Osmosis (PRO): This type of osmosis is an intermediate of the previous two since it uses the difference between the osmotic pressure and the hydraulic pressure. The driving force is the difference between the osmotic pressure and the hydraulic pressure, the former being greater than the latter. Therefore, it has an intermediate flow and it is a process that is used for the production of energy, called blue energy.

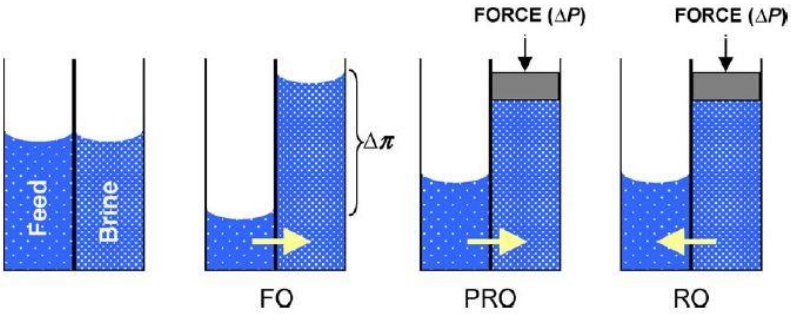

Figure 5. Flow direction in the different osmosis processes. *(Tzahi Y. Cath et al, 2006).*

1.2.2. Draw solutions

Is called draw solution to the concentrated solution which is on the permeate side of the membrane; this solution is the source of the driving force FO process. Depending on which publications or books are consulted, the draw solution receives different names besides this one, such as osmotic agent, driving motor, osmotic media, conduction solution, sample solution or brine. When selecting a draw solution, the main criterion is usually that it has a high osmotic pressure and considerably higher than that of the feeding solution. Even so, depending on what is being treated, it is possible to take draw solutions with moderate osmotic pressures, always higher than that of the feed solution, due to toxicity or difficulty of recovery at the end of the process, among other causes.

Currently there are programs that allow you to predict and calculate the osmotic pressure of a certain draw solution, one of those programs is the OLI Stream Analyzer 2.0 (OLI Systems

Inc., Morris Plains, NJ). This program is a software that uses thermodynamic models based on experimental data in order to predict the properties of multiple solutions in a wide range of concentrations and temperatures.

As previously stated, one of the criteria in FO applications is that the draw solution recovery process, that is, its reconcentration, does not have a high cost and therefore is relatively simple. It is very common to use NaCl solutions since they have a high solubility and, in addition, it is easy to reconcentrate it by RO without high costs or risks of fouling. It is important to take into account the diffusion of the solute from the draw solution through the semipermeable membrane; therefore in some cases multivalent ion solutions are better, such as when a high rejection is desired.

Accordingly, as can be understood from the above, the choice of the solute in the draw solution is very important and has a great impact on both the performance and the viability of the process, so its choice is as important as the chosen properties of the FO membrane. Theoretically, the ideal draw solute should be stable, inexpensive, highly soluble, obviously non-toxic, and have a molecular size large enough to prevent or limit the flow of draw solute through the membrane but at the same time small enough to be highly mobile and mitigate internal concentration polarization (ICP). In addition, having easy recovery at the end of the FO process.

Due to the high difficulty in meeting these requirements, some of them even contradictory, the search for this ideal extraction solute has been called: the hunt for the Holy Grail of osmosis, since finding it would lead to the maximum industrial explosion of FO, RO and PRO making them the most profitable processes such as separation process and clean energy production process.

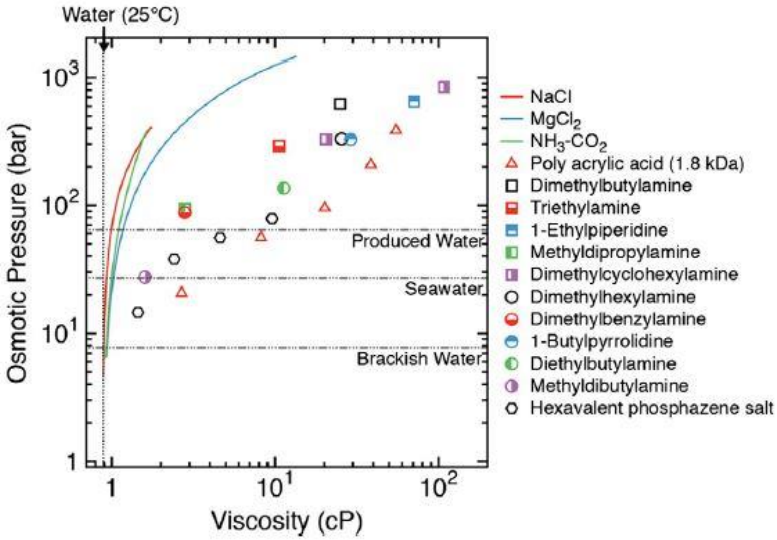

Figure 6. Relationship between osmotic pressure and viscosity for different draw solutions**.** *(Devin L. Shaffer et al, 2014).*

1.2.3. Applications of osmosis processes

As mentioned briefly in the previous sections, various applications for osmosis are being studied, specifically for FO that is less used in industry than RO. Today commercial applications, still quite limited, are emerging in the field of water purification, such as extraction bags, and in the pharmaceutical industry, such as osmotic pumps. This section will speak in general since many of the applications contain FO, RO and / or PRO at the same time. In addition, it will focus on energy production because today part of humanity, especially the West, intends to reduce pollution on our planet and osmosis has much to contribute in this regard. Today, there are various plants for the clean production of energy through osmosis processes in various parts of the world.

It is important to know how it is possible that energy can be obtained through osmosis. For this, the concept of osmotic power must be briefly explained. Osmotic power, which is also known as salinity gradient power or directly blue energy, is energy that can be obtained by the difference in salinity between seawater and river water. So the waste obtained from the process is only brackish water, that is, water with an intermediate salinity between sea or ocean water

and river or lake water. As previously mentioned, it is a process that does not emit greenhouse gases or pollute it in any other way, which is why it is considered renewable energy and has great potential in large river regions.

Two membrane technologies are currently being used and developed that are complementary to Pressure Delayed Osmosis (PRO) and Reverse Electrodialysis (RED). The development of obtaining energy through PRO processes came from Professor Sidney Loeb in 1973 who used the bases theorized by Professor Pattle in the 1950s, when he explored the idea that there was an untapped energy source when a river mixes with the sea in terms of loss of osmotic pressure.

As already mentioned above, one of the most important current challenges that humanity must face is guaranteeing the supply of electricity and drinking water to a growing population, trying not to harm the planet. Regarding energy production, an osmotic power plant uses at least two tanks, one for fresh water and one for salt water, divided by a semi-permeable membrane. As in all osmosis processes, the water in the fresh water tank will pass through the nanopores, while the salts will be retained, so as to increase the volume of water in the saltwater tank. This increase in volume implies an increase in the pressure inside the tank that can be exploited by a turbine and in this way, so conceptually simple, clean energy can be obtained.

It is estimated that a 1 m^2 membrane could produce the energy necessary to operate $5 \cdot 10^4$ light bulbs. Blue energy could be able to cover up to 40% of the world's electricity demand, another example, to imagine its potential, is that a power plant the size of a soccer field could produce enough energy for $3 \cdot 10^4$ homes.

A 2012 Yale University study estimated that 0.75 kWh, or 2.7 MJ, was dissipating when a cubic meter of fresh river water was mixed with a cubic meter of seawater. The International Energy Agency (IEA) estimated that the global potential of the salinity gradient could reach $2 \cdot 10^3$ TWh / year. Furthermore, according to the European Center for Excellence in Sustainable Water Technology, blue energy could reach 2 TW of energy, a value close to the current demand for electricity.

Some of the osmotic plants that are in operation will be briefly mentioned. Australia is one of the countries that has bet the most on osmosis, especially for the production of drinking water, since Oceania, especially Australia, is the driest habitable continent. After the enormous drought

that the country suffered between 1997 and 2009, the governments decided to build desalination plants that make the water drinkable using reverse osmosis technology. The first large-scale plant was the Kwinana plant in Perth, they currently have more than 30 nationwide, many of these use wave or wind farms in addition to running on solar energy. In Norway the state company Stratkraft has created osmosis plants for energy production.

It can be observed the different numbers that the experts give, but they all lead to the same thing, the great potential that osmosis has and the promising future that it may have.

2. OBJECTIVES

This work or study aims to improve, through the modification of thin-film composite (TFC) membranes, the operation of the FO process. Thus, to achieve this objective, others must be achieved previously, such as the characterization of the different membranes used, that is, knowing their parameters. An attempt will also be made to experimentally determine the permeability of the membrane to both the solvent and the solute used, using various assumptions, since it is not possible, with the means available, to do it exactly. The effectiveness of the modifications applied to the membrane will be studied. Given the results obtained, the retention of ethanol by the TFC membranes used will be determined and the importance of the ECP factor in our system will be experimentally analyzed by applying different agitations and, therefore, less and greater turbulence.

3. MATHEMATICAL MODEL

Mass transport across the semipermeable membrane in osmosis processes is a thermodynamic process that can be described using flow equations. For the solvent flow we have:

$$J_W = A \cdot (\sigma \Delta\pi - \Delta P) \quad (1)$$

Where J_w is the flow of the solvent through the membrane, $\Delta\pi$ is the osmotic pressure difference between the two solutions, A is the permeability of the membrane to the solvent, σ is the reflection coefficient and finally ΔP is the hydraulic pressure difference between the two sites of the membrane.

The ideal equation that governs the flow of the solute depends on the concentration difference between the two solutions, the draw and feed solutions:

$$J_s = B \cdot (1 - \sigma) \cdot \Delta C \quad (2)$$

Where B is the permeability of the membrane to the solute "s".

Using Van't Hoff's law, osmotic pressure is described as a function of solute concentration:

$$\pi = jRTC \quad (3)$$

Where j is the speciation factor that depends on the type of solute you have, R is the gas constant, T is the temperature and C is the concentration.

In the case of non-ideal mixtures there are other non-linear approaches, although in these cases the experimental data sources and software are more reliable. The units of the variables of all the equations must be those of the International System.

3.1. **CONCENTRATION POLARIZATION IN THE OSMOSIS PROCESSES**

As mentioned above, one of the most important membrane problems is concentration polarization. In osmosis processes it can be seen how the difference in osmotic pressure ($\Delta\pi$) through the active layer is considerably less than the difference in bulk and this means that the solvent flow is less than expected so that the process efficiency is much lower than desired and this occurs due to various transport phenomena associated with the membrane.

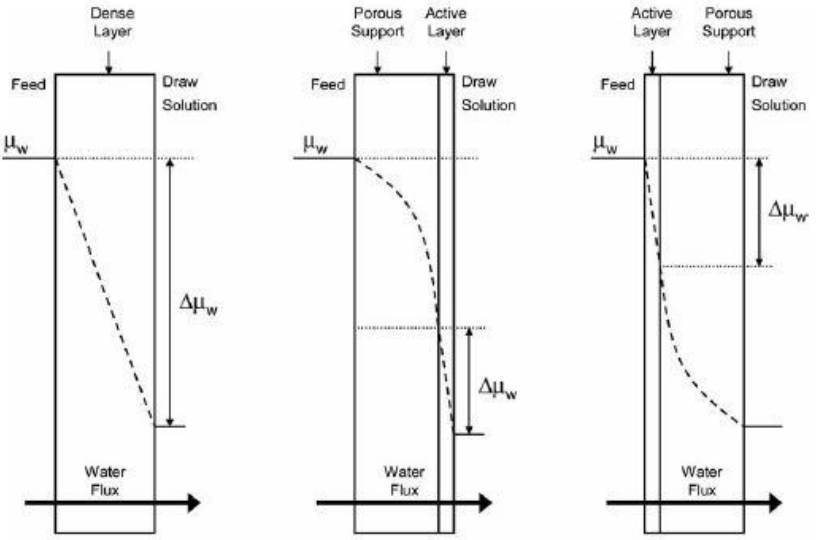

Figure 7. Driving force profiles (chemical potential, μ_w) and effect of CP. *(Tzahi Y. Cath et al, 2006).*

There are two types of concentration polarization that are caused by different factors:

Polarization of the external concentration (ECP): in the operation of the process, the flow that passes through the membrane is practically pure solvent, unlike the bulk solution that has its own concentration, so that this concentration difference it is the cause of a concentration gradient forming between the membrane walls and the bulk solution. On the feed solution side, the solute goes to the membrane but is rejected by it, so that its concentration increases. In contrast, on the draw solution side, the solvent that passes through the membrane dilutes the draw solution in the areas near the membrane. It can be deduced that this type of problem basically depends on the rheological conditions of the solution, so a high turbulence will allow a greater mixing of the solution, considerably reducing the ECP.

$$\frac{dc}{dt} = D\nabla^2 c - v\nabla c \tag{4}$$

In this equation it can be seen how a solution with a high convention term v∇c with a high turbulence will create a better homogenization of the concentration, that is, a lower concentration differential.

Furthermore, the ECP depends on the flow through the membrane, being important when the flows are high. The equation that models the diffusive and convective transport of the solute that occurs in the membrane in a stable state is this:

$$J_w = J_s - D\frac{\delta c}{\delta x} \tag{5}$$

Where D is the diffusivity of the solute in the solvent.

If we integrate equation 5 between each bulk solution and its membrane wall, the following equations are obtained:

$$c_{fa} = c_f \exp\left(\frac{J_w}{k_f}\right) + \frac{J_w}{J_s}(\exp\left(\frac{J_w}{k_f}\right) - 1 \tag{6}$$

$$c_{sd} = c_s + \exp\left(-\frac{J_w}{k_d}\right) + \frac{J_w}{J_s}(\exp\left(-\frac{J_w}{k_d}\right) - 1 \tag{7}$$

Where c_{fa} and c_{sd} are the concentrations in the walls of the membrane (f stands for feed solution and d for draw solution, k_f and k_d are the mass transfer coefficients in the feed and in the draw solution which depend on the Reynolds number (Re), and the Schmidt number (Sc), both depending on the hydrodynamics of the fluid.

Internal concentration polarization (ICP): in low flow osmosis processes, such as those of FO, this factor is more relevant than ECP. As its name indicates, this factor is proud inside the PSL, which causes gradients in the concentration of the solvent towards the active layer. Depending on the orientation of the membrane in the solution, the flow that passes through the active layer (DSL) can dilute or concentrate the solution within the PSL. This factor considerably reduces the effective osmotic pressure and depends solely on the geometry of the porous layer. So that by integrating equation 5 of the two sides of the PSL, the equation is obtained that indicates the internal concentration in contact with the active layer:

$$c_{as} = c_{sd}\exp(-\frac{J_w S}{D}) + \frac{J_w}{J_s}(\exp\left(-\frac{J_w S}{D}\right) - 1) \quad (8)$$

Where c_{as} is the concentration inside the membrane, between DSL and PSL, c_{sd} is the concentration in the external wall of PSL, D is the diffusivity of the solution in the support layer and S is a structural parameter of the support layer that can be calculated using the following equation:

$$S = \frac{\delta\tau}{\epsilon} \quad (9)$$

Where δ is the thickness of the support layer, τ is the tortuosity and ϵ is the porosity. These variables can be manipulated to minimize the value of S. The objective of many industries and researchers is to minimize this factor. One of the models to calculate the S is:

$$S = \frac{D}{J_w}(ln\frac{B+A\cdot\pi_{D,b}}{B+J_w+A\cdot\pi_{F,m}}) \quad (10)$$

Where D is the diffusivity of the solute, $\pi_{D,b}$is the osmotic pressure of the bulk draw solution and $\pi_{F,m}$ is the osmotic pressure of the feed solution at the membrane interface. The above parameters do not define the structure of the membrane and changes in them should not influence the structure of the support.

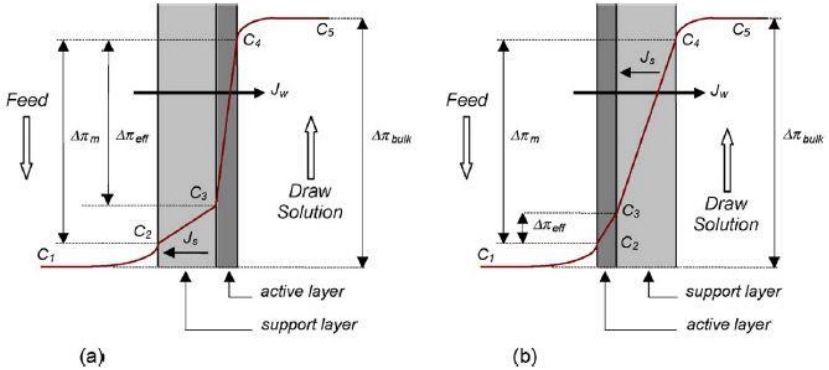

Figure 8. Concentratation polarization CP, (a) concentrative internal and (b) dilutive interal across a composite or asymetric membrane in FO. *(Tzahi Y. Cath et al, 2006).*

In this figure it can be seen how the driving force, which is the osmotic pressure difference (Δπ) is greater in configuration (a), where the active layer is in contact with the draw solution. In the case of this work, it has been considered that, although the process would be slower, use the second configuration (b) to thus protect the active layer of the membrane.

4. EXPERIMENTAL PROCEDURE

4.1. SOLUTIONS USED

The main objective of this study is to determine the permeability of the different membranes that will be put to work in forward osmosis processes. Different solutions have been used for this. It has worked with ethanol, pure water and glycerine (or glycerol) to create different solutions.

First of all we have the feed solution that consists of a solution of water and ethanol at 10% by mass. Ethanol is used because it is wanted to investigate if it is possible to reduce alcohol from hydroalcoholic drinks so that none of its organoleptic properties are lost. In addition, it is also sought to determine if the membranes used are capable of retaining or rejecting ethanol.

On the other side of the membrane, we have the draw solution consisting of a 40% by mass solution of water and glycerin. Although glycerin has a lower osmotic pressure than could be obtained with NaCl solutions, glycerin is used, because as we have said before, it can be used for food, so the small amount of NaCl that could pass to the other would vary the flavor and other substances are directly toxic, so glycerin has been considered more suitable.

4.2. EXPERIMENTAL CELLS

They are one of the most important elements of the laboratory instruments used. The experiments are carried out in these cells. They are used two by two, so that the compartments are separated by the semipermeable membrane. The cells have been specifically designed and assembled for these experiments. The cells consist of a rectangular space in which the membrane will be placed. So that between the two metal plates of the cells, there are two silicone gaskets and the membrane will be placed between the gaskets, thus avoiding any type of leakage.

As it has been said in the previous sections, the problem of concentration polarization is very important and to avoid it, it is necessary to generate turbulence in the system so that the concentration in the bulk solution is equal to or very similar to the concentration of the solution in the areas close to the membrane.

For this, a magnetic stirring system is used. So that the speed of rotation of the internal magnet can be adjusted manually, therefore also that of the agitator. Each cell has a square base of 10 cm per side, in each cell there is a scale that measures the height of the solution in cm, knowing the equivalence that each centimetre is equivalent to 100 mL. To compensate for the space of the membrane that is very thin, a piece of plastic is used that occupies the same volume as the free space left for the membrane. The dimensions of the membrane are 100 mL long by 50 cm high.

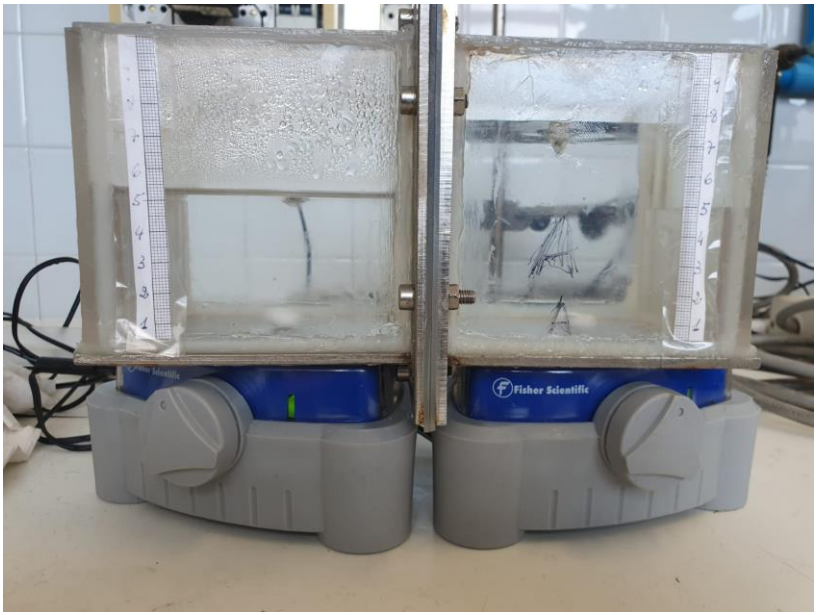

Figure 9. Experimental cells in operation.

Therefore, since we have the scale to measure the height of the solution and we can measure the time with a stopwatch, what we have done is measure the height every hour, in this way we can calculate the flow that passes through the membrane:

$$J_w = \frac{dV}{dt} \tag{11}$$

Therefore, since the function is a derivative, it will be calculated in such a way that the points of the linear regression of the experimental results will be made (Volume-time) or also fitting the points to a polynomial and taking the derivative.

4.3. **CONCENTRATION MEASURAMENT**

The objective of this work is to study and estimate the permeability of the different membranes used for each component, it is necessary to determine the final concentration at the end of each experiment. The initial concentration is known.

4.3.1. Ethanol concentration determination

As previously explained, at the end of each experiment the concentration of ethanol in the feed solution is measured, since it is easier than measuring it in the draw solution since there are 3 compounds in it: water, ethanol and glycerin; while in feed solution we have only two: water and ethanol.

In the laboratory there was no direct concentration meter and it could have been indirectly measured by electrical conductivity, but it was considered more appropriate to do it by means of density measurements, since this method has the adequate precision and is also easier since the densities of mixtures of ethanol and water are experimentally tabulated. Therefore, pycnometers, specifically 3, were used, by means of which the density of the feed solution was calculated after each experiment.

Before that, pycnometers must be calibrated. For this, pycnometers are weighed empty several times on an analytical scale that has a precision scale of 0.0001 g. The pycnometers filled with distilled water are then weighed, the water temperature is measured. With temperature we can know the density of the water at that T, so we can know the mass of water

inside. And in experiments, know the mass of water and ethanol, so its concentration is determined. Density values have been obtained from the Perry's Encyclopedia.

Table 1. Pycnometers calibration

Pycnometer	Dry mass [g]	Volume [mL]
A	17.2646 ± 0.0008	10.5288 ± 0.0012
B	17.2074 ± 0.0004	10..4489 ± 0.0035
C	18.0017 ± 0.0007	10.1795 ± 0.0024

Therefore, once the densities of the final solutions of the different experiments are obtained, they must be compared with the densities table in the Chapter "Densities of aqueous organic solutions" in the Perry's Encyclopedia. In the Perry's Encyclopedia there are not all the possible mixtures between water and ethanol, so the concentration cannot be determined directly, but rather a two-dimensional interpolation function, concentration and temperature, had to be created, whose coefficients have been found by means of a regression of least squares:

$$\rho(c,T) = A\,c + B\,T + C\,c^2 + D\,T^2 + E\,c\,T + F + Gc^3 + H\,T^3 + I\,c\,T^2 + J\,c^2T \quad (12)$$

Where c is the concentration of ethanol expressed in% by mass, T is the Temperature of the solution and ρ the density of the solution.

Once we have the table and the function, the coefficients of the polynomial are determined using the 'Solver' tool from 'Excel'.

Table 2. Interpolation coefficients.

A	B	C	D	E
$-2.0209 \cdot 10^{-3}$	$-3.5953 \cdot 10^{-4}$	$5.4212 \cdot 10^{-5}$	$1.5146 \cdot 10^{-5}$	$4.6705 \cdot 10^{-6}$

F	G	H	I	J
1.0023	$-8.7146 \cdot 10^{-7}$	$-3.6011 \cdot 10^{-7}$	$-1.0969 \cdot 10^{-7}$	$-6.0792 \cdot 10^{-7}$

The polynomial and the coefficients are true assuming that at the end of each experiment there is only water and ethanol in the feed solution and that if glycerin has passed through the membrane from the draw solution, it is insignificant. Later this assumption will be verified as true. Therefore, with this polynomial and obtaining the T and density results from the experiments, the concentration of each of the solutions can be known.

Due to the fact that the process was going to be done repetitively, a macro has been programmed in Excel to speed up the calculation of concentrations. The error that the results of the polynomial have with respect to the values of the Perry's Encyclopedia has been calculated. The absolute average error of this method is 0.0037 and the maximum error found has been 0.092 for the 104 tabulated points.

The error propagation has also been calculated in this method. For this, it has been considered that the absolute error when estimating the density is ± 0.0002 g / mL, while the thermometer has an error of ± 0.1 ºC, so it has been estimated that 95% of the errors are below ± 0.18% by mass of ethanol, that is, the absolute error for each result is ± 18% with a degree of confidence of 95%.

4.3.2. Gycerin concentration determination

The measurement of the concentration of glycerin is carried out on the feed solution side since we are interested in the passage of glycerin from the draw solution through the membrane; in this aspect the draw solution is not important, only the draw solution is important for the subsequent recovery of glycerin.

For the determination of the concentration a heat treatment is applied. This treatment can be carried out thanks to the great difference in boiling temperature. Ethanol has a boiling point at 78ºC, water at 100ºC and glycerin at 290ºC, so you can apply enough temperature to evaporate ethanol and water without losing glycerin (or that the loss is insignificant).

Thus, samples are taken in vials of the feed solution at the end of each experiment and placed at 110ºC in an oven for 24 hours. All vials are the same or very similar, are heavy before and after use, and all have the same fluid surface area that determines the amount of glycerin that can be evaporated.

In order to interpret the results, the method must be calibrated. In this case, different samples of different known concentrations of glycerin have been prepared and subjected to the same conditions, at 110ºC. So the concentration obtained by the method is compared with the concentration that was actually present.

Table 3. Results of the calibration of the measurements of glycerol. 0.05% glycerin is lost.

Real Glycerol concentration (%m)	**Measured remaining glycerol (%m)**
0	-0.0024
0.2396	0.1846
0.5007	0.4509
0.7710	0.7152
0.9535	0.9071

With calibration you can do a linear regression:

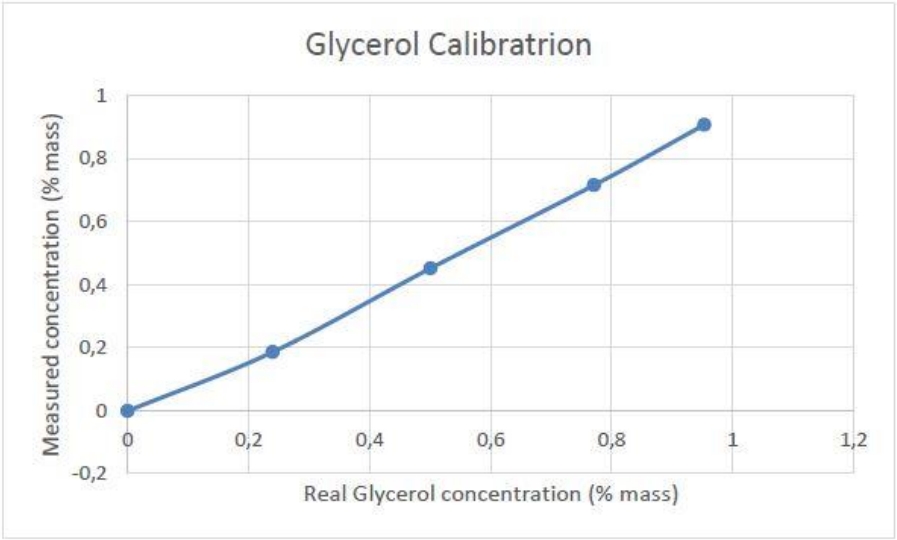

Figure 10. Linear regression of the calibration of the glycerol measurement.

From this regression we obtain the following equation:

$$c_m = c_{real} - 0.0236 \tag{13}$$

Where c_m is the concentration measured with the method and c_{real} is the concentration that the sample actually has. The value of R2 is 0.9979.

4.4. **MEMBRANE THICKNESS AND POROSITY MEASUREMENT**

As mentioned above, it is important to measure the thickness and porosity of the membranes in order to calculate the permeability. In this work a micrometer has been used to measure the thickness. The micrometer is mounted on a flat marble surface. Accuracy is one micron. The process consists of making a total of 10 measurements in different sides of the membrane and taking the average.

In the case of the porosity of the membranes, a rectangular portion is cut out and its area is calculated by measuring the sides (width and length). Subsequently, with the thickness that had previously been calculated, the volume can be estimated. So the porosity is calculated as follows:

$$\epsilon = 1 - \frac{m}{v\,\rho} \tag{14}$$

Where m is the mass of the membrane, V is the volume of the membrane and ρ the density of the material. The thin-film composite (TFC) membranes used are made of polysulfone, while the amount of polyamide is considered negligible. The density used of the polyamide is 1,245 g/cm^3.

4.5. **OBSERVATION AND STUDY OF THE SURFACE OF THE MEMBRANES**

In order to carry out an adequate study of the TFC membranes, it has been considered necessary to observe them by light microscopy. The reason is that the membranes have been modified by different methods and it was necessary to know if the membrane had broken, the pores had become blocked or if the membrane was still functional. The light microscope can reach magnifications of x1000, but for this study they have been used in the range of x100 to x200.

4.6. **AGITATION SPEEDS ESTIMATION**

As stated in the previous sections, it is necessary to shake the solutions to minimize concentration polarization. Therefore, each cell has a magnetic stirrer. All stirrers are the same size but in some experiments they operate at different speeds with the intention of being able to estimate the effect of stirring on the speed of the process.

To estimate the speed of the stirrer, the operation of the stirrer at different speeds was recorded in slow motion with a stopwatch. In this way, it is easy to calculate the time it takes for the agitator to complete one turn on itself. Keep in mind that the draw solution, having 40% by mass of glycerin, is much thicker than the feed solution, so the speeds in the draw solution will be lower.

Table 4. Results of the RPM on each side of the solutions

Cell and mode	rpm
Draw solution fast mode	1142
Draw solution slow mode	176
Feed solution slow mode	281
Feed solution fast mode	1333

5. RESULTS AND DISCUSSION

In this study, experiments have been carried out with 5 different membranes. One of these membranes is a commercial Forward Osmosis membrane which in this study has been named Membrane F. The other four membranes are from Reverse Osmosis, which have been named A, B, D, and E membranes. These names are used by confidentiality reasons. Although they are Reverse Osmosis membranes, they will be used in FO processes, so a treatment has been applied that consists of removing part of the porous structure that consists of cellulose, which gives it extra resistance to withstand pressure. Membrane A has also undergone further modifications because it showed more interesting results.

Since membrane F was the fastest, it was the membrane with which 4 extra experiments were carried out to determine the effect on the performance of the process of the stirring speed. The rest of the membranes have operated at all times at the maximum stirring speeds to, as previously stated, minimize the effect of ECP.

During the experiments, at the beginning of the experiments, it was observed how the performance of the membranes improved if they were previously wet. The explanation for these events is that if they are previously moistened, the air that may have trapped between the pores is eliminated since the water occupies those spaces, so that the diffusion process between the pores is greater.

Therefore, different experiments have been carried out under different conditions both of the stirring speed and of whether the membrane has previously been in water for a few days to facilitate diffusion. So below is a summary table of the previously exposed conditions.

Table 5. Experimental conditions

Experiment	Membrane used	Conditions
1	B	Dry membrane, 1142 rpm of agitation in the draw side and 1333 rpm of agitation in the feed side.
2	A	Dry membrane, 1142 rpm of agitation in the draw side and 1333 rpm of agitation in the feed side.
3	E	Dry membrane, 1142 rpm of agitation in the draw side and 1333 rpm of agitation in the feed side.
4	F	Dry membrane, 1142 rpm of agitation in the draw side and 1333 rpm of agitation in the feed side.
5	D	Dry membrane, 1142 rpm of agitation in the draw side and 1333 rpm of agitation in the feed side.
6	F	Wet membrane, 176 rpm of agitation in the draw side and 281 rpm of agitation in the feed side.
7	F	Wet membrane, 176 rpm of agitation in the draw side and 1333 rpm of agitation in the feed side.
8	B	Wet membrane, 1142 rpm of agitation in the draw side and 1333 rpm of agitation in the feed side.
9	A	Wet membrane, 1142 rpm of agitation in the draw side and 1333 rpm of agitation in the feed side.

10	E	Wet membrane, 1142 rpm of agitation in the draw side and 1333 rpm of agitation in the feed side.
11	D	Wet membrane, 1142 rpm of agitation in the draw side and 1333 rpm of agitation in the feed side.
12	F	Wet membrane, 1142 rpm of agitation in the draw side and 281 rpm of agitation in the feed side.
13	A	Further modified membrane in dry conditions, 1142 rpm of agitation in the draw side and 1333 rpm of agitation in the feed side.
14	A	Further modified membrane in wet conditions, 1142 rpm of agitation in the draw side and 1333 rpm of agitation in the feed side.
15	F	Wet membrane, 1142 rpm of agitation in the draw side and 1333 rpm of agitation in the feed side.

5.1. **THICKNESS AND POROSITY RESULTS**

As previously mentioned, by means of equation 9 the value of S can be estimated with the calculated values of porosity and thickness. In the bibliography studied on the tortuosity investigations of the material it is between 1.1 and 1.6, as indicated by the researcher S. Manickam. Therefore, it has been decided to take the average value to make the estimates, so in this work the tortuosity will be 1.35.

Table 6. Results of Thickness, Porosity and Parameter S.

	Membrane A	Membrane B	Membrane D	Membrane E	Membrane F	Modifed Membrane A
Average Thickness [mm]	0.040	0.041	0.044	0.048	0.084	0.030
Porosity	0.561	0.593	0.562	0.615	0.530	0.561
Parameter S [μm]	95.41	93.32	105.05	105.84	213.96	105.16

As explained above, concentration polarization, both internal (ICP) and external (ECP) is one of the biggest problems with osmosis. The value of the parameter S is extremely important since it directly influences the ICP of the membranes. The lower the value of parameter S, the greater performance the membrane has, since the driving force is greater.

As can be seen, it is strange how membrane F, which is the commercial FO membrane, has the highest value of parameter S, since it is supposed to be the best membrane of all. What happens in this case is that the porosity and tortuosity values are estimated and can vary quite a bit. Especially in the case of membrane F, which had an internal network of a material that could not be determined, so that the density and the other variables may be different from those previously assumed.

Observing the results, it can be affirmed that the modification that was made to membrane A has not been adequate, since its parameter S has increased, which could cause an increase in the ICP phenomenon.

5.2. **FLUX RESULTS**

The method that has been decided to calculate the water flow through the membrane has been to perform a linear regression of the volume over time and taking the slope of the line. The problem is that with this method it is assumed that the flow is constant throughout the experiment, and this cannot be true since the concentration of the draw solution is diluting, resulting in a decrease in the driving force. Still, over the duration of each experiment, this variation can be very small. This is why the results fit the regression and most of the experimental results have an R^2 greater than 99%.

The equation to estimate the flow is as follows:

$$J_w = \frac{m}{S} \tag{15}$$

Where m is the slope of the concentration versus time and S is the section of the membrane, which in all cases is 0.005m^2.

Assuming that the feed solution flows through the membranes contain water and ethanol, the following is obtained:

Table 7. Membrane fluxes obtained from liner regression.

Experiment	Membrane used	Jw (LMH)
1	B	0.380
2	A	0.671
3	E	0.568
4	F	1.87
5	D	0.466
6	F	2.11
7	F	2.24
8	B	0.973
9	A	1.09

10	E	0.928
11	D	0.848
12	F	2.17
13	A	1.29
14	A	0.862
15	F	2.57

It can be seen how the 'wet membrane' factor is very important. Leaving the membrane in water for several days implies a considerable improvement in performance. Proof of this is that experiments 1 and 8, 2 and 9, 3 and 10, 4 and 15 and finally 5 and 11 have been carried out in exactly the same conditions with the only difference that some are with 'dry membrane' and others with a 'wet membrane'.

It can also be seen that the increase in flow ranges between 38% more and 156% in the case of membrane B. The only membrane that does not improve is the modified membrane A, which, as previously mentioned, the modification caused an increase in the parameter S and therefore of the ICP, in addition to which damage to its structure could have been generated, thus worsening its performance.

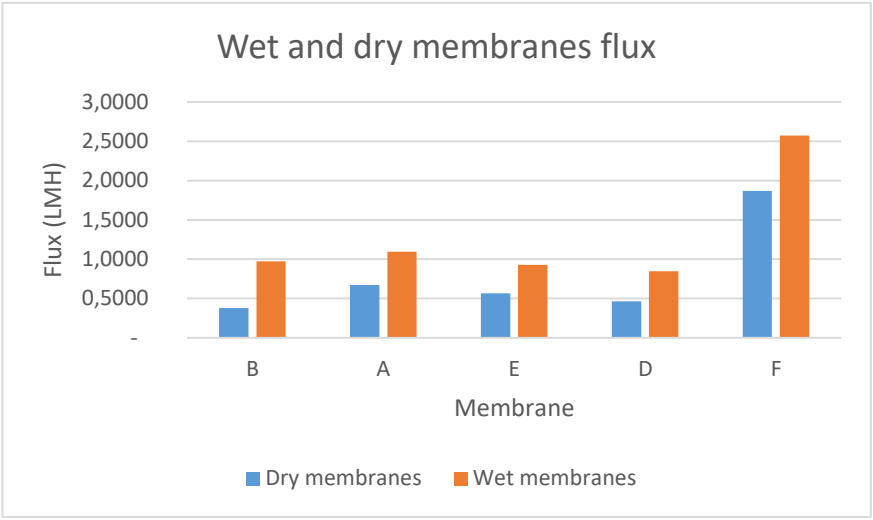

Figure 11. Comparison of fluxes results.

From the results obtained, it can be deduced that ECP has not been a relevant problem. Agitation is a factor to consider but it has been proven that the performance of the membranes increases slightly when agitation is optimal. It could be deduced that for such low solution flows the effect of the ECP is low, it should be taken into account, but it is not decisive.

With these results it can be affirmed that all the membranes seem to improve with respect to the membranes in unmodified conditions. However, no membrane manages to achieve performance or flow of commercial FO membrane, the membrane F. is most interesting is the membrane A which reaches 42.5% of the performance of the membrane F.

5.3. **CONCENTRATIONS OF ETHANOL AND GLYCERIN**

To carry out experiments, initial solutions of ethanol and glycerin were made for several experiments, that is, many of them have the same initial conditions. The initial concentration of glycerin in the feed solution is always 0%, the same as the initial concentration of ethanol in the draw solution is 0%. The following table shows the initial and final conditions:

Table 8. Concentration results.

Experiment	**Membrane used**	**Initial ethanol concentration (% mass)**	**Final ethanol concentration (% mass)**	**Final glycerol concentration (feed solution) (% mass)**
1	B	10.1	8.28	0.637
2	A	10.1	9.04	0.290
3	E	10.1	7.67	0.300
4	F	10.1	8.95	0.788
5	D	10.0	7.85	0.236
6	F	10.0	9.36	0.667
7	F	10.0	9.66	0.513

8	B	10.0	9.49	0.419
9	A	10.0	10.2	0.327
10	E	10.0	8.46	0.466
11	D	10.0	8.52	0.357
12	F	10.0	9.88	0.477
13	A	10.0	9.11	0.304
14	A	9.95	8.72	0.731
15	F	9.95	9.35	0.539

As can be seen in Table 8, the results of the experiments show a considerable drop in the final concentration of ethanol with respect to the initial one. Initially, the first 5 experiments, it was thought that this could be due to the fact that samples were taken during the experimental process of the cells, and when opening them, some of the ethanol could be lost. For this reason, it was decided to take the samples of ethanol concentration only at the end of each experiment, thus ensuring tightness of the cells, avoiding any type of leakage.

Despite this change in methodology, the difference persisted, so the hypothesis of loss of ethanol through evaporation when opening the cells was considered erroneous. Therefore, it was thought that perhaps the missing ethanol could be in the internal atmosphere of the cell, so that before taking samples, the cells were manually shaken to achieve redissolution of the ethanol. It has been estimated that the ethanol that the ethanol that could have evaporated supposes only 0.5 g, that this has an effect of 0.1% of the final concentration of ethanol, therefore this cannot explain this loss of ethanol either.

Therefore, the results are surprising since the ethanol molecule is considerably larger than that of water and therefore it should have difficulties to cross the membrane. This happens on all membranes except wet A membrane.

The rejection of a membrane is a parameter that depends on both the membrane and the solutes used and it is defined as follows:

$$r = \frac{c_f - c_D}{c_f} \cdot 100 \quad (16)$$

Where c_f is the concentration of feed solution, c_D is the concentration of draw solution. The rejection towards certain solvents is one of the parameters that define the membranes. In this work, the rejection of glycerin largely depends on the duration of the experiment, since the mechanism it uses to cross the membrane is diffusion.

The results obtained are consistent since they follow what is indicated by the specifications of the different membranes. The rejection of the membranes to NaCl is: A> B> D> E, with membrane F being between membranes A, B and D. Therefore, it is true that membrane A has a higher rejection.

On the other hand, it can be seen how the results of the glycerin concentrations do not meet the rejection assumption for this compound. And this is because the experiments have different durations and the diffusion of glycerin mainly depends on time. Therefore, a better measure is the flow of glycerin that passes through the membrane. And to solve this it is necessary to make a matter balance of glycerin in the feed solution cell:

$$\frac{d(Vc_g)}{dt} = SJ_s \quad (17)$$

Where V is the volume within the feed solution cell and can be estimated as follows:

$$V = V_0 - J_W t \quad (18)$$

Where c_g is the concentration of glycerin, S is the section of the membrane (0.005m^2), J is the flow of the solvent (in this case the glycerin) and Vo is the initial volume of the cell. If we integrate equation 17 in time and knowing that the volume is governed by equation 18, also considering that the initial concentration of glycerin: c_g (t = 0) = 0, we obtain this flow equation:

$$J_s = \frac{(J_W S t) c_g}{S\, t} \quad (19)$$

The variable J_s is expressed with the LMH units, the concentration in this case in % by volume and the product J_w S t can be expressed as V_f, final volume of the solution.

Applying everything explained above, the following results are obtained:

Table 9. Solute flux through the membrane and glycerin rejection.

Experiment	Membrane used	J_s (LMH)	Rejection to glycerin (%)
1	B	0.0043	98.57
2	A	0.0032	99.35
3	E	0.0036	99.33
4	F	0.018	98.23
5	D	0.0029	99.47
6	F	0.021	98.50
7	F	0.019	98.85
8	B	0.0062	99.06
9	A	0.0054	99.27
10	E	0.0069	98.95
11	D	0.0053	99.20
12	F	0.016	98.93
13	A	0.0096	99.32
14	A	0.012	98.36
15	F	0.015	98.79

The results presented in the previous table show how the rejection of the membranes to glycerin does not follow the same sequence as with the rejection of ethanol and salt. In this case the sequence is: D≈A> B≈E> F.

It can also be seen how the modified membrane A allows both ethanol and glycerin to pass through more easily, this may be because the modification may have caused damage to the active layer of the membrane.

It is also proven that the higher the stirring speed in both the feed solution and the draw solution it increases, and it is even more noticeable when the two cells are running at maximum speed.

5.4. **MEMBRANE PERMEABILITY**

In this study, it was decided to use two methods to calculate the permeability of the membrane and then they will be compared with each other.

Using the first method, this is based on the experimental results of porosity, thickness and equation 9. Instead, with the second method, parameters A and B can be found by solving equation 10.

We have chosen to neglect the influence of ethanol on itself to estimate the osmotic pressure since the reflection coefficient of ethanol in these membranes and in equation 3 we will assume that j is 1 since glycerin does not dissociate in ions. Keep in mind that the glycerin concentration decreases with time due to the dilution of the draw solution, therefore an average value between the initial and final pressure will be used.

As the agitation is very high, both the ECP and equations 6 and 7 will be considered negligible. In contrast, the ICP described in equation 8 will be taken into account with a diffusivity of $0.72 \cdot 10^{-5}$ cm^2 /s.

Table 10. Permeabilities to feed solution and glycerin of the membranes by method 1.

Experiment	Membrane used	A σ [LMH/atm]	B (1- σ) [LMH]
1	B	$4.49 \cdot 10^{-3}$	$1.56 \cdot 10^{-4}$
2	A	$8.06 \cdot 10^{-3}$	$1.15 \cdot 10^{-4}$
3	E	$6.56 \cdot 10^{-3}$	$1.27 \cdot 10^{-4}$
4	F	$2.65 \cdot 10^{-2}$	$7.77 \cdot 10^{-4}$
5	D	$5.20 \cdot 10^{-3}$	$9.78 \cdot 10^{-5}$
6	F	$2.97 \cdot 10^{-2}$	$9.04 \cdot 10^{-4}$
7	F	$3.12 \cdot 10^{-2}$	$8.08 \cdot 10^{-4}$
8	B	$1.19 \cdot 10^{-2}$	$2.32 \cdot 10^{-4}$
9	A	$1.32 \cdot 10^{-2}$	$1.97 \cdot 10^{-4}$
10	E	$1.12 \cdot 10^{-2}$	$2.54 \cdot 10^{-4}$
11	D	$1.01 \cdot 10^{-2}$	$1.91 \cdot 10^{-4}$
12	F	$3.03 \cdot 10^{-2}$	$7.00 \cdot 10^{-4}$
13	A	$1.49 \cdot 10^{-2}$	$3.38 \cdot 10^{-4}$
14	A	$1.01 \cdot 10^{-2}$	$4.34 \cdot 10^{-4}$
15	F	$3.99 \cdot 10^{-2}$	$7.03 \cdot 10^{-4}$

The permeability of the feed solution is A, since it contains water and ethanol. The estimation of the permeability to ethanol is made by means of the measured concentrations of ethanol. So you get:

$$J_{et} = \frac{V_0 c_0 - V_f c_f}{s\, t} \tag{20}$$

Where c_0 and c_f are the initial and final concentration of ethanol, while V_0 and V_f are the initial and final volumes of the cells.

The concentration of ethanol that passes through the membrane can be calculated by:

$$\frac{J_{et}}{J_{et}+J_{H_2O}} \cdot 100 \quad (21)$$

Table 11.Ethanol and water permeability and its effects on fluxes and concentration of feed solution.

Exp	Membrane used	J_{et} [LMH]	J_{H20} [LMH]	Ethanol permeability [LMH/atm]	Water permeability [LMH/atm]	Ethanol concentration [%vol]
1	B	0.068	0.312	$8.04 \cdot 10^{-3}$	$3.69 \cdot 10^{-3}$	17.9
2	A	0.111	0.560	$1.31 \cdot 10^{-3}$	$6.61 \cdot 10^{-3}$	16.5
3	E	0.125	0.443	$1.47 \cdot 10^{-3}$	$5.23 \cdot 10^{-3}$	22.0
4	F	0.297	1.57	$3.51 \cdot 10^{-3}$	$1.85 \cdot 10^{-2}$	15.9
5	D	0.112	0.353	$1.33 \cdot 10^{-3}$	$4.17 \cdot 10^{-3}$	24.1
6	F	0.307	1.80	$3.62 \cdot 10^{-3}$	$2.12 \cdot 10^{-2}$	14.6
7	F	0.324	1.91	$3.83 \cdot 10^{-3}$	$2.26 \cdot 10^{-2}$	14.5
8	B	0.131	0.842	$1.55 \cdot 10^{-3}$	$9.94 \cdot 10^{-3}$	13.5
9	A	0.145	0.948	$1.71 \cdot 10^{-3}$	$1.12 \cdot 10^{-2}$	13.2
10	E	0.151	0.777	$1.78 \cdot 10^{-3}$	$9.17 \cdot 10^{-3}$	16.3
11	D	0.140	0.708	$1.65 \cdot 10^{-3}$	$8.36 \cdot 10^{-3}$	16.5
12	F	0.280	1.89	$3.30 \cdot 10^{-3}$	$2.23 \cdot 10^{-2}$	12.8
13	A	0.161	1.08	$1.90 \cdot 10^{-3}$	$1.27 \cdot 10^{-2}$	12.9
14	A	0.149	0.713	$1.76 \cdot 10^{-3}$	$8.42 \cdot 10^{-3}$	17.3
15	F	0.331	2.24	$3.91 \cdot 10^{-3}$	$2.65 \cdot 10^{-2}$	12.9

In the previous table it can be seen how the permeability of the membrane to ethanol is high in these membranes, this indicates that they do not easily reject ethanol, quite the contrary; the solution that passes through the membrane has a higher concentration than original concentration of the feed solution.

The results indicate that those with the best retention of ethanol are A and F, an expected fact since they were the membranes with the highest rejection. These two membranes could be used to concentrate ethanol solutions above 13% by volume.

In contrast, membranes E and D are the most dilute, so they could be used to dilute concentrations of less than 16-23% by volume of ethanol.

Now we will proceed to use the second method, so that we can compare the parameters S and permeabilities obtained and see how far the approximation is:

Table 12. Permeabilities to feed solution and glycerin of the membranes obtained by method 2.

Experiment	Membrane used	Aσ[LMH / atm]	B (1- σ) [LMH]	S [m]
1	B	$4.43 \cdot 10^{-3}$	$1.56 \cdot 10^{-4}$	$1.37 \cdot 10^{-6}$
2	A	$7.86 \cdot 10^{-3}$	$1.13 \cdot 10^{-4}$	$8.19 \cdot 10^{-7}$
3	E	$6.42 \cdot 10^{-3}$	$1.24 \cdot 10^{-4}$	$8.03 \cdot 10^{-7}$
4	F	$2.27 \cdot 10^{-2}$	$6.73 \cdot 10^{-4}$	$3.34 \cdot 10^{-7}$
5	D	$5.11 \cdot 10^{-3}$	$9.63 \cdot 10^{-5}$	$8.16 \cdot 10^{-7}$

6	F	$2.49 \cdot 10^{-2}$	$7.66 \cdot 10^{-4}$	$2.67 \cdot 10^{-7}$
7	F	$2.59 \cdot 10^{-2}$	$6.76 \cdot 10^{-4}$	$2.30 \cdot 10^{-7}$
8	B	$1.15 \cdot 10^{-2}$	$2.25 \cdot 10^{-4}$	$5.89 \cdot 10^{-7}$
9	A	$1.26 \cdot 10^{-2}$	$1.90 \cdot 10^{-4}$	$4.68 \cdot 10^{-7}$
10	E	$1.08 \cdot 10^{-2}$	$2.47 \cdot 10^{-4}$	$5.72 \cdot 10^{-7}$
11	D	$9.76 \cdot 10^{-3}$	$1.86 \cdot 10^{-4}$	$5.86 \cdot 10^{-7}$
12	F	$2.54 \cdot 10^{-2}$	$5.89 \cdot 10^{-4}$	$2.45 \cdot 10^{-7}$
13	A	$1.42 \cdot 10^{-2}$	$3.22 \cdot 10^{-4}$	$3.05 \cdot 10^{-7}$
14	A	$9.81 \cdot 10^{-3}$	$4.23 \cdot 10^{-4}$	$5.32 \cdot 10^{-7}$
15	F	$3.23 \cdot 10^{-2}$	$5.72 \cdot 10^{-4}$	$2.77 \cdot 10^{-7}$

From the results of the previous table, it can be seen how the values estimated by equation 9 are greater than those estimated by equation 10. This is because when using equation 10, the ICP is less taken into account. Giving an estimate of the greater driving force that end up being lower values for A and B. It can be affirmed that equation 10 serves to estimate the values of S, if there were no other way, since S does not seem to have an impact on the parameters A and B.

5.5. **MASS TRANSFER COEFFICIENTS**

In this section of the work, the mass transfer coefficients that have been omitted in the other sections will be taken into account. Experiments performed show that for low stirring speeds, the flow through the membrane and the concentrations of the solutes can vary substantially compared to high stirring speeds.

To estimate these coefficients, it will be assumed that in the four experiments carried out with membrane F, at different stirring speeds, they have the same parameters A, B and S. Therefore, with the same conditions except for ECP. With equations 6 and 7 you can model the ECP and with 8 the ICP, experimentally having S.

The average values of A and B obtained with the first method can be used as an approximation. It has not been possible to obtain the same values of the coefficients for a stirring value, therefore, a solution has not been found for all the experiments. The cause of this may be that the stirring speed varies over time as the volumes vary. Values that are not greater than 10^6 have been recovered using the 'Solver' tool in Excel, an excessively large value since the ECP is negligible after 10.

Table 13. Mass transfer coefficients

		Draw solution speed			
		176 rpm		1142 rpm	
		K_f [LMH] Feed Sol.	K_f [LMH] Draw Sol.	K_f [LMH] Feed Sol.	K_f [LMH] Draw Sol.
Feed solution speed	281 rpm	0.0507	0.00725	0.000633	10^6
	1333 rpm	10^6	0.00928	10^6	10^6

the values obtained are the maximum imposed by the iteration. Instead, as previously predicted, at very slow speeds ECP becomes an important factor. In the case of the feed solution for the same agitation value, it gives very different coefficients, on the other hand, in the draw solution. Therefore, the viscosity influences, being very low in the feed solution which may have caused significant variations in stirring speed.

6. CONCLUSIONS

- The membranes used in this study have yielded interesting and therefore promising results in the Forward Osmosis process.
- The Membrane F, which is the commercial one from Forward Osmosis, has a higher flow of water and ethanol than the rest of the membranes. Therefore, in this aspect, it is more efficient.
- The Membrane F has less rejection of glycerin than the rest of the membranes. Therefore, in this aspect, it is less efficient.
- In the light microscope it was observed that the membrane F had a complex structure, which affected the calculations of density, porosity and tortuosity.
- It is observed how the ICP is the factor of control of the flow of alcohol and water. Flow is related to thickness, regardless of rejection.
- The effect of ECP on flow is less than that of ICP. It depends on the hydrodynamics of the fluid near the membrane. Large changes in hydrodynamics near the membrane, without agitation or very high, can produce changes in the flow of water and alcohol through the membrane, approximately 20%.
- The membrane must be kept for at least three days in water before being put into operation, since a notable difference in the flows of water and alcohol has been demonstrated.

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ACRONYMS

$\in$: porosity (-)
τ: tortuosity of the pores (-)
A: Permeability of feed solution
B: Permeability of solute
D: solute diffusivity in water (m^2/s)
DSL: Dense selective layer (or active layer)
ECP: External concentration polarization
EDF: Effective driving force
FO: Forward Osmosis
ICP: Internal concentration polarization
J_{et} : Ethanol flux (LMH)
J_{H2O}: Water flux (LMH)
J_S : Solute (glycerin) flux (LMH)
J_w: Solvent flux (LMH)
K_f: mass transfer coefficient (LMH)
LMH: Liter per meter squared and hour (L m-2h-1)
PRO: Pressure retarded osmosis
PSL: Porous selective layer
RO: Reverse Osmosis
S: Structural parameter of the membrane
S: structural parameter of the support intervenes (m)
t: thickness of the support (m)
TFC: Thin-film composite
δ: Thickness of the laminar layer (m)