

Faculté des bioingénieurs

Cobalt-coordinated chitosan membranes to separate a dimethyl carbonate and methanol mixture by pervaporation

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ABSTRACT

Dimethyl carbonate, an eco-friendly organic component, has gained much attention in the chemical sector due to its wide range of applications. However, its separation from its precursor in its production process, methanol, can be challenging as it forms an azeotrope. Pervaporation offers an energy efficient solution for separating azeotropes and was used within this thesis with the aim to separate the dimethyl carbonate/methanol mixture using a chitosan-based membrane.

Chitosan is a biopolymer derived from biowaste that has shown to be effective in the separation of the aforementioned mixture. However, with growing interest in this field, it has been demonstrated that inserting inorganic material within the biopolymer membrane can significantly enhance its separation performance. The aim of this thesis was to develop a cobalt formate metallic organic framework within the chitosan membranes, as this crystalline framework could act as a size-selective sieve for methanol. Unfortunately, in-situ crystal nucleation and growth did not occur. The evidence gathered in this work demonstrates that cobalt-coordinated chitosan membranes were formed.

Metal ion coordinated chitosan had never been used in pervaporation. However, our new aim was to investigate the separation performances of these novel membranes. Our work shows that the presence of cobalt ions within the biopolymer served as a crosslinker, increasing the membrane's stability. The presence of cobalt also enhanced the membrane's hydrophilicity, increasing its selectivity towards methanol. The 20% cobalt loaded membranes that were developed managed to invert the molar fraction ratio found in the feed. A 11:89 methanol:dimethyl carbonate molar ratio in the feed resulted in a 89:11 ratio in the permeate. These results are similar to what has been found when metal organic frameworks are present within chitosan membranes to separate this mixture. Nonetheless, the production process of the cobalt-coordinated chitosan membranes is more facile and generates less waste, resulting in an effective and more sustainable solution for the separation of dimethyl carbonate/methanol mixtures that are rich in dimethyl carbonate.

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LIST OF ABBREVIATIONS

Most recurring:

DMC = **Dimethyl carbonate**

MeOH = **Methanol**

PV = **Pervaporation**

CS = **Chitosan**

Co FA = **Cobalt formate**

Co(Ac)₂ = **Cobalt acetate tetrahydrate**

MMM = **Mixed matrix membrane**

MOF = **Metallic organic framework**

HSP = **Hansen Solubility Parameters**

PAN = **Polyacrylonitrile**

IPCC = **Intergovernmental Panel on Climate Change**

GHG = **Greenhouse gas**

DMS = **Dimethyl sulphate**

VOC = **Volatile Organic Compound**

MeI = **Methyl Iodide**

AE = **Atom Economy**

MI = **Mass index**

MTBE = **Methyl tert-Butyl Ether**

GLC = **Glycerol carbonate**

PVA = **Polyvinyl alcohol**

PPy = **Polypyrrole**

PA = **Polyamide**

PAA = **Polyacrylic acid**

PEEK = **Polyether ether ketone**

PDMS = **Polydimethylsiloxane**

PIMs = **Polymers of intrinsic microporosity**

PVDF = **Polyvinylidene difluoride**

GA = **Glutaraldehyde**

MWNT = **Multi-Walled Carbon Nanotubes**

GO = **Graphene Oxide**

STA = **Silicic acid**

PCP = **Porous coordination polymers**

PEBA = **Poly(ether block amide)**

BTPA = **Bis [3-(trimethoxysilyl)propyl] amine**

MAPTS = **Trimethoxy [3-(methyl amino)propyl] silane**

APTES = **3-Aminopropyl triethoxy silane**

ZIF = **Zeolitic Imidazolate Framework**

XRD = **X-ray Diffraction**

SEM = **Scanning Electron Microscope**

EDX = **Energy-Dispersive X-ray Spectroscopy**

ATR = **Attenuated Total Reflectance**

FTIR = **Fourier Transform Infrared Spectroscopy**

GC = **Gas chromatography**

FID = **Flame ionization detector**

TCD = **Thermal Conductivity Detector**

PMMA = **Polymethyl Methacrylate**

ANOVA = **Analysis of variance**

1 INTRODUCTION

AR6, the sixth Assessment Report of the Intergovernmental Panel on Climate Change (IPCC), has conclusively shown that Earth's surface temperature has risen by 1,09°C since the 19th century due to the effects of man-made greenhouse gas (GHG) emissions. Moreover, it was revealed that there is more than a 50% chance that the 1,5°C threshold will be reached or exceeded in the near-term (before 2040). The consequences of such a rise in global surface temperature include severely damaging all living ecosystems, reducing food and water security and inducing extreme weather events which all contribute to increasing human vulnerability in the future (IPCC, 2023).

Since 2010, GHG emissions have increased in all major sectors, and it is estimated that 24% of net global GHG emissions come from the industrial sector (the second biggest contributor after the energy sector) (IPCC, 2023). Within the industrial sector, the chemical industry accounted for 15% of GHG emissions in 2010 and has since shown a yearly 2,5% increase (data issued until 2018) (IPCC, 2022; Minx et al., 2021).

The need for a greener chemical industry, reliant on greener processes, is thus a crucial component to mitigate the negative consequences of climate change. However, it has become more than a moral obligation as – since 2008 – Article 3.3 of our European Constitution states that: *“The Union shall [...] work for the sustainable development of Europe based on balanced economic growth [...] aiming at [...] a high level of protection and improvement of the quality of the environment. It shall promote scientific and technological advance.”* (OPOCE, 2008).

Separation techniques are at the forefront of many chemical processes. Distillation, the most prominent separation technique within the industry, which relies on the difference in boiling points of the components within a mixture to separate them, is considered to be responsible for about 40% of all the energy used in the chemical industry (Kiss & Smith, 2020). However, putting its high energy consumption aside, traditional distillation has a chemical shortcoming. It is incapable of separating mixtures, the components of which have the same boiling point and composition when distilled or vaporized (Hilmen, 2000). These mixtures are called azeotropes.

A surge in the research and development of processes that could remedy this shortcoming has led to the increasing usage of pervaporation (PV). Although PV's inception dates back to 1917, it is still considered to be a developing technology, which has recently garnered more popularity and is undergoing rapid development (Nagy, 2019).

PV is a process that enables the separation of a liquid mixture, often an azeotrope, by passing the latter through a dense membrane (Crespo & Brazinha, 2015). Both permeation and evaporation occur as one of the components within the mixture has more affinity with the membrane and passes through it. The combination of these two processes explains its etymology, as PV originates from the amalgamation of “permselective” and “evaporation” (Luis, 2018).

Beyond breaking azeotropes, PV is capable of separating heat sensitive substances, doesn't involve heavy equipment, involves low operational temperatures and pressures, is regarded as a flexible operating system, results in high purity products and has low capital, maintenance, and operating costs. Its main drawbacks are that the feed needs to be purified and lower

temperatures are often synonymous with transmembrane flux reduction. All of the above lead to PV being eco-friendlier and more economical than traditional separation processes (Khan et al., 2013; Kiss & Smith, 2020; Stewart Slater et al., 2012; Wu et al., 2020).

However, these criteria are dependent on PV set-ups using selective membranes. The more selective the membrane, the more the PV separation will be effective (Nagy, 2019).

Moreover, a greener chemical sector is dependent not only on its processes but also on its reagents. As a wider range of reagents are being discarded due to their toxicity, the search for their sustainable alternatives has never been greater.

The aim of this thesis will be to develop novel membranes, which are biopolymer-based and which will separate an azeotrope through PV. The azeotrope consists of an eco-friendly reagent, that is both non-toxic and biodegradable, dimethyl carbonate (DMC) and its precursor in its production process – methanol (MeOH).

2 STATE OF THE ART

2.1 CONTEXT: DIMETHYL CARBONATE, A GREEN REAGENT

Platform molecules serve as building blocks for the creation of higher-value materials and chemicals that are used in everyday life. From pharmaceuticals and plastics to the clothes we wear, these everyday-life objects went through induced chemical changes so that they can become the products we use and cherish.

Methylation and carbonylation reactions are examples of such induced chemical changes and have become routine reactions in the chemical sector. However, the reagents used to perform these essential organic and inorganic synthesis reactions can be toxic to humans as well as our ecosystems. Common examples of these platform molecules that enable such reactions are dimethyl sulphate (DMS), methyl halides and phosgene.

However, all of the latter are highly toxic chemicals with severe health risks. Dimethyl sulphate, despite its widespread use, is potentially fatal if inhaled and may cause genetic defects and cancer. Methyl halides and phosgene are also toxic and carcinogenic, with methyl bromide being phased out due to its ozone-depleting effects (ECHA, 2023; Rippey & Stallwood, 2005; Montreal Protocol, 2007). The dangerous nature of these reagents and their impact on the environment have been recognized as a major concern, their use is thus being increasingly controlled. The search for greener, and more sustainable alternatives has begun with some already garnering much attention and being increasingly used in industrial applications.

Greener solvents are considered as such if they respect some of the following principles related to green chemistry: avoiding or reducing the use and production of auxiliary chemicals considered toxic or dangerous, promoting the use of renewable materials, choosing catalysts over stoichiometric reagents, preventing waste and/or using energy-efficient processes (Aricò & Tundo, 2010; Schäffner et al., 2010).

DMS, methyl halides and phosgene are all very toxic and corrosive, they require copious quantities of other solvents (such as strong bases) and produce vast amounts of waste in the form of inorganic salts. On the other hand, organic carbonates offer the same alkylation and carboxylation opportunities as the aforementioned reagents, however they possess low toxicity and are completely biodegradable. They are also stable under ambient conditions and do not generate any salt related by-products (Aricò & Tundo, 2010). Within the organic carbonate family, the short-chained dialkyl carbonates have been placed in the spotlight due to their numerous advantages and applications, namely dimethyl carbonate (DMC) and diethyl carbonate (DEC). Of the latter, this thesis will solely focus on DMC.

DMC is a carbonate ester, which is classified as a flammable liquid. It is a colourless liquid, has a similar smell to methanol and has no irritating or mutagenic effects (Pyo et al., 2017). Its density at room temperature is 1,07 g/cm³. It has good miscibility with water and is a polar aprotic solvent (Schäffner et al., 2010). It is shown on Figure 1, on the right.

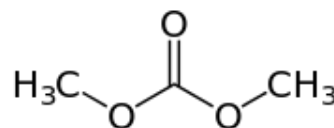


Figure 1 : Dimethyl carbonate molecule

Its non-toxicity and biodegradability into H₂O and CO₂ as well as versatility as a methylation and carboxymethylation reagent all point to it being a suitable alternative to its harsher counterparts. Under different temperature and catalytic conditions and in the presence of a nucleophile (labelled as Y⁻ on Figure 2 below), DMC will yield either carboxymethylation or methylation (Tundo & Selva, 2002).

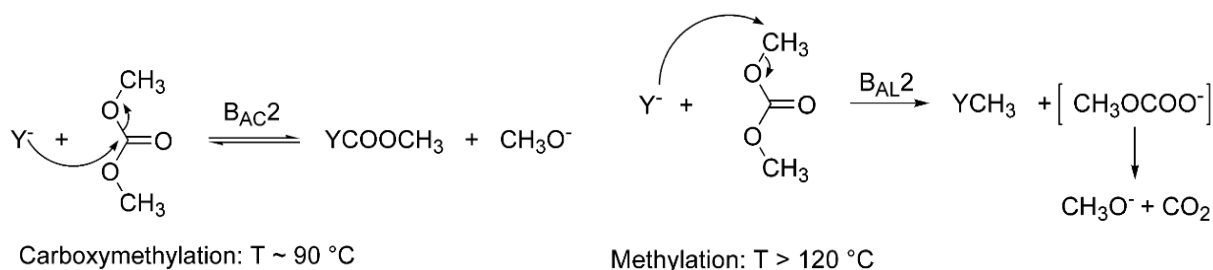


Figure 2 : Mechanisms of nucleophilic substitution on DMC (Tundo & Selva, 2002)

In Selva & Perosa's (2008) study, DMC's efficiency as a methylating reagent was compared to DMS and methyl iodide (MeI), for 33 different procedures that are commonly found in the pharmaceutical, cosmetic, fragrances and dyestuffs industries. Atom economy¹ (AE) and mass index (MI), being indicators of process efficiency, were compared between the three compounds. DMC was not only cheaper, but its AE was found to be superior or equal to that of DMS and superior to MeI. Moreover, DMC's MI was found to be inferior to that of DMS and MeI. Indicators such as these tend to confirm DMC's reputation as a greener reagent.

DMC demonstrates remarkable reactivity and selectivity towards various nucleophilic substrates, making it a versatile compound for organic synthesis. In addition to its applications in organic chemistry, DMC has proven to be a viable alternative to methyl tert-butyl ether (MTBE) in gasoline, significantly reducing harmful emissions (S. Huang et al., 2015; Tan et al., 2018). It also shows potential as a solvent in lithium-ion batteries and finds use in cosmetics, co-solvent cleaning, lacquer applications, and other industries (Schäffner et al., 2010).

Although GHG emissions related to the chemical sector are substantial, they are still vastly inferior to GHG emissions related to the energy sector. With demand for fossil fuels continuously increasing, their prices (both economic and environmental) are pushing us to find energy sources based on renewable feedstocks. A persuasive alternative is biodiesel. Based on biomass, plants and animal fats, its environmental footprint has shown to be considerably smaller (Mota et al., 2017). Biodiesel production has been steadily increasing over the past decades, with one of its main production processes being the transesterification reaction (shown below on Figure 3) (IEA, 2021). The latter is one of the most economic and high yielding methods for its production (Knothe et al., 2010; Quispe et al., 2013).

$$^1AE = \frac{Mw_{product} (g/mol)}{\sum Mw_{all reagents} (g/mol)} * 100$$

$$MI = \frac{\sum (reagents+catalysts+solvents) (kg)}{Desired product (kg)}$$

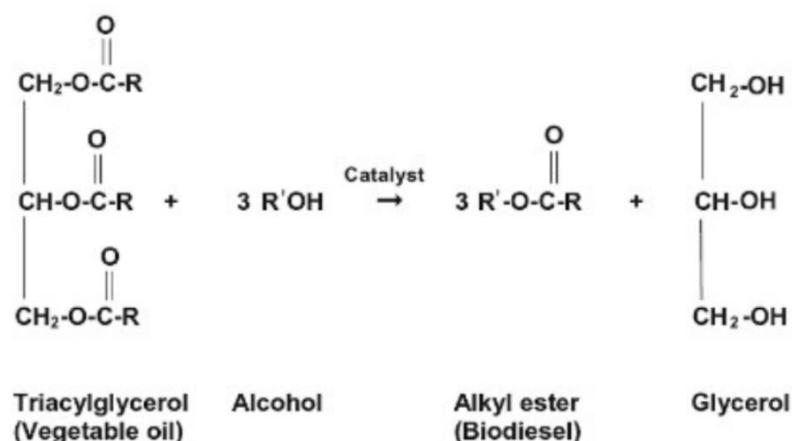


Figure 3 : Transesterification reaction mechanism for the production of biodiesel (methanol is typically the alcohol used) (Knothe et al., 2010)

However, from triglyceride transesterification, waste in the form of glycerol (accounting for 10% weight) is produced. As biodiesel production increases, the amount of glycerol needing to be treated is complementarily rising. In order to make biodiesel more prominent and improve its environmental and economic viability, adding value to its by-products is also a necessity (Mumtaz et al., 2017).

In this context, DMC may have an important role to play. In the presence of DMC ($\pm 1500\$/\text{ton}$), there is transesterification of glycerol ($\pm 2500\$/\text{ton}$) into glycerol carbonate (GLC) ($\pm 8000\$/\text{ton}$) (see Figure 4 below) (ChemAnalyst, 2023). GLC is a glycerol ester that has low toxicity, is not flammable, has a high boiling point and is also biodegradable. Having both nucleophilic (1 site) and electrophilic (3 sites) sites, its role in organic synthesis is assuredly versatile (Teng et al., 2014). GLC has already been used successfully in the semiconductor, agricultural, chemical, pharmaceutical, construction, cosmetics and polymer industries (Gade et al., 2022; Ishak et al., 2017; Ochoa-Gómez et al., 2012; Okoye et al., 2016).

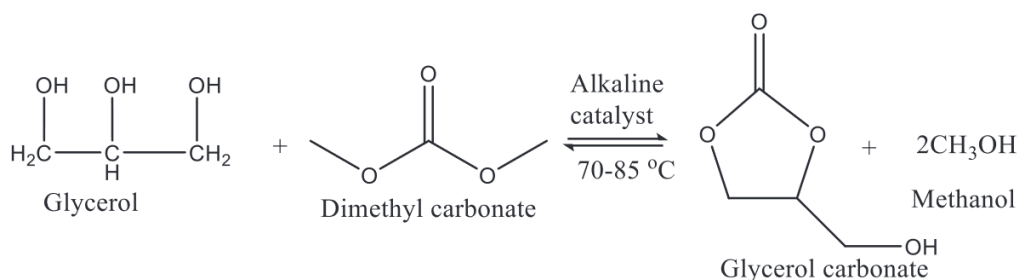


Figure 4: Glycerol transesterification pathway with DMC for glycerol carbonate synthesis (Okoye et al., 2016)

The growing applications of DMC have spurred advancements in its production methods. The phosgene alcoholysis process (top left of Figure 5), once widely used, has now been phased out due to environmental and toxic concerns and has been replaced by the direct oxidative carbonylation of alcohol in a gas-phase method (middle left of Figure 5) (S. Huang et al., 2015). Another process that has been shown to work on an industrial scale is methylnitrite carbonylation which avoids water production (prolonging the usage of the catalyst) but emits toxic gases, contradicting with green chemistry principles (bottom left of Figure 5).

Furthermore, CO_2 can be utilized in three main routes for DMC synthesis: direct carbonylation (top right), urea alcoholysis (middle right), and transesterification of cyclic carbonates with alcohol (bottom right of Figure 5) (S. Huang et al., 2015). While direct carbonylation faces challenges with low yields and reversible reactions, urea alcoholysis is gaining popularity. The transesterification of cyclic carbonates is the most established CO_2 -based process, but it relies on the production of expensive and hazardous epoxides. Propylene carbonate and DMC are produced through a series of reactions, with propylene glycol being a valuable by-product (Deng et al., 2019). More information detailing the evolution of DMC production can be found in section 8.1.1 (p.84).

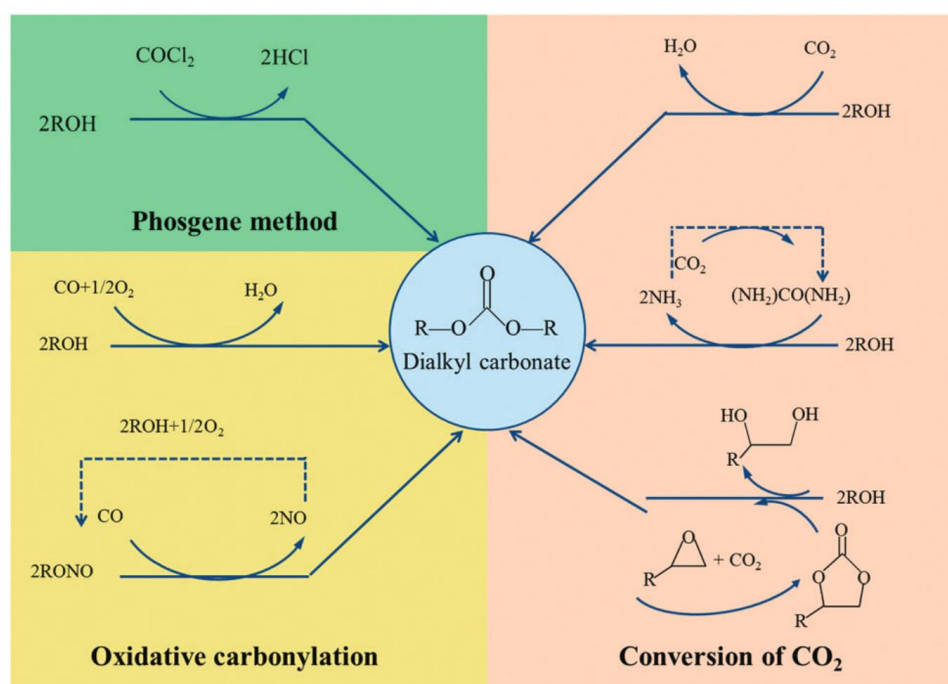


Figure 5 : Synthetic routes for dimethyl carbonate (when $\text{R} = \text{CH}_3$) (S. Huang et al., 2015)

The different processes for DMC synthesis all have their advantages and disadvantages. However, two obstacles are present within all these processes. Firstly, water risks hydrolysing the formed product. It creates a harder end-product to separate and also deactivates catalysts (S. Huang et al., 2015). Water thus needs to be avoided or reduced at all times. Secondly, separating the DMC from its production process precursor, MeOH. Be it through its production cycle, or by reacting with glycerol to form GLC, MeOH is always present within the system and forms an azeotrope with DMC.

2.2 AZEOTROPY: DMC/MEOH MIXTURES

An azeotrope signifies that the components within a mixture share equal vapor and liquid compositions at a specific temperature and pressure (Hilmen, 2000). MeOH has a boiling point of 337,85K and DMC has a boiling point of 363,5K. However, the MeOH/DMC azeotropic mixture has a boiling point =336,9K (Cho et al., 2014).

Therefore MeOH/DMC mixtures are defined as being a minimum-boiling azeotrope (or positive azeotrope). This label comes from the fact that the mixture's boiling point is lower than either of the pure components' boiling temperatures. The mixing enthalpy is thus negative as the interactions between MeOH molecules and DMC molecules are less favoured than the interactions between molecules of the same type, making the liquid mixture less stable than in an ideal mixture, where intermolecular interactions between different and same species molecules are equal (Atkins, 2016, Li et al., 2020). This is seen on Figure 6 below, at the 86,5% molar MeOH composition on the vapor-liquid equilibrium (held at a constant pressure of 1 bar absolute). The various vapor mole fractions of MeOH are displayed on the y-axis and the various liquid mole fractions of MeOH are represented on the x-axis. The data used for this graph are given in section 8.1.2. Above the diagonal line - which represents the coexistence of vapor and liquid phases at equilibrium - lies the vapor phase, under it lies the liquid phase.

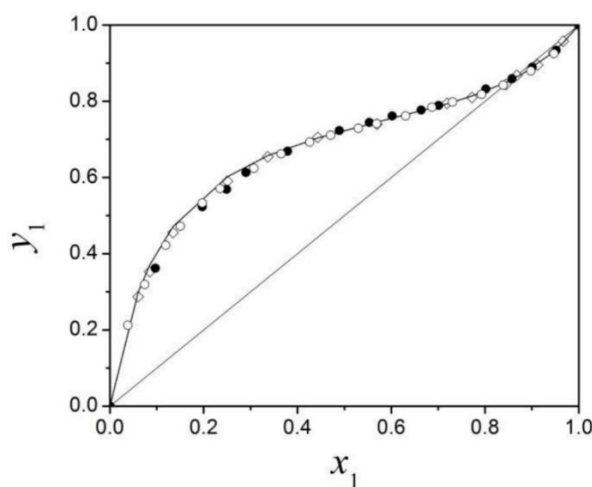


Figure 6 : Isobaric vapor-liquid equilibrium of a MeOH/DMC binary mixture (y_i = vapor mole fraction of MeOH, x_i = liquid mole fraction of MeOH (Z. Zhang et al., 2016)

Figure 6 shows that a higher concentration of MeOH is found in the vapor phase when its molar composition is low in the liquid phase. However, when MeOH reaches an 86,5% molar concentration in the mixture's composition, a plateau is formed. This is an indicator that the mixture has reached a constant boiling composition. As both liquid and vapor phases have the same composition at this point, MeOH forms an azeotrope with DMC. After this point, there is DMC enrichment in the vapor phase.

The 86,5% molar MeOH composition indicates the point at which vapor pressure will be maximum (which is directly correlated to the minimum boiling temperature of 336,9K), indicating that there is thus no change in composition when the mixture is boiling. This can also be visualised as a positive deviation from Raoult's Law on a pressure-composition phase diagram which can be correlated to a temperature-composition phase diagram, shown on Figure 7, below.

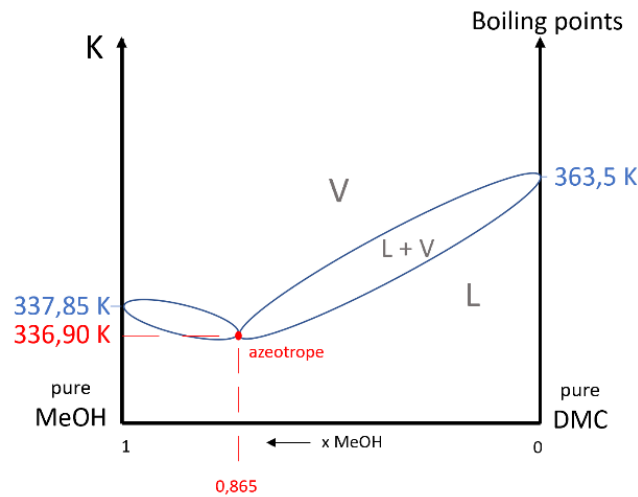


Figure 7 : Temperature-composition phase diagram (L= liquid phase, V =vapor phase)

On the figure above, we can see that vapour pressure and boiling temperatures are inversely proportional as a higher vapour pressure corresponds to a component being more volatile.

Traditional distillation processes will be unable to fully separate this binary mixture into two pure components due to the occurrence of a constant boiling temperature associated when the azeotrope's composition is reached. Based on the concentration of the feed, the azeotrope will find itself either at the bottom or the upper flow of a distillation column. Specific distillation process such as heteroazeotropic distillation, extractive distillation (Qi et al., 2023) and pressure swing distillation (H. M. Wei et al., 2013) have been shown to work for MeOH/DMC mixtures. In the former case, entrainers such as ionic liquids or eutectic solvents are often used as special agents to facilitate the separation of the mixture (due to their low volatilities and high thermal stabilities). However, all these processes rely on either the usage of extra solvents and/or higher energy consumptions due to the utilisation of heavier equipment (also incurring extra costs).

2.3 PERVAPORATION

Pervaporation (PV) circumvents all these complications as it does not use the boiling point to separate the mixture. PV is a process that enables the separation of one of the components within a feed liquid mixture to selectively pass through a dense membrane (Crespo & Brazinha, 2015). A difference in partial pressures on either side of the membrane is needed to assist in the passage through the membrane and acts as the main driving force (Luis, 2018). Habitually, a vacuum is applied on the other side of the membrane, or more rarely, an inert purge flow, in the form of air or steam, is used (Feng & Huang, 1997).

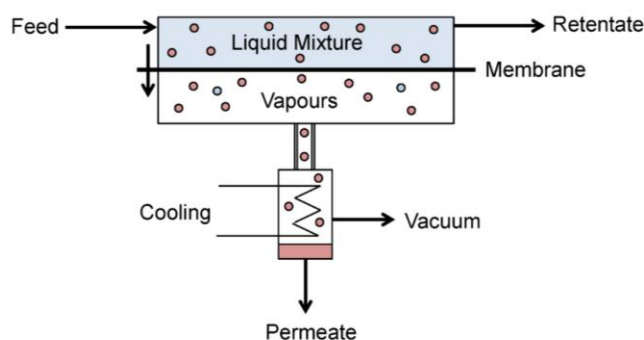


Figure 8: Pervaporation unit (Davey et al., 2016)

The components from the feed will firstly adsorb on the membrane's surface (Crespo & Brazinha, 2015). The adsorption rate is determined by the components affinities for the membrane's polymeric material. The components will then diffuse within the membrane, the of rate which is principally determined by the free volume within the polymeric matrix of the membrane, the size of the components as well as the chemical potential gradient (Seader et al., 2011). The components' different affinities for the membrane will affect their transport rate, enabling selective separation (Koros & Zhang, 2017). Evaporation of the components happens somewhere within the membrane (W. Li et al., 2019). As the targeted component selectively passes through the membrane, it finally desorbs on the other side of the membrane as vapor. This vapor is recovered, which is designated as the permeate, and is subsequently (often) condensed. The feed mixture that hasn't passed through the membrane is called the retentate and is recycled into the feed. A simplified scheme of the PV process is shown above, on Figure 8.

The permeation of the component is independent of the liquid-vapor equilibrium but is strongly dependent on its solubility and diffusion rate within the membrane (Luis, 2018). It is thus the membrane's composition which is the decisive element within this process, as it is how selective the membrane is to one of the feed's elements that attests to its efficiency (Crespo & Brazinha, 2015). However, selective permeability of the targeted component through a membrane is not only dependant on the membrane's composition, but also on the membrane's thickness, the chemical nature of the components that are in the feed, the feed's composition as well as its temperature (Jyoti et al., 2015; Pulyalina et al., 2015; Seader et al., 2011; S. Zhang et al., 2017).

PV is considered to be a safer and a "green" process due to the easy handling of the operating parameters, the closed-loop nature of the process preventing emissions due to additional streams, the fact that no additional chemicals are added to the feed and its low energy requirements as compared to other mainstream separation processes (Castro-Muñoz et al., 2019).

PV's uses are mainly found in the separation of azeotropic mixtures. These can be surmised into three categories: water-organic mixtures, organic-water mixtures as well as organic-organic mixtures (Castro-Muñoz & González-Valdez, 2019).

Currently, PV's most widespread use concerns water-organic mixtures being dehydrated. Water is thus separated from its organic counterpart; the water molecules permeate through a hydrophilic membrane and the mixture is separated into an aqueous and an organic phase (an

example of this would be the dehydration of alcohols such as (bio)ethanol and isopropanol). Removing these water traces increases the purification degree of the organics. As of yet, over one hundred industrial scale PV setups are used for this purpose and have been reported to be successful (Castro-Muñoz et al., 2019). Although PV's main focus has been on binary azeotropes, it has also proved successful in the separation of ternary systems such as the removal of water from DMC/MeOH mixtures for example (Smitha et al., 2004; Won et al., 2003a).

Organic-water mixtures pertain to the removal of the organic component from an aqueous solution. In this case, it is the organic component that becomes the permeate, as the membrane is hydrophobic (an example of this would be the removal of toluene from wastewater). These procedures however have not been used on such a wide scale (Smitha et al., 2004).

Lastly, organic-organic mixtures are mixtures composed of several organic components, where one of the components will selectively pass through the membrane. The PV process will separate the mixture into two distinct organic phases with different compositions. Although the possibilities linked to the separation of these mixtures via PV are countless, it is also - by far - the least prevalently used in the chemical sector due to the complications it entails (Smitha et al., 2004). As opposed to the two previous categories of mixtures mentioned, where separation is considered much easier due to the large difference in polarity between water and the organic compound, organic-organic mixtures don't benefit from these considerable contrasting properties. Using solely the difference in polarity with such mixtures will not yield the best selectivity. Membranes thus need to be better tailored to the organic compound sought to be separated within the mixture (Galiano et al., 2016; Van Der Bruggen & Luis, 2014).

2.4 MEMBRANE SEPARATION OF ORGANIC-ORGANIC MIXTURES

The organic-organic family of mixtures, being vast and diverse, can be subdivided into the four following subgroups as per Figoli et al. (2015):

- Polar / non-polar mixtures
- Aromatic / alicyclic mixtures
- Aromatic / aliphatic mixtures
- Isomer mixtures

Polar and non-polar (P/NP) mixtures can be separated in a multitude of ways; however, most P/NP separation processes nowadays often use both membrane polarity (Galiano et al., 2019) and size sieving (Fazlifard et al., 2017a; Jia & Wu, 2016a). The combination generally leads to an improved separation efficiency (S. Liu et al., 2022a). The structure of the membrane's polymeric matrix can lead to selective size sieving of the mixture as the smaller compound will pass more easily through the matrix than its bigger counterpart (Saw et al., 2019). The dielectric constant (ϵ), which measures a component's ability to insulate charges from another component, is often used as an indicator to measure solvent polarity (Xie et al., 2022).

Aromatic and aliphatic mixtures both share weak polarity, however aromatic compounds possess delocalized pi electrons which may be polarized under the induction of polar groups (S. Liu et al., 2022a), they will thus polarize with the former polar groups much more easily than the aliphatic compounds. Altering the polarity of one of the initial components has shown promising results as it can improve their affinity to the pores within certain membranes (Zhang et al., 2020).

Aromatic and alicyclic mixtures share very similar chemical properties, it is therefore their physical properties that are used to separate them. The molecule's size and weight will be the determining factor in the separation as the molecules diffuse through the membrane (Figoli et al., 2015). However, in contrast to the aromatic and aliphatic mixtures, tuning the chemical properties of the membranes has proved successful (Kyu Park et al., 1994).

Isomer mixtures are the most recent subgroup to have undergone separation through PV due to their near identical chemical and physical properties. The defining component of this breakthrough seems to have been made through the creation of zeolite membranes (Liu et al., 2022). A zeolite is an aluminosilicate mineral which possesses a framework structure based on interconnected cavities formed by large metal ions (Britannica, 2022). Their uniform micro-pore structure, thermal stability and overall mechanical and structural strength make this crystal's use in separating isomers consistent and reliable (A. Huang et al., 2007). The crystals are formed and then dissolved within a polymer solution which will then set as a membrane (Zah et al., 2006). Steady results have been observed, most recently with the separation of dichlorobenzene isomers and xylene isomers (He et al., 2021; Kim et al., 2022).

Below, Table 1 encapsulates the most widely used techniques to selectively separate one of the components within the feed based on the organic-organic mixture at hand. An x mark denotes the usage of the technique/mechanism for separating the organic-organic feed mixture.

Table 1: Prevalent membrane separation techniques and mechanisms used to separate the mixture at hand

organic-organic mixture subgroups	prevalent mechanisms and properties used to separate the mixture at hand				
	membrane polarity	size sieving	chemical alteration of a component in the feed	chemical alteration of the membrane	insertion of filler material in the membrane
polar/non-polar	x	x			
aromatic/aliphatic	x		x		
aromatic/alicyclic	x	x		x	
isomers		x	x		x

MeOH and DMC mixtures are both polar compounds, however their mixture belongs to the P/NP mixture subgroup. Looking at their dielectric constants, as $\epsilon_{\text{DMC}} = 3,2$ and $\epsilon_{\text{MeOH}} = 37,9$, we can deduce that the difference in polarity between both components is considerable and DMC can be regarded as the non-polar compound in the mixture. A higher dielectric constant corresponds to a solvent being more easily polarized (Bezman et al., 1997; S. Lee & Park, 2012; Pyo et al., 2017). Moreover, it is interesting to keep note of the alternate possible routes to increase selective permeation that exist for organic-organic mixtures. As interest in this subject has been steadily increasing, techniques used on different mixture types have inspired the development of membranes using a combination of these mechanisms. It is the particular physicochemical properties of the components within the mixture that will lead to the modifications that need to be made to the membrane that will separate them. Effective mass transport and the membrane's selectivity (which is intrinsically linked to its composition) are resolutely correlated (Luis & van der Bruggen, 2015).

2.5 SOLUTION-DIFFUSION MODEL

To describe the selective transfer of components through a membrane, several mathematical models can be used depending on the membrane's porosity. As polymeric membranes are considered dense, the solution-diffusion model is used, and the flux is described as diffusive (As opposed to the pore-flow model which is used for porous membranes where the transport mechanism is described by convection) (Luis & van der Bruggen, 2015; Luis, 2018).

The solution-diffusion has been proven to be a good approximation and simple to use for the modelling of mass transport for pervaporation through polymeric membranes (Bettens et al., 2007). This model describes the mass transport in three steps (Lipnizki & Trägårdh, 2001):

- 1- Sorption of the permeating compound(s) into the polymer.
- 2- Diffusion through the polymer along the gradient of the chemical potential.
- 3- Desorption at the permeate side.

The main assumptions for this model as well as Figures showing the concentration gradient of the components across the membrane as well as chemical potential, pressure and activity gradients along the membrane during this mass transfer are given in section 8.2.1 (p.89).

2.5.1 Membrane performance indicators

As per the solution-diffusion model, it should be known that the main indicators assessing a membrane's performance are its **flux**, **permeance**, **separation factor** and **selectivity**.

A membrane's **flux** (J) can be assessed experimentally via Wijmans & Baker's (1995) equation which evaluates the total weight of the permeate (w), which was collected over a specific period of time (Δt) over the effective surface area (A) of the membrane such as:

$$J_{permeate} = \frac{w}{A\Delta t} \quad (1).$$

This is not to be confused with permeability, however, which is an indicator of the driving force's normalized productivity of a dense membrane. J_i corresponds solely to the flux of component i , P_i is the permeability of component i across the membrane, l is the thickness of the membrane and $a_{F,i}$ and $a_{P,i}$ correspond to the difference of partial vapor pressures (or activities) of component i on the feed and permeate side of the membrane, respectively (Wijmans & Baker, 1995).

$$J_i = \frac{P_i}{l} (a_{F,i} - a_{P,i}) \quad (2).$$

The activity of component i can be calculated using Raoult's law (section 8.2.1.1) which will allow us to determine a membrane's **permeance** and permeability.

To assess a membrane's selectivity, the **separation factor** ($\beta_{i/j}$) is generally used and is determined by dividing the molar ratio of i in the permeate ($\frac{y_i}{y_j}$) by the molar ratio of i in the feed ($\frac{x_i}{x_j}$) such as:

$$\beta_{i/j} = \frac{y_i x_j}{y_j x_i} \quad (3).$$

Although the separation factors tells us what compound is found more abundantly in the permeate, it does not consider the components' volatilities. As the vapor phase will attract the component with a higher volatility, the separation factor can therefore not distinct the membrane's actual selectivity as volatility may play an important role in the mass transfer. This is why **selectivity** is used, which is given by the ratio between permeabilities (Luis, 2018) such as:

$$\alpha_{i/j} = \frac{P_i}{P_j} = \frac{P_i l}{P_j l} = \frac{P_i}{P_j} \quad (4).$$

Through the use of the components' permeances, their volatilities are taken into account, giving us the membrane's true ability in separating the components within the mixture. Flux and separation factor are consistently divulged in the literature when assessing a membrane's performance, however, permeance and selectivity are seldom mentioned.

2.6 MEMBRANE SEPARATION OF MEOH/DMC MIXTURES

As the membrane can be considered to be the heart of the pervaporation process, it goes without saying that the material it is made of is of crucial importance. Membranes are typically classified into three distinct families: polymeric, inorganic and mixed matrix membranes which are also known as hybrid membranes.

2.6.1 Polymeric membranes

The polymer chosen as a polymeric membrane will be chosen for its adsorption towards the components in the mixture and for the diffusion it is able to procure for the component(s) in the mixture within its free volume (Gugliuzza & Basile, 2013).

The identification of the best polymeric membranes for MeOH/DMC separation greatly benefited from pre-existing scientific literature on the PV of MeOH/MTBE mixtures (Won et al., 2002). MTBE and DMC share many physicochemical similarities. They have similar polarities and are both bigger in size than MeOH. However, it should be noted that MBTE has a bigger kinetic diameter (6,2 Å) as compared to DMC (which ranges from 4,7 to 6,3 Å) (X. Xu et al., 2022).

Synthetic polymers such as polyvinyl alcohol (PVA), poly(phenylene oxide), polypyrrole (PPy), polyelectrolytes such as Nafion® and Polyacrylonitrile (PAN) as well as biopolymers such as chitosan (CS), cellulose and agarose were tested on the PV separation of MeOH/MTBE mixtures (Won et al., 2002). Of the latter, PVA and CS showed the best results and have since, also proved to be ideal candidates for MeOH/DMC separation as well. These show preferential affinity for MeOH, being hydrophilic polymers, and the size within their polymer matrix –

determining their free volume capacity – has shown preferential diffusion for MeOH as well (Gugliuzza & Basile, 2013; G. Liu & Jin, 2021; Won et al., 2002). A more detailed look at CS membranes will be given in section 2.7.

Polyamide (PA), polyacrylic acid (PAA), Polyether ether ketone (PEEK) as well as the hydrophobic polydimethylsiloxane (PDMS) and polymers of intrinsic microporosity² (PIMs) have also been tested on MeOH/DMC mixtures, the latter two being DMC-selective (H. Zhou et al., 2014; Golubev et al., 2022).

For organic-organic separation, chemical and mechanical resistance play a bigger role as the molecules within the mixture are bigger, applying more pressure on the membrane's polymeric network.

It is therefore important to find techniques that increase chemical, thermal and mechanical resistance to guarantee membrane stability and durability (Gugliuzza & Basile, 2013). Composite membranes can be used to face this challenge. Composite membranes consist of non-reactive polymers which serve as a thicker porous underlayer to the nonporous (dense) selective membrane. These guarantee better mechanical resistance, without playing any role in the actual separation process, as their polymer matrix is much too wide (Galiano et al., 2016). PAN and polyvinylidene difluoride (PVDF) are often used as composite membranes in the separation of MeOH/DMC mixtures. Another popular option to increase membrane stability is polymer crosslinking. This refers to the alteration of the polymer's physical properties by linking polymer chains together through chemical linkages (Won et al., 2003b). This increases the polymer's rigidity but will also negatively affect the feed's solubility within the membrane as the polymer's network size decreases. Glutaraldehyde (GA) is a common crosslinking reagent used in PV (J. H. Chen et al., 2016; Migneault et al., 2004; Yong Nam & Moo Lee, 1999). Moreover, blending another polymer with the membrane's polymer can also be used for increasing overall membrane resistance as reactions can occur between the polymers, increasing the degree of crosslinking between them and also increasing their selectivity (Ong et al., 2016; L. Wang et al., 2007).

Finally, we should note that the main advantages of polymeric membranes are that they are low cost, easy to manufacture and produce and their scale up possibilities are thus broad. However, as opposed to inorganic membranes, which we will look at in the following subsection, their separation capabilities are qualified as moderate and their thermal and chemical resistance are low (Gugliuzza & Basile, 2013).

Obtained results of hydrophilic (CS excluded) and hydrophobic polymeric membranes for the separation of MeOH/DMC mixtures via PV are given below in Table 2 and Table 3 respectively.

² PIMs belong to a group of polymers characterized by high free volume. They hold significant potential in the advancement of membranes and adsorbents for achieving highly efficient molecular separations. The interconnected intermolecular voids create an uninterrupted cohesive and rigid network, notable examples include polybenzodioxanes, triptycene or binaphthyl (Budd, 2019).

Table 2: Hydrophilic polymeric membranes (MeOH selective) for MeOH/DMC separation via PV

membrane	feed solution (wt% MeOH)	temperature (°C)	flux (g/m ² *h)	separation factor ($\beta_{\text{MeOH/DMC}}$)	reference
Polyamide: PA-6	20	50	199	6	(Kopeć et al., 2013)
	50	50	209	3	
PVA (crosslinked with GA)	70	50	390	8,3	(L. Wang et al., 2009)
PAA / PVA blend (70wt% PAA)	60	60	577	13	(L. Wang et al., 2007)
PAA / PVA blend (10wt% PAA)	70	70	510	2,8	(L. Wang et al., 2007)
PAA / PVA blend (10wt% PAA) (crosslinked with GA)	70	70	248	37	(L. Wang et al., 2009)
PEEK-WC	3,8	30	140	13,4	(W. Li et al., 2018)
Nafion [®]	70	40	5080	1,5	(Kludský et al., 2018)
	10	40	930	10,6	

Table 3: Hydrophobic polymeric membranes (DMC selective) for MeOH/DMC separation via PV

membrane	feed solution (wt% MeOH)	temperature (°C)	flux (g/m ² *h)	separation factor ($\beta_{\text{DMC/MeOH}}$)	reference
PDMS (on PVDF composite)	72	40	490	3,95	(H. Zhou et al., 2014)
PIM-1	62	40	1000	2,3	(Golubev et al., 2022)

Through the results that are shown on the tables above, we can observe the variables that seem to benefit or impede overall mass transfer through the membranes as well as its selectivity. Firstly, is the choice of polymer, however other factors seem to intervene.

As is discussed in Wang et al.'s (2007) study, using polymer blends was used to increase membrane stability. We see that increasing the PAA weight percentage within the PVA membrane seems to increase flux and yields a higher separation factor. The higher the PAA content, the higher the degree of crosslinking, as the PAA crosslinks with PVA through esterification reactions. Although, it should be noted that crosslinking is often correlated to a higher selectivity and not to an increase in flux.

Their results also cover the reduction of swelling via crosslinking. Membrane swelling (or membrane plasticization) occurs when solvents exhibit strong affinity for the membranes, the latter thus penetrate and then react within the polymer matrix (Galiano et al., 2016). This is due to the solvent's interaction with the membrane's polymers which might be stronger than the polymer-polymer interactions leading to the partial dissolution of the membrane (Li, 2019). This causes both the permeability and the selectivity of the membrane to decrease because the preferred permeable component's diffusion coefficient will be negatively affected (Shao & Huang, 2007). If the swelling degree is important, it can completely change the structure of the

membrane, making it more open, and thus easier for all of the feed's components to pass through.

We can also see the effect of feed composition, especially on the PA membrane in Kopeć et al.'s (2013) study. When the weight percentage of MeOH within the feed increases, we see that flux is hardly affected and that the separation factor decreased, which is intriguing as the membrane is hydrophilic. It could be possible that MeOH induces a swelling effect on the membrane, an increase in its initial concentration will then decrease the membrane's selectivity. However, a higher increase in flux at the same time would also be expected (Garcia Villaluenga & Tabe-Mohammadi, 2000). Feed composition is shown to directly affect permeation activation energies (Pulyalina et al., 2015; B. Wang et al., 2010). Let us assume that DMC has a permeation activation energy of $E_{a\text{ DMC}}$ and MeOH has a permeation activation energy of $E_{a\text{ MeOH}}$ and $E_{a\text{ DMC}}$ is bigger than $E_{a\text{ MeOH}}$. The change in composition can therefore cause $E_{a\text{ MeOH}}$ to become greater than $E_{a\text{ DMC}}$, inverting the kinetics of sorption and diffusion for both components which may lead to a switch in the overall permeation of the components (Li, 2019; Smitha et al., 2004). This is called the coupling effect. This was shown in Pulyalina et al.'s study (2015) as the methanol percentage in the composition increased, MeOH's permeation E_a decreased and became smaller than that of ethanol. This led to preferred permeation of MeOH as opposed to ethanol. We can add that the coupling effect can also be caused by the addition of extra components to the feed (Luis, 2018).

Hydrophobic membranes for MeOH/DMC separation through PV generally tend to show smaller separation factors and higher fluxes, as the transport is more heavily reliant on the affinity between the diffusing compound and the membrane as size sieving plays virtually no role (Golubev et al., 2022).

2.6.2 Inorganic membranes

Inorganic membranes are generally composed of materials that are crystalline and microporous such as zeolites made of TiO_4 frameworks which possess "well-defined and rigid pore structures" (G. Liu & Jin, 2021). Other porous materials such as ceramics, silicas and glass metal can be used (Luis & van der Bruggen, 2015). Zeolites are renowned for uniform, molecular-sized pores which gives them considerable active surface per volume and abundant free volume for the permeate to pass through. These characteristics gives inorganic membranes high permeability and selectivity with greater thermal and mechanical stabilities than polymeric membranes (Gugliuzza & Basile, 2013). The pores within the zeolites can be tuned, generating selective sub-nanometre tubes reaching molecular separations that are really efficient. Moreover, they generally possess better natural chemical, thermal and mechanical resistance properties. Their main disadvantages are that they are much more expensive, rendering manufacturing and scale-up possibilities sparse.

Obtained results of inorganic membranes for the separation of MeOH/DMC mixtures via PV are given below in Table 4.

Table 4: Inorganic membranes for MeOH/DMC separation via PV

membrane	feed solution (wt% MeOH)	temperature (°C)	flux (g/m ² *h)	separation factor ($\beta_{\text{MeOH/DMC}}$)	reference
nano-tuned SiO ₂	7	50	3600	156	(Tsuru et al., 2011)
BTESA (acetylene bridged silica)	10	50	3000	120	(Dong et al., 2020)
Ni-BTPA (aminosilica)	10	50	750	280	(Anggarini et al., 2022a)

The results shown in Table 4 above show fluxes and separation factors that are much (much!) higher than for polymeric membranes (Tables 2 & 3), attesting to the efficiency of inorganic membranes. Their selectivity and resistance characteristics inspire awe; however, their costly nature is their drawback. We can however still use some of their advantages without the economic setback.

2.6.3 Mixed matrix membranes (MMMs)

Mixed-matrix membranes (MMMs) uses properties from the two previous families. They succeed in combining the low cost, production ease and scale-up possibilities of the polymeric membrane family with the more efficient selectivity and higher transport rates of inorganic membranes, which have sieve-like properties (Galiano et al., 2016). This is done by dispersing inorganic material within the polymer matrix. A difficulty that arises in the making of these membranes is the homogeneity of the filler's dispersion within the polymeric matrix and compatibility or how well it will adhere to the matrix (Gugliuzza & Basile, 2013). Commonly used inorganic fillers are zeolites, carbon molecular sieves, silica or metal-based frameworks (G. Liu & Jin, 2021; Galiano et al., 2016). Moreover, when in contact with a fluid, MMMs have been shown to be less affected by swelling than their unaltered –polymeric- counterparts (Luis & van der Bruggen, 2015). Results pertaining to MMMs are shown in the following subchapter, in Table 5.

2.7 CHITOSAN MEMBRANES

Chitosan (CS) is a linear semicrystalline polysaccharide comprised of N-acetyl-2-amino-2-deoxy-D-glucose (glucosamine, GlcN) and 2-amino-2-deoxy-D-glucose (N-acetylglucosamine, GlcNAc) residues. It is the deacetylated derivative of chitin, which is mainly found in the exoskeleton of crustacea, but also in algae, fungi cell walls and even the cuticles of insects (Al-Rooqi et al., 2022). A scheme of the structural framework of CS is given below (Figure 9). CS is insoluble in basic media, poorly soluble in neutral media, however, its large number of primary amines on the C-2 position of the glucosamine units make it easily soluble in acid solutions as the amines protonate (Aranaz et al., 2021).

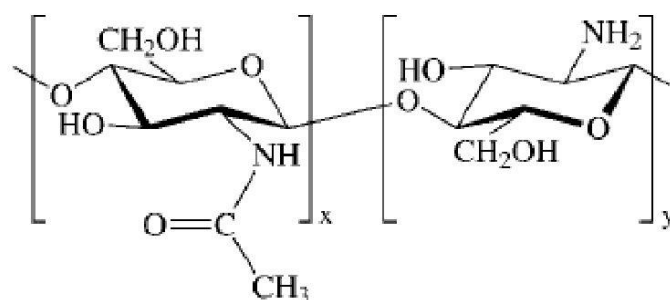


Figure 9: Chitosan molecule if $y > 50\%$ ($x=0$ if chitin is completely deacetylated into chitosan) (Patrulea et al., 2022)

CS has anti-inflammatory, antioxidant, antimicrobial, antifungal and wound healing properties (Aranaz et al., 2021). All of these have caused an increased interest in this biopolymer, however, the most prevalent area of interest in CS remains in material science and its usage as a polymeric membrane in PV has been extensively studied for numerous mixtures, including MeOH/DMC mixtures (Al-Rooqi et al., 2022; Castro-Muñoz & González-Valdez, 2019). It is naturally biodegradable and possesses good hydrophilicity, and overall shows good membrane-forming and chemical stability properties (S. Liu et al., 2022b). A visualisation of pure CS membranes' performances separating MeOH/DMC mixtures at various feed compositions and operating temperatures can be seen in Figure 10, below.

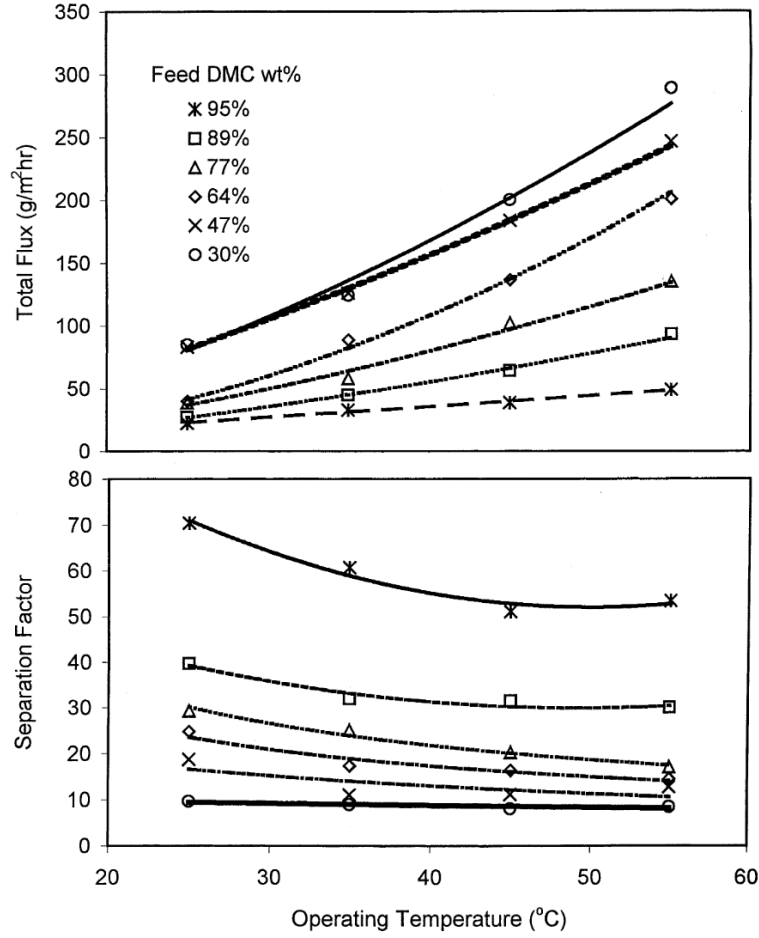


Figure 10: PV separation of MeOH/DMC mixtures at different feed concentrations and operating temperatures using CS membranes (Separation factor = $\theta_{\text{MeOH/DMC}}$) (Won et al., 2002)

The pre-existing data on the separation of MeOH/DMC mixtures via pure CS membranes shows us that it is preferentially permeable to MeOH (Won et al., 2002). At a constant operating temperature, as MeOH's weight percentage increases, flux increases yet the separation factor decreases. Another clear demonstration of the effect of feed composition, as seen in subchapter 2.6.1. Similarly, as the feed composition remains constant and temperature increases, flux increases yet the separation factor decreases. It has been shown that an increase in temperature favours the increase in the partial flux of DMC more so than MeOH's.

As per Luis (2018), it has been shown that permeability and temperature are dependent on each other via the following Arrhenius equation:

$$\frac{P_i}{l} = \frac{P_{i\infty}}{l} \exp\left(-\frac{1000E_a}{RT}\right) \quad (5).$$

Where $\frac{P_{i\infty}}{l}$ is the permeance value given for temperatures nearing infinity and E_a is the pervaporation activation energy of the permeable compound. The E_a can be described as the sum of the sorption enthalpy and the activation energy of diffusion. The E_a measures how sensitive the component's permeation is to temperature. If the E_a is negative, the equation tells us that permeance is set to decrease while temperature increases. However, if the E_a is positive,

the permeation process is said to be controlled by diffusion (Verhoef et al., 2008, S. Zhang et al., 2017). This rise in temperature might lead to the preferred diffusion of the unwanted component in the mixture as seems to be the case here (Adymkanov et al., 2008).

Temperature also affects the vapour pressure of components. As was seen in equation (2) the driving force through the membrane uses component activity which is directly correlated to vapour pressure (section 8.2.1.1, equation (A12)). In the latter formula, P_i^0 is the saturated vapour pressure which can also be calculated via the Antoine equation:

$$P_i^0 = 10^{\left(A - \frac{B}{C+T}\right)} \quad (6).$$

where A, B and C are specific parameters to a component and T is the temperature (Z. Wang et al., 2022). Via the latter equation, we can see that when temperature increases, the vapour pressure will also increase, resulting in a greater driving force. This directly leads to an increase in transmembrane flux. Lastly, a change in feed composition has been shown to directly influence the temperature effect as the component's sorption and diffusion kinetics will have changed (Smitha et al., 2004).

2.7.1 Mixed Matrix Chitosan Membranes

Although CS membranes show overall good performance when it comes to the MeOH/DMC mixture, it has been demonstrated that adding inorganic material to CS can increase its selectivity and overall thermal and mechanical stability (Castro-Muñoz & González-Valdez, 2019). Materials such as silicates, titanosilicates, multiwalled carbon nanotubes (MWNTs), graphene oxide (GO), zeolites, metallic-organic frameworks (MOFs) and more have been inserted into CS with conclusive results (Hung et al., 2017; Langari et al., 2018; Zhao et al., 2013). However, this being an emerging class of membrane, available scientific literature concerning mixed matrix CS membranes isn't vast and mainly addresses water-organic mixtures (Jia & Wu, 2016b; S. Liu et al., 2022b). The Table A1 in section 8.1.3 demonstrates a variety of these fillers inserted within CS, the different mixtures that were separated (MeOH/DMC mixtures excluded) and their astonishing results. Expectedly, both fluxes and separation factors are greater when compared to no inorganic filler being present. However, most impressive is the extent of this increase in performance. The median flux had increased by a factor of 1,39 whereas the median separation factor had increased by a factor of 6,17. This paves a very promising future for PV using mixed matrix CS membranes.

Concerning MeOH/DMC mixtures being separated by mixed matrix CS membranes, available scientific literature is sparse. Below, Table 5 incorporates all the results pertaining to all types of CS membranes and MeOH/DMC separation, ranging from pristine (pure) CS, crosslinked CS, to MMMs and MOF-CS membranes.

Table 5: Chitosan membranes used for MeOH/DMC separation through pervaporation

membrane	feed solution (wt% MeOH)	temperature (°C)	flux (g/m²*h)	separation factor (β _{MeOH/DMC})	reference
Pristine CS					
CS	30	30	170	28	(J. H. Chen et al., 2007)
	30	40	220	22	
	30	50	259	16,6	
	50	50	252	15,8	
	70	50	300	13,5	
Crosslinked CS					
CS crosslinked with H ₂ SO ₄	29	25	81	38	(Won et al., 2003b)
	29	35	122	31	
	29	45	170	22	
	29	55	215	19	
	52	55	370	13	
	70	55	498	9	
Mixed matrix CS					
CS- silica crosslinked with APTEOS	30	30	890	49	(J. H. Chen et al., 2007)
	30	40	1050	45,3	
	30	50	1158	41,4	
	50	50	1125	39,4	
	70	50	1275	29,8	
Hollow fiber CS (CSHF)	13	50	150	22,8	(Xiao et al., 2010)
	70	50	510	5,1	
Silicatungtic acid hydrate (STA) filled CS crosslinked with GA	10	50	1030	90,5	(J. H. Chen et al., 2016)
	70	50	1290	63,3	
STA filled CS crosslinked with GA (using cardo-polyetherketone (PEK-C) substrate	10	30	910	120,3	(J. H. Chen et al., 2016)
ZSM-5 zeolite into chitosan	70	55	990	2,4	(B. Liu et al., 2007)
MOF CS					
UiO66-CS MOF	10	50	355	337	(Zhu et al., 2022)
ZIF 8 - CS MOF (30 μm)	3,8	50	84,2	66	(X. Xu, Hartanto, et al., 2022)
(40μm)	3,8	50	45	71,2	

In the table above, we can observe the effect that feed composition and temperature have on the membrane's performance. Secondly, the positive impact crosslinking has on a membrane's performance cannot be underestimated. Thirdly, the addition of inorganic material generally increases both flux and the separation factor. Lastly, as can be seen at the very bottom of the table, the membrane's thickness also has an effect.

The scientific consensus seems to be that with greater membrane thickness comes greater selectivity yet a poorer transmembrane flux due to permeation resistance (Jyoti et al., 2015; Baker et al., 2010). Membrane thickness is a key factor in the trade-off between permeability and selectivity in the decision-making process of membrane production. As very selective membranes often possess low permeability (and are therefore not very productive) and conversely, productive membranes are not very selective (Gugliuzza & Basile, 2013; X. Xu et al., 2022). Moreover, Qunhui et al.'s study (1995) showed not only that a CS membrane's selectivity increased with the membrane's thickness, but that swelling decreased as the membrane got thicker.

2.7.2 MOF Chitosan membranes

Our attention will now be focused on one particular subset of MMMs, namely metallic-organic frameworks (MOFs). The use of MOFs (which are also known as porous coordination polymers (PCPs)) has steadily increased as they counteract the limitation set by the inherent trade-off between the permeability and the selectivity of a polymer. They decrease a polymer's tendency to swell and also increase their durability (as organic vapour has been shown to inflict damage to some polymers - this is called physical aging) (C. Zhou et al., 2004). They are one of the latest organic-inorganic hybrid materials to be used in separation processes. The nodes (metal ions or clusters) form coordination bonds with linkers (organic ligands) thus creating uniform cavities within their structure. This is exactly how they differ to zeolites (which are solely composed of inorganic materials) as MOFs possess this organic-inorganic duality (X. Xu et al., 2022). MOFs thus offer more flexibility as their framework structures can endure guest-induced modifications which is much more complicated on rigid, covalent bond-based structures such as zeolites. Moreover, MOFs possess a considerably larger surface area than zeolites (Krishna, 2015). These changes, as well as the versatility of the many existing metal ions and organic ligands, can be used to obtain more selective separations through the range of different pore size frameworks that can be created chemically (Krishna, 2015; Mí Nguéz Espallargas & Coronado, 2018).

There are two types of MOFs: pure MOF crystalline membranes and particulate filler MOFs which will be inserted within a polymer. We will concentrate on the latter.

MOFs increase a membrane's performance in three ways. Firstly, the coordination complexes form crystals that act as channels or nanopores, creating the molecular sieve effect inorganic membranes are distinguished for. This thus leads to the desired molecules in the mixture to pass through the latter pores, leading to higher selectivity (X. Xu et al., 2022). Secondly, a certain MOF can have preferential affinity to one of the compounds, increasing preferential adsorption to the membrane. Thirdly, they can enlarge a polymer's matrix free volume improving general permeation, this could lead to a decrease in selectivity, however (Y. Li et al., 2016a; X. Xu et al., 2022). Additional (yet weaker) mechanisms enabling MOFs to separate compounds in a

liquid mixture via pervaporation also exist. These mechanisms are induced by the MOF's electric field, namely physisorption and induced dipole moments. Supplementary information regarding this is given in section 8.1.4.

As of yet, the following metallic ions that have been used for the development of MOF CS membranes are: zirconium-based (UiO-66, MOF 801); iron-based (MIL-53); zinc-based (ZIF 7, ZIF 8) and aluminium-based MOFs (DUT-5, Al(OH)(MBA)]-(CYCU-7), Al(OH)(SBA)]-(CAU-11)) (Kachhadiya & Murthy, 2023; Kang et al., 2013; Q. Li et al., 2017; F. Wu et al., 2017a; X. Xu et al., 2022).

Other metals that have been used for the synthesis of MOFs in the literature are copper, europium, chromium, nickel, titanium, samarium and cobalt (X. Xu et al., 2022). As of yet, only two MOF-based MMM CS membranes have been developed for the separation of MeOH and DMC, they are UiO-66 and ZIF 8 (Zhu et al., 2022). The wide range of different affinities between metal ions and linkers creates numerous possible pore sizes which offers some customizability in relation to the mixture that needs separating which is why MOFs are garnering increasing attention in molecular separation techniques.

However, preparing MOF MMMs has its challenges as both the polymer and the MOF's properties need to be taken into account. For example, if the metal ion shows poor compatibility with the polymer matrix, this can result in the metal ion's nanocrystals being dispersed heterogeneously within the polymer, they can agglomerate creating interfacial voids which will then decrease selectivity as the pores may become too wide (Y. Li et al., 2016b).

2.7.2.1 *In-situ MOF synthesis*

To mend this shortcoming, a novel way of developing MOFs has come to light whereby they are directly synthesized within the matrix. This has been shown to drastically reduce the nonselective voids between the MOF and the polymer matrix and be a more sustainable method of MOF production as less solvents are used (H. Zhang et al., 2014).

MOFs are generally produced in the following manner. Firstly, there is inorganic material dissolution. A stirring and/or centrifuging step is often necessary as the organic precursor is added to the solution hereafter. The organic linkers thus attach to the metal ions. Subsequently, the unreacted solvents are evaporated, a washing step is then present to purify the generated particles. The generated MOF particles are then dried. The MOFs are then ready to be inserted within a polymer (this step is called 'blending') (X. Xu et al., 2022; Y. Zhang et al., 2016a).

In-situ MOF precipitation bypasses most of these latter steps. The inorganic precursor is dispersed in an aqueous phase, and the organic precursor is dispersed in an organic phase. The polymer is dissolved within one of these solutions, thereafter the two solutions are mixed. As both the organic and inorganic precursors meet, they generate MOFs directly into the polymer. This technique allows for greater MOF particle content and interfacial voids - that are commonly found when solid MOFs particles are inserted within the polymeric solution - are avoided (X. Xu et al., 2022; H. Zhang et al., 2014).

The in-situ precipitation of calcium phosphate (CaP) within CS is discussed in Park et al.'s article (2017) as to test its viability as bone cement. The CaP nanoparticles formed as KH_2PO_4 and $\text{CaCl}_2 \cdot \text{H}_2\text{O}$ were added to dissolved CS (in 2% acetic acid). In Nie et al.'s (2020) article, ZIF-8 MOFs were generated within CS to assess their potential as hazardous particulate matter removers in the air. CS was dissolved in a 2% acetic acid solution, to which $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was added. A mixed solution of NaOH and methylimidazole was prepared on the side. The latter solution was then added dropwise in the CS solution. ZIF-8 precipitated within the latter solution. CS served as an economical retainer of the MOF particles, reducing particle destruction or wastage as its synthesis was both more efficient and facile as compared to the conventional MOF synthesis techniques. Y. Zhang et al. (2018) also developed in-situ ZIF-8 MOFs within CS and showcased its efficiency as a copper adsorber. As of yet, no articles pertaining to in-situ MOF synthesis within CS for PV applications can be found in literature. Mao et al. (2019) do however discuss the in-situ synthesis of ZIF-8 within PDMS for ethanol-selective PV.

2.7.2.2 Cobalt formate MOF

Within the vast families that belong to the MOF group, metal formates ($\text{M}_3(\text{HCOO})_6$) have proved to be advantageous in the following ways: their preparation conditions are relatively easy and they are low cost (Z. Wang et al., 2007). Metal ions that have been used to create metal formates are manganese, iron, cobalt, nickel, zinc and magnesium, the linker used is the formate anion. They all share the same MOF structure. The metal ion (M) forms a tetrahedron with four other metal ions (MM_4), and each of those latter metal ions have an octahedral geometry. Moreover, when the metal formates superimpose, they form channels in a zigzag fashion. Figure 11 below shows the metal formate family framework.

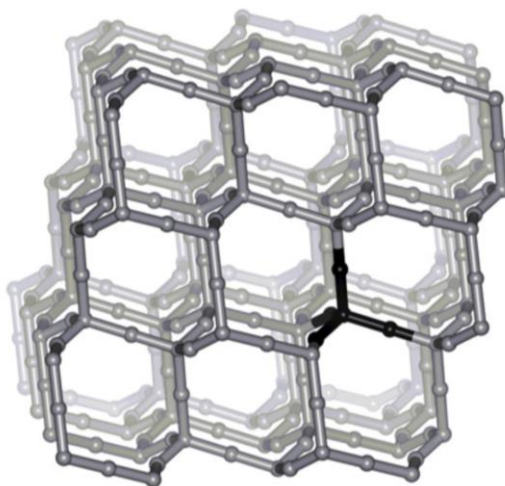


Figure 11: Metal formate diamondoid framework (Z. Wang et al., 2007)

The distance between the metal and the formate linker varies on the nature of the metal used, affecting the size of the pore as well as the void space within the framework, as is shown in the Table 6 below. The short nature of the ligand used, in this case formate, is beneficial as they create nanopores possessing strong and thick walls, which emphasizes its porous nature by preventing the architecture from falling upon itself (this is called interpenetration) (Mí Nguéz Espallargas & Coronado, 2018; Z. Wang et al., 2005).

Table 6: Summary of $[M_3(\text{HCOO})_6]$ porosity measurements (Ar adsorption) (Hu et al., 2016)

Metal formate	BET surface area (m^2/g)	micropore volume (cm^3/g)	pore diameter ($\text{\AA}$)
$[\text{Mg}_3(\text{HCOO})_6]$	307	0,108	4,9
$[\text{Mn}_3(\text{HCOO})_6]$	271	0,098	5,5
$[\text{Co}_3(\text{HCOO})_6]$	296	0,102	4,6
$[\text{Ni}_3(\text{HCOO})_6]$	233	0,087	4,3

Cobalt formate (Co FA, $[\text{Co}_3(\text{HCOO})_6]$ or $[\text{Co}(\text{HCOO})_2]$) has already been used in a vast array of preferential adsorption tests such as xenon/krypton, acetylene/ CO_2 and methane/ N_2 as well as methane/ CO_2 separation (Hu et al., 2016; H. Wang et al., 2013; Z. Wang et al., 2005; X.-J. Zhang & Chen, 2022).

Throughout such experiments, the following data have been revealed. Co FA has proved to be easily preparable chemically and its porous structure stays intact up to 220°C and starts decomposing at 260°C , proving excellent thermal stability (Z. Wang et al., 2005, 2007). Beyond its general robustness, Co FA hasn't yet shown any preferential affinity towards peculiar compounds, be they polar or non-polar, only its framework size seems to be the limiting factor for component separation (Mí Nguéz Espallargas & Coronado, 2018).

However, it is for the following reasons that it is interesting to think about using Co FA specifically as a MOF in a CS membrane.

Based on the adsorption tests used, Co FA's pore size ranges from $4,6 \text{ \AA}$ to $5,5 \text{ \AA}$ which makes it ideal for a MeOH/DMC mixture as MeOH's kinetic diameter is smaller and DMC's is bigger. This metal formate framework would thus act as a preferentially selective size sieve to MeOH (Hu et al., 2016; Z. Wang et al., 2005; Zou et al., 2011).

Secondly, of all the metal formates that have been investigated, only Co FA has been used as a filler in a polymeric membrane to separate an organic-organic mixture. Indeed, Y. Zhang et al.'s (2016) study showed that the toluene/n-heptane (aromatic/aliphatic) mixture could be separated using Co FA within a poly(ether block amide) (PEBA) membrane through PV. The addition of Co FA, which was blended into the polymer, made the latter more robust, it had increased its fractional free volume and increased its affinity to the aromatic compound, enhancing solubility. As compared to a pristine PEBA membrane, the addition of Co FA increased the permeate's flux as well as its separation factor. However, when the overall weight percentage (loading) of Co FA within the polymeric membrane was too high, the separation factor decreased (as flux increased). When Co FA's concentration was too high within the membrane, the filler particles aggregated provoking this decrease in selectivity. It should be stated that, in this case, Co FA was not used for the aromatic compound to pass through as the size of its pores would be too small. It was used as a polarizer of the aromatic pi-bond to increase the membrane's affinity with toluene (as was discussed in section 2.4). Improving the membrane's affinity to toluene and increasing its fractional free volume enable it to have a higher flux than other MOFs tested on this mixture and its separation factor was competitive with other MOFs and remained the cheaper option.

2.7.3 Cobalt-ion coordinated chitosan

Despite its numerous assets, the stability of Co FA crystals is not yet known within a CS solution. Direct metal-ion coordination to CS has however already been studied. Such polymers containing metal centres are also called metallopolymers.

The hydroxyl group in the C3 position on the glucosamine and, more importantly, the amino site on the glucosamine are both nucleophilic and have both been shown to be reactive for metal ions (Ramos et al., 2003). High purity CS will lead to more chelation due to the higher number and better distribution of the amino groups, as compared to chitin. The process is dependent on the pH of the solution but also on the nature of the cation. The latter will determine the ease of the interaction mechanism. At a pH of 5, we can see, on Figure 12 below, the affinity between a CS film and different metal cations (Rinaudo, 2006).

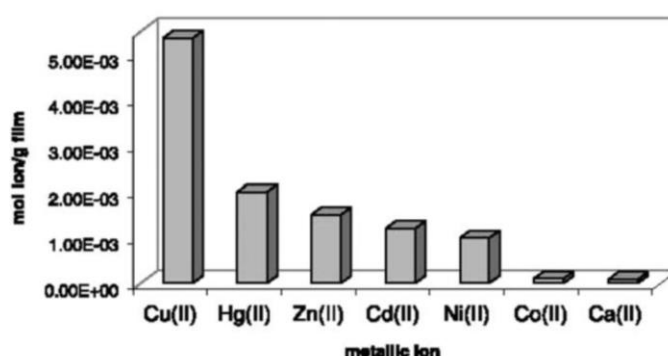


Figure 12: Cation selectivity of chitosan (mol of divalent cations fixed per gram of chitosan film) (Rinaudo, 2006)

Based on XPS and electrical conductivity data, the cobalt-chitosan coordination polymer has been shown to have the chemical structure shown on Figure 13, below. The cobalt divalent cation is surrounded by two CS units, and it has a coordination number of four within the CS polymer (Huai-Min & Xian-Su, 2004; Ravishankar & Dhamodharan, 2020).

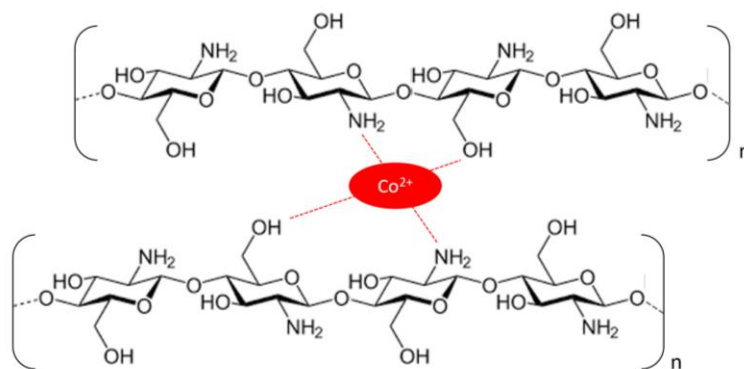


Figure 13: Chemical structure of cobalt-ion coordinated chitosan (Ravishankar & Dhamodharan, 2020)

Cobalt- ion coordinated CS has already been used as a catalyst, selectively catalysing the polymerization of vinyl acetate and methyl methacrylate (Götz et al., 2021). There lies, as of yet, the main use of metal-ion coordinated CS polymers. They are most commonly found for their heterogenous catalysis processes. Copper, palladium, nickel, cobalt and ruthenium have been used within CS to catalyse reactions such as ring-opening metathesis polymerization for olefins, aminations, Suzuki cross-coupling, cycloadditions, etc. The improved polymers'

durabilities, due to the crosslinking, and the ease with which it is possible to recuperate the metal catalyst via filtration are also frequently mentioned. More recently, metal-ion coordinated CS polymers have been used as novel drug delivery mediums. However due to CS's efficient tendency to absorb these metals, CS is thus more often used as a cation removal medium from industrial sewerage or wastewater (Lima & Airoidi, 2004).

More generally, metallopolymers have a wide array of uses that span from optical electronics (as they can both harvest and emit light), stimuli-responsive (thermal, redox, etc) or self-assembling polymers, biomedicine and, as we saw earlier, catalysis (Götz et al., 2021). As the possible uses for this type of polymer is ever growing, we can note one recent CS related example where it selectively separated ions based on their size and charge. Copper-coordinated CS was used as a high-performance hydroxide exchange membrane (which is used to transport anions between electrodes in fuel cells). It enabled rapid ion transportation while exhibiting excellent hydroxide conductivity at ambient temperature. Additionally, the incorporation of the Cu^{2+} coordination increased the membrane's mechanical durability (M. Wu et al., 2022).

The use of metallopolymers in pervaporation has not been the focus of much research as of yet. Most of their applications are related to the desulfurization of petroleum products. They have been shown to be particularly adept at facilitating the transport of thiophene across the membrane, a heterocyclic compound with one sulfur atom whose lone electron pair interacts with the metal ion's unoccupied orbitals. Such membranes include silver-coordinated PDMS or copper, lead or manganese-coordinated poly[bis(p-methyl phenyl) phosphazene] (PMePP) (S. Liu et al., 2022c).

Within inorganic membranes, metal coordination has already been proven to be effective in separating organic-organic mixtures. Bis [3-(trimethoxysilyl)propyl] amine (BTPA) is an amino functional silane; it has both amine and methoxy groups that are attached to its silane core. BTPA will thus show more affinity to polar compounds. Via pervaporation, BTPA separated a 10 wt% MeOH/toluene (azeotropic) mixture at 50°C with a separation factor of 442 and a flux of 40 g/m²h (Anggarini et al., 2021). Additionally to its greater affinity with MeOH as toluene (similarly to DMC) is a polar aprotic solvent, BTPA's microporous structure will inherently facilitate the diffusion of methanol as compared to the cumbersome aromatic hydrocarbon.

However, the addition of nickel was shown to form bonds with BTPA's amino units that act as robust ligands with electron-donating properties. Crosslinking BTPA, nickel enabled the membrane to be more stable and to better regulate its micropore framework. Ni-coordinated BTPA increased the flux from 40 to 2800 g/m²h and its separation factor from 442 to 907 (Anggarini et al., 2021).

Based on these promising results, Anggarini et al., (2022b) used Ni-BTPA, and two other nickel-coordinated amine functionalized organosilica membranes, namely trimethoxy [3-(methyl amino)propyl] silane (MAPTS), and 3-aminopropyl triethoxy silane (APTES), to separate a 10 wt% MeOH/DMC mixture at 50°C in his following study. They added different molar ratios of nickel to the membranes, and their results are shown in Table 7 below.

Table 7: Nickel-coordinated organosilica membranes' performances in MeOH/DMC separation through pervaporation (Anggarini et al., 2022b) (number next to the membrane refers to the molar ratio of Ni/membrane)

membrane	feed solution (wt% MeOH)	temperature (°C)	flux (g/m ² *h)	separation factor ($\beta_{\text{MeOH/DMC}}$)
Ni-BTPA 0,5	10	50	750	280
Ni-MAPTS 0,25	10	50	1750	13
Ni-MAPTS 0,5	10	50	570	11
Ni-APTES 0,25	10	50	980	39
Ni-APTES 0,5	10	50	24100	2,57

Firstly, we observe that the separation factor of Ni-BTPA 0,5 has decreased from 907 for toluene to 280 for DMC. The size of the pores within the membrane will be less efficient in separating MeOH from DMC as the latter's kinetic diameter is smaller than that of toluene. The difference in performance between the different types of organosilica membranes can be explained via their chemical structures, shown below in Figure 14 (when they are coordinated with nickel).

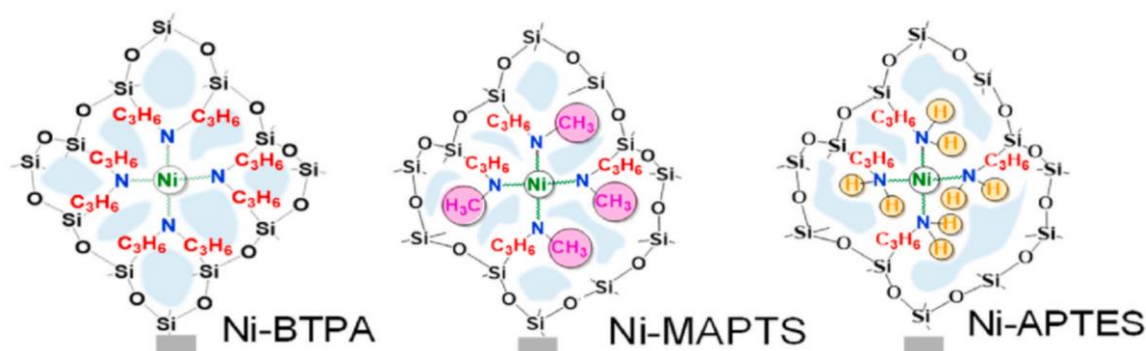


Figure 14: Chemical structures of Nickel-coordinated amine-functionalized alkoxysilanes: BTPA, MAPTS and APTES (Anggarini et al., 2022b)

BTPA has a pore size of 0,46 nm. MAPTS and APTES have relatively smaller pores sizes, being 0,44 nm and 0,41 nm respectively. APTES and MAPTS would thus be more efficient than BTPA in separating MeOH from DMC had they not been coordinated with nickel. However, the nickel coordination is hindered by their basicity. APTES has a primary amine group as compared to BTPA and MAPTS which possess secondary amine groups. The nickel cation will thus link preferentially to BTPA (most stable secondary amine, thus more basic) and then MAPTS. Moreover, the presence of the unattached methyl groups in Ni-MAPTS reduces the selective transport of MeOH as the pore sizes are wider, as compared to Ni-BTPA. Lastly, we observe that increasing the concentration of nickel for Ni-APTES leads to a decrease in performance. Due to the poorer chemical affinity between the nickel cation and its less basic primary amine groups, the nickel will tend to agglomerate and form larger interparticle pores leading to non-selective diffusion (Anggarini et al., 2022b).

However, Anggarini et al. (2021) also show through organic-vapor isotherm tests that the membrane's MeOH adsorption capacity increased as the concentration of nickel dopant increased. They ascribe this adsorption increase to the change in the lone pair of electrons that is found on the nitrogen. As the metallic cation coordinates with the amine, the cation's lower electronegativity will have an electron-withdrawing effect which, as a consequence, leads to the nitrogen's lone pair being more susceptible to interacting with polar compounds. As per their findings, the membrane thus becomes more hydrophilic, facilitating the sorption of MeOH. For Ni-BTPA, this enabled a strong polarization for MeOH, with its adsorption to the membranes increasing roughly linearly to nickel concentration.

We have thus seen that membranes separating the MeOH/DMC mixture via pervaporation can also benefit from metal-coordination, making the membranes both more hydrophilic and their polymer matrix more size selective through crosslinking. The addition of cobalt to CS has been shown to be both easily attainable and to enhance its mechanical and physical properties leading to increased stability and reusability (Begum et al., 2021). Although the use of metallopolymers in PV has only been shown for inorganic membranes, cobalt-ion coordinated CS could prove to be an effective inorganic filler for the separation of the MeOH/DMC mixture.

To summarize and conclude this literature review, we should highlight the fact that CS has proved to be naturally successful in separating MeOH/DMC mixtures through PV (Won et al., 2002). The separation performance of membranes can however be enhanced by the addition of inorganic fillers such as MOFs. More sustainable MOF synthesis techniques such as in-situ synthesis are gaining more traction. Metal formates are cheap and stable, which is promising for the conception and development of new MOF-based mixed matrix membranes. Y. Zhang et al.'s (2016b) study discussing Co FA – specifically – shows it has the ability to be a filler within a polymeric membrane. Although its results are promising for aromatic/aliphatic mixtures, Co FA's MOF pore size could prove to be a valuable asset in the separation of MeOH/DMC mixtures. It remains to be seen whether this MOF can be synthesized within a CS solution or whether cobalt-coordinated CS will be obtained.

3 OBJECTIVES & STRATEGY

This master's thesis is inspired by the preliminary work done by Xiao Xu. Also focusing on the separation of the MeOH/DMC mixture, his work has shown that inserting a MOF within CS, namely ZIF-8, or Zeolitic Imidazolate Framework-8, greatly enhanced its separation properties with conclusive and impressive results. The three-dimensional inorganic porous structure with uniform, well defined, pore sizes enabled a separation factor superior to 70 (and selectivity of 11,2) towards MeOH, inverting the molar ratio of the binary mixture from a 10:90 molar percentage ratio of MeOH/DMC feed to a ~90:10 molar ratio permeate.

3.1 OBJECTIVES

The aim of this work is firstly to see whether the addition of cobalt to CS will lead to an improvement in the membrane's ability to separate the MeOH/DMC mixture. The intention is to synthesize in-situ Co FA MOFs within CS as opposed to adding already-made crystals to the biopolymer. Developing Co FA crystals directly into a CS solution has never been tempted before. In the event that MOF formation does not occur, the speculated alternative is the formation of cobalt-coordinated CS, which could also be effective due to its crosslinking capabilities. The consequences of the metal coordination on CS's hydrophilicity would have to be assessed.

Ultimately, the aspired objectives this thesis at answering can be presented as the following questions:

- Will cobalt crystals form within CS?
 - If so, will homogenous cobalt formate MOFs develop within CS membranes?
 - If not, what will be the architecture of the filler within the CS membrane?
- Will the resulting membrane show more affinity towards MeOH or DMC?
- Will the cobalt loaded membranes improve upon a pure CS membrane's performance regarding the separation of the MeOH/DMC mixture through pervaporation?
- How will an increase in cobalt loading affect all these prior questions?

3.2 RESEARCH STRATEGY

The protocol that was developed to synthesize cobalt formate MOFs within CS will be explained in the following chapter. Once the membranes were made, they were tested within the set up to see whether they positively or negatively affected the separation of the mixture, as compared to a pure CS membrane that was tested beforehand.

As they had a positive effect, the proportion of filler loading was gradually increased as to assess the cobalt filler's impact on the separation of the mixture.

Subsequently, the membranes underwent different membrane characterization techniques in order to obtain as much information as possible concerning the nature of the filler particle within the membranes.

4 MATERIALS & METHODS

4.1 CHEMICALS

A low molecular weight (50 -190 kDa) chitosan – Poly (D-glucosamine) (C₁₂H₂₄N₂O₉) powder from Sigma-Aldrich (USA) was used (Product number: 448869 ; CAS number: 9012-76-4).

Cobalt (II) acetate tetrahydrate powder ((CH₃COO)₂Co · 4H₂O, > 98%) (molecular weight: 249.08 g/mol), which can be seen on Figure 15 below, was obtained from Sigma-Aldrich (USA) (Product number : 403024 ; CAS number: 6147-53-1).

Formic acid (HCOOH, 98-100%) (molecular weight: 46,03 g/mol) was purchased from Merck (Germany) (Product number: 100264 ; CAS number: 64-18-6).

Methanol (CH₃OH, 100%) (molecular weight: 32,04 g/mol) was obtained from VWR International (Belgium) (Product number: 1060351000 ; CAS number: 67-56-1).

Ethanol euro-denatured³ (C₂H₅OH, 99%) (46,07 g/mol) was obtained from VWR International (Belgium) (Product number: 85823.360 ; CAS number : 64-17-5).

Sodium hydroxide pellets (NaOH, 98,9%) (molecular weight: 40,00 g/mol) were purchased from VWR International (Belgium) (Product number: 28244.262 ; CAS number : 1310-73-2).

Dimethyl carbonate (C₃H₆O₃, 99%) (molecular weight: 90,08 g/mol) was purchased from Alfa Aesar (Germany) (Product number: A13104 ; CAS number : 618 – 38 – 6).

Polyacrylonitrile (PAN) (100kDa) flat ultrafiltration hydrophilic membrane from Snyder Filtration (United States) (Product number: 10338 ; P.W.T. ID : 1.14) and served as the support of the synthesized composite membrane.

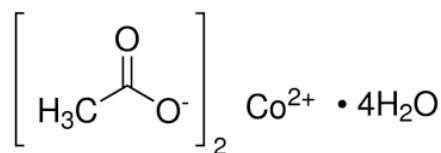


Figure 15: Cobalt acetate tetrahydrate molecule

4.2 MEMBRANE

4.2.1 Membrane synthesis

Firstly, a 2% HCOOH solution is prepared by mixing 10g of HCOOH in 490mL of deionized water. 24,5g of the 2% HCOOH solution is then mixed with 24,5g of MeOH in a sealed glass jar. 0,042g of (CH₃COO)₂Co·4H₂O is dispersed within the aforementioned solution. This is mixed using a magnetic stirrer at 500 rpm for 120 minutes. Subsequently, 1g of CS powder is added to the solution. It is then mixed at 500 rpm using a magnetic stirrer for 180 minutes.

³ The denaturant is in compliance with European legislation (1% isopropanol, 1% methyl ethyl ketone and denatonium benzoate) (*Éthanol Eurodenatured* ≥99 %, *TechniSolv*® (1 : 1 : 1), 2023).

A 1 molar NaOH solution is prepared by mixing 20g of NaOH pellets in 500mL of deionized water in a graduated cylinder (which is sealed). This basic solution is mixed at 300 rpm using a magnetic stirrer and heated at 30°C. A sheet of PAN membrane is placed within this heated basic solution for 90 minutes. Through this process, the PAN membrane develops a yellowish tint. This is an indication that PAN hydrolysis has occurred. The nitrile bonds in the polymer backbone are broken, leading to the formation of carboxylate groups. This chemical modification of PAN makes it more hydrophilic. Subsequently, the PAN membrane is placed in another graduated cylinder, full of deionized water, for 120 minutes, to rinse it. The water within the cylinder is changed every 40 minutes.

The PAN membrane is then placed on a clean glass plate. Stainless steel retainer rings (diameter: 10,9 cm – height: 3 cm) are placed atop the PAN membrane. 5,25g of the cobalt-CS polymer solution is weighed and poured and spread evenly within the retainer ring. The retainer rings are covered with paper towel to avoid dust from setting on the membrane. The cobalt-CS polymer solution - atop the PAN polymer - then goes through a 48-hour room-temperature drying process. This enables the membrane to set and the HCOO-MeOH solvents to evaporate.

All weighing is done using an analytical balance (DeltaRange® AE260 Mettler, from Mettler-Toledo, United States). The magnetic stirrer used is a Bioblock Scientific, AM 3003 control. All these experiments are done under a fume hood.

Once the drying and evaporation process is terminated, the resulting MOF-based MMM layer is solid and has completely adhered to the PAN membrane. The cobalt-CS membranes are then carefully cut out from their retainer rings using a razor blade knife and placed in airlocked bags with 5mL of MeOH to avoid them bending and twisting upon themselves. The bags are then labelled with their date of production, their loading percentage and kept in a dark storing unit at room temperature until they are used.

The cobalt loaded CS membranes' loading percentage is defined as follows:

$$w_{Co-lid} = \frac{m_{Co-lid}}{m_{CS} + m_{Co-lid}} \times 100\% \quad (7).$$

Where w_{Co-lid} represents the amount of cobalt loading, m_{Co-lid} represents the mass of cobalt acetate tetrahydrate powder put into the solvent and m_{CS} represents the mass of CS.

In the aforementioned experiment, the cobalt loaded CS membrane's particle loading was 4%. In this thesis, the following cobalt loaded particle loadings were made and tested: 0%, 4%, 8%, 12%, 16%, 20% and 24%.

4.2.2 Membrane characterization

To undergo characterization techniques, free-standing membranes need to be made. These consist of the same polymer solution however in this case, they are not poured over the PAN composite membrane as the latter would tamper the characterization results. The polymer solution is directly poured in their retainer rings on cellophane and then left to dry. They are then cut out using a razor blade knife. The dried polymer solution detaches itself naturally from the cellophane. These free-standing membranes then underwent the following characterization techniques to describe the physical and chemical attributes of the membranes that are made.

4.2.2.1 XRD

X-ray diffraction (XRD) is a non-invasive method that presents the crystallographic structure, and physical properties of the subjected material. The latter is exposed to incident X-rays. The intensities and scattering angles that emanate from the material are then measured and can be correlated to known diffraction peaks to determine the chemical composition of the material (Hilal et al., 2021). Membranes, the CS powder, the cobalt acetate tetrahydrate powder and the formed crystals (section 4.3) were placed on a polymethyl methacrylate (PMMA) sample holder. The membranes were also ground into a powder using a pestle and mortar. The powdered membranes also underwent XRD analysis. A Bruker *D8 Advance* X-Ray diffractometer (Germany) with cobalt radiation, $\lambda = 1,78897 \text{ \AA}$, in the 5° to 100° range (step size = $0,02$; time step = $2,4$ seconds) was used. Diffrac.EVA software was used for result analysis.

4.2.2.2 SEM

Scanning Electron Microscopy (or SEM) uses a focused electron beam that interacts with the sample to generate a topographical image of the sample's surface. The surface can be magnified at the nanometre scale (Hilal et al., 2021). Double-sided adhesive tape was placed on a metal sample holder. Both membranes and powders were deposited on it. To analyse the membrane's cross-sections, the membranes were put into liquid nitrogen for 30 seconds and were then torn in half. The new perpendicular cut of the membrane that stems from this tear is analysed. A Balzers Union FL9496 Balzers *SCD 030* (Principality of Lichtenstein) sputter coater was used to deposit a thin layer of gold and palladium under vacuum on the membranes on the sample holder. A Zeiss *UltraTM 55* (Germany) Scanning Electron Microscope, with an Electron High Tension (EHT) (electron gun voltage) of $3,00 \text{ kV}$, was used.

4.2.2.3 EDX

Energy-dispersive X-ray spectroscopy (or EDX) is an analytical method utilized for the elemental analysis of materials as an electron beam from the SEM excites the sample, where excited atoms emit X-rays specific to the corresponding element (Hilal et al., 2021). EDX can measure the elemental composition at concentration levels above $0,1\%$. It was used for qualitative analyses and to detect possible contaminations on the membranes. A Bruker *123eV* (Germany), High Voltage (HV): $10,0 \text{ kV}$; Working Distance (WD) $7\text{-}8\text{mm}$, was used. The EDX spectroscope and was included in the Zeiss SEM.

4.2.2.4 FTIR

The Attenuated Total Reflection - Fourier Transform Infrared Spectroscopy (ATR - FTIR) technique enables the identification of chemical bonds within a molecule through the generation of an infrared absorption spectrum (Hilal et al., 2021). A Thermo Scientific *NicoletTM iN10* (United States) infrared microscope, with the ATR collection mode was used. The detector was cooled using liquid nitrogen. The wavenumber analysis ranged from 4000 cm^{-1} to 600 cm^{-1} , and a germanium ATR tip was used for this analysis (64 scans, aperture width: $150 \text{ }\mu\text{m}$, aperture height: $150 \text{ }\mu\text{m}$). Omnic Picta software was used for result analysis.

4.3 CRYSTAL SYNTHESIS

0,4421g of cobalt acetate tetrahydrate was placed in a glass jar containing a 35g 2% HCOOH and 35g MeOH solution. Its lid was placed upon it but was not sealed. The jar was placed in a Pyrex bowl containing heating oil. The latter was placed on the magnetic stirrer (300 rpm) and heated to 90°C for 48 hours. When small amounts of solvents were left, the magnetic stirrer's rotating speed was decreased to 100 rpm until all the solvents had evaporated. The crystals were then collected and also underwent the characterizations techniques listed in the section above. For FTIR analysis, the crystals were ground with KBr powder using a pestle and mortar to disperse the material and offer an inert structural support. The homogeneous powder was then put into a mould and turned into a solid pellet using a manual press. Transmission-FTIR analysis was used utilizing the same Thermo Scientific microscope (and software) under the same conditions as the membranes.

4.4 PERVAPORATION

4.4.1 Experimental set-up

One litre of liquid feed is poured in a 1,5 L feed tank. A heating bath (Julabo heating bath with an internal pump and stirrer, model *MA*, Germany) is used to set and control the temperature within the feed tank. The feed is transported from the tank to the membrane holder via a circulation pump (Speck Pumpen Systemtechnik GmbH, Germany). This circulation pump also serves in bringing the retentate back to the feed tank. The membrane cell (constructed by Sulzer Chemtech AG, Switzerland) possesses a metal porous disc that serves as a support for the PV membrane that is to be made and placed atop it. A vacuum pump is used to create a vacuum on the permeate side of membrane holder (model *VE235D*, from Thermo Fischer Scientific, United States). This helps the permeate travel to the ethanol-filled cold trap bath (Witeg, model *WCT-80*, Germany). A temperature sensor (Digitalthermometer *GMH 3230* from GREISINGER Electronic, Germany) controls the temperature in the membrane holder. A pressure sensor (model *DVR2* provided by VACUUBRAND, Germany) controls the pressure on the permeate side of the membrane holder and a flow rate meter at the entrance of the feed tank (*DK34* from KROHNE Messtechnik GmbH, Germany) is also used. The setup is schematised on Figure 16, below. The operating conditions are given in Table 8 (p.38).

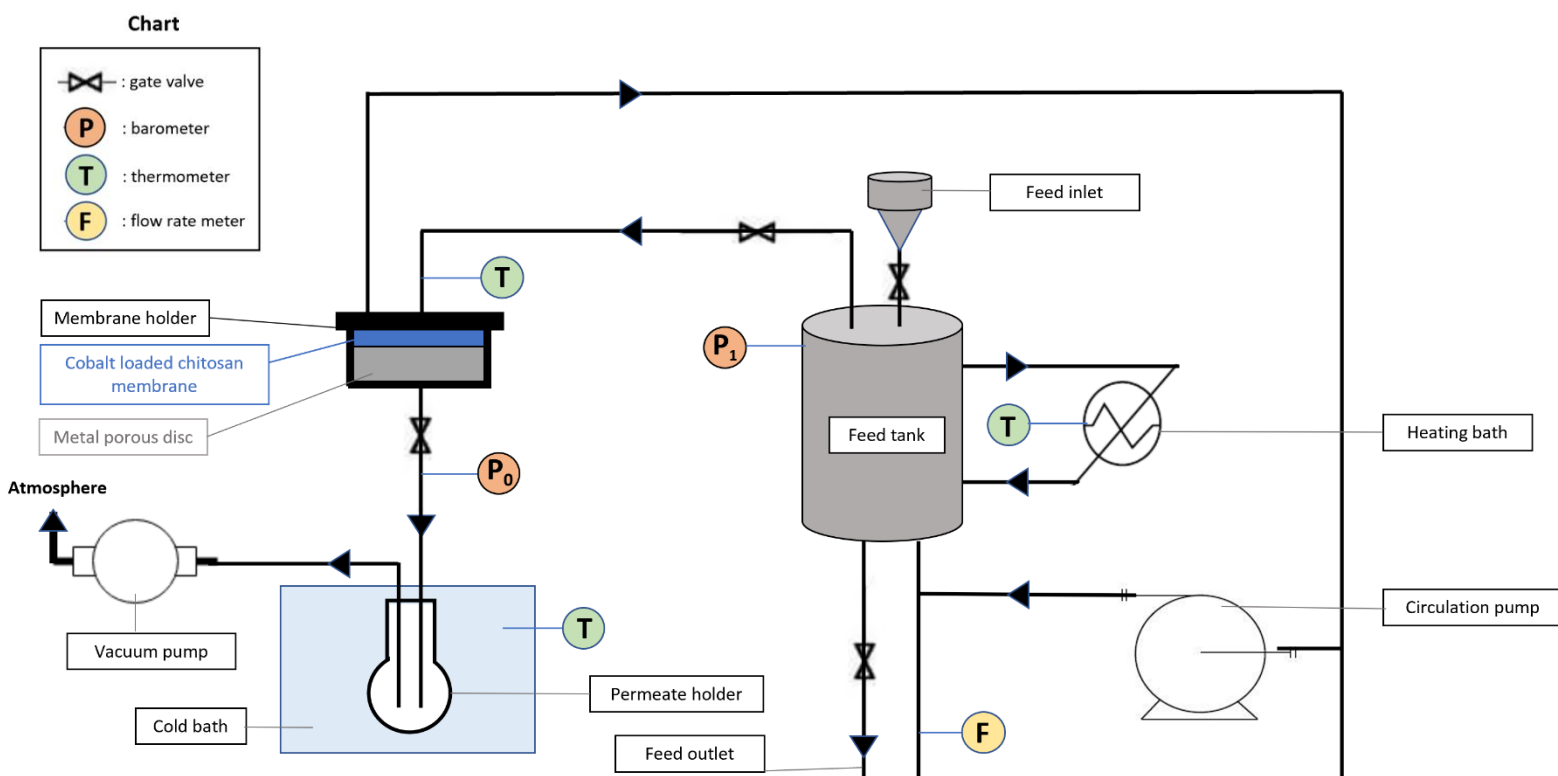


Figure 16: Experimental pervaporation set-up

4.4.2 Membrane preparation

When a membrane is to be tested within the set-up, it is taken from its zip-locked bag and cut to a 7 cm diameter circle using scissors. The membrane is then placed in the membrane holder, atop the metal porous disc that has been previously dried using compressed air. An elastic rubber ring seal is placed around/on top of the membrane to ensure that there are no gaps between the membrane's edge, the metal porous disc and the membrane holder. The vacuum pump is turned on and we wait for the pressure sensor to reach 0-2 mbar. This ensures that the membrane is not faulty – i.e., there are no cracks in the membrane and/or that there are no gaps between the rubber ring seal and the membrane holder. Once the pressure is reached, the membrane holder is hermetically locked, and the circulation pump can be turned on. The feed solution is circulated for 60 minutes (at 80L/h) before the beginning of the permeate collection experiment begins.

4.4.3 Feed and permeate analysis

Depending on the membrane, the permeate is collected every 60 to 120 minutes. The permeate sample is weighed using the analytical balance and then analysed using gas chromatography to determine its relative concentrations in MeOH and DMC.

4.4.3.1 Gas chromatography

A Thermo Scientific™ – TRACE 1300 Gas Chromatograph (GC) - with a helium mobile phase - equipped with a flame ionization detector (FID) (air flux: 350 mL/min, hydrogen flux: 30 mL/min, nitrogen flux (carrier gas): 40 mL/min) is used to analyse the relative compositions of MeOH and DMC within the feed and the permeate samples that are collected. The Thermal

Conductivity Detector (TCD) is set at 110°C and the FID is set at 250°C. The packed column is a Stabilwax (Length: 30 m, Internal Diameter: 0.32 mm, DF: 1.0 µm). The feed sample is taken before the feed is poured within the feed tank. The calibration curves enabling us to convert the relative area % to weight fraction % are given in sections 8.2.4 & 8.2.5.

4.4.3.2 Karl Fischer Titrator

Coulometric Karl Fischer titration (899 Coulometer from Metrohm, Switzerland) was done to determine the quantity of water within the pure solvents and the feed mixture. Vials were dried in a 110°C oven for 2 hours to eliminate the moisture within the vials. The dried vials were injected with 2mL of pure DMC, pure MeOH and the feed mixtures. A hermetic cap was then placed upon the vial. Argon, an inert gas, is injected into the headspace of the vial to eliminate the air. 0,1mL of each solution were collected then successively injected into the coulometer. The collected volume is titrated with a solution consisting of iodine and sulfur dioxide. The iodine consumption is proportional to the water content within the sample, when excess iodine is detected, the titration finishes. Built-in software directly gives the water content in ppm.

4.4.4 Membrane solvent uptake

To test the affinity of the cobalt loaded CS membranes with the solvents, solvent uptake tests in pure MeOH and DMC were done. Two separate 1 cm² pieces of every differently loaded free-standing membrane were cut using scissors. Every piece was weighed. One of those pieces was placed in a sealed sample bottle containing 10 mL of pure MeOH, while the other was placed in a sealed sample bottle containing 10 mL of pure DMC. All these sample bottles were then placed in a 50°C oven (WTC Binder model 78532, Germany) for 48 hours.

Thereafter, the pieces were collected from the bottles using tweezers, dried using paper towel and then weighed on the analytical balance. In the meantime, the solvent within the sample bottles was thrown away. The weighed pieces were then put back into their respective empty sample bottle, with the lid being placed upon it, but it was not sealed. The samples went back in the oven for 72 hours at 50°C. Thereafter, they were weighed again.

4.4.5 Separation performance tests

A 10/90 mol% (or 4/96 weight%) MeOH/DMC feed mixture was used to test whether the cobalt loading in a CS membrane had a meaningful effect on the separation process. The different cobalt loadings were tested using the same experimental conditions (shown in Table 8, below). Subsequently, the performances of the membranes were analysed in the PV set-up.

Table 8: Summary of the experimental conditions

symbol	instrument	location	experimental conditions	units
P ₁	barometer	feed	≈ 1000	mbar
F	flow rate	feed	≈ 80	L/h
T	thermometer	membrane holder inlet	50	°C
T	thermometer	heating bath	≈ 55	°C
P ₀	barometer	permeate	< 2	mbar
T	thermometer	cold bath	< - 80	°C

5 RESULTS & DISCUSSION

Firstly, we will present and discuss the results regarding crystal and membrane characterization, then their solubility and affinity towards the solvents present in the mixture. Subsequently, the membranes' performances separating the MeOH/DMC mixture will be presented. Each of these subchapters will be concluded with a brief general discussion.

5.1 CHARACTERIZATION RESULTS

Firstly, the SEM results will be presented in order to visualize the general morphology and distinct surface characteristics of the crystals and the membranes at the micro and nanoscale. EDX will then help us determine and compare - qualitatively - the composition of the membranes. Thereafter, XRD will assess the phase compositions of the membranes. We will thus have confirmation regarding crystal presence or absence within the membrane. Finally, FTIR will ensue to identify the chemical composition and the interactions between the membrane and the added filler. This will enable us to gradually shift our focus from a surface-level understanding to the underlying structure of the developed membranes.

5.1.1 SEM Results

5.1.1.1 Crystals

Below on Figure 17, we can observe the morphology of the cobalt acetate tetrahydrate ($\text{Co}(\text{Ac})_2$). Its particles are significantly large and do not appear to have a clear crystalline symmetry. Their sizes range between $25\mu\text{m}$ and $500\mu\text{m}$.

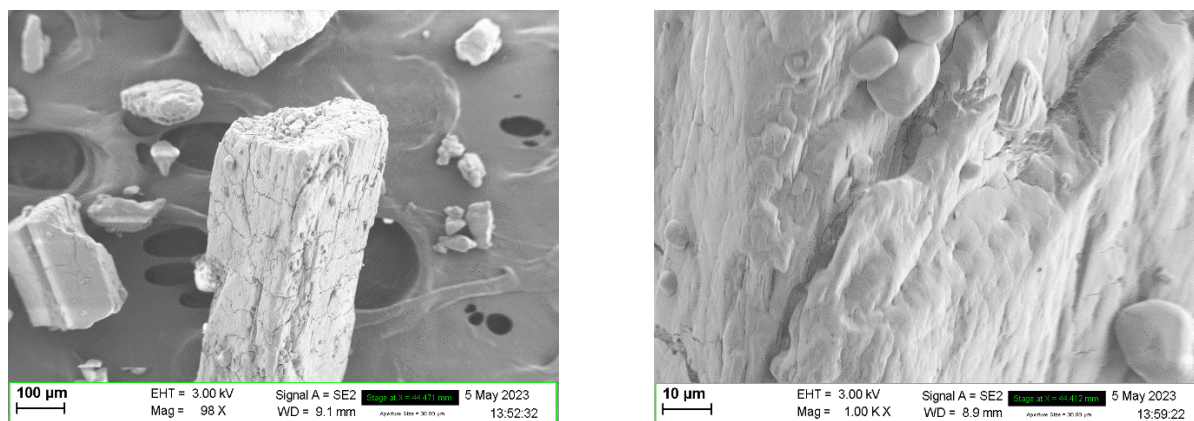


Figure 17: Cobalt acetate - SEM images at 98x [left] and 1 000x magnification [right])

Figure 18 below, shows the dried product of $\text{Co}(\text{Ac})_2$ dissolved in a formic acid/MeOH solution (section 4.3). The resulting particles have a clear crystalline structure. They are much smaller than $\text{Co}(\text{Ac})_2$ particles, ranging from a couple of hundred nanometres to $100\mu\text{m}$ at most. This is believed to be Co FA. However, confirmation regarding its nature cannot yet be determined.

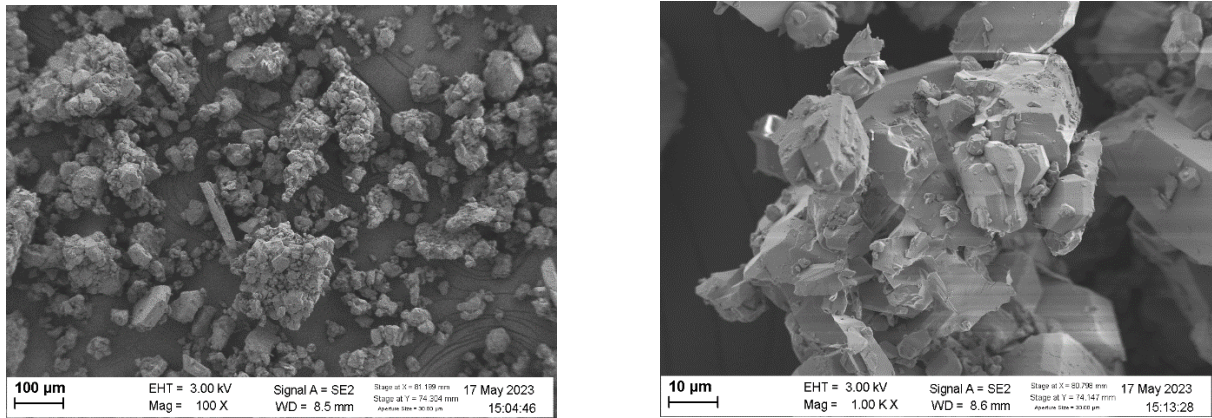


Figure 18: Cobalt formate(?) - SEM images at 100x [left] and 1 000x magnification [right]

5.1.1.2 Membrane surface

On Figure 19, below, are images of the surface of the pristine CS membrane. Its surface is relatively smooth, and no gaps are visible. We observe a homogeneous covering. We have visual confirmation that a CS membrane is dense. There are only a small number of defects or impurities, examples of which could be the white specks on the image on the left. At higher magnifications (image on the right), we can observe the formation of small black cuts which is due to the SEM electron beam interacting more intensely with the sample.

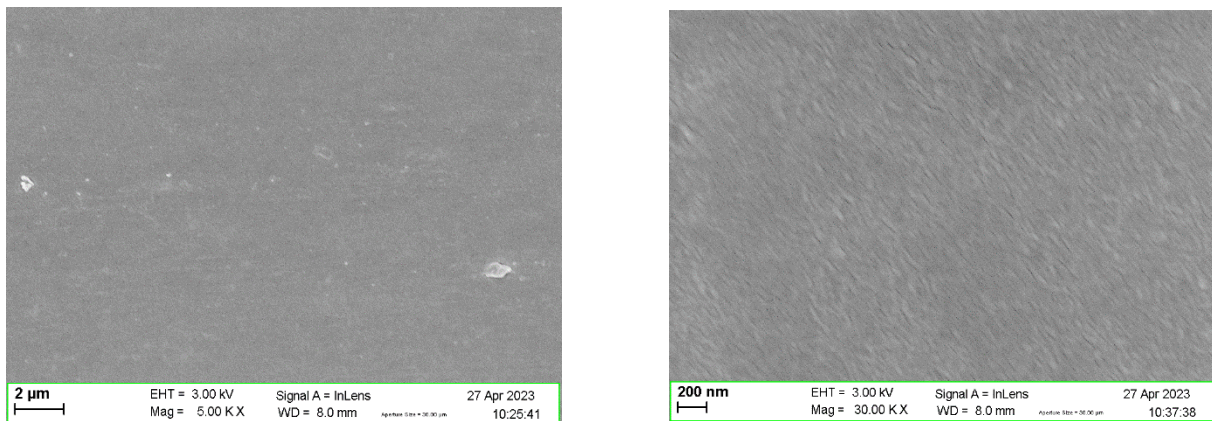


Figure 19: Pristine chitosan membrane surface - SEM images at 5 000x [left] and 30 000x magnification [right]

Figure 20 below, shows the surface of a 20% cobalt loaded membrane. There are no visible differences between the surface of the 20% cobalt loaded membrane and the pristine CS membrane shown above. At higher magnifications, the SEM's production of small black cuts seems to exhibit a decreased rate of propagation.

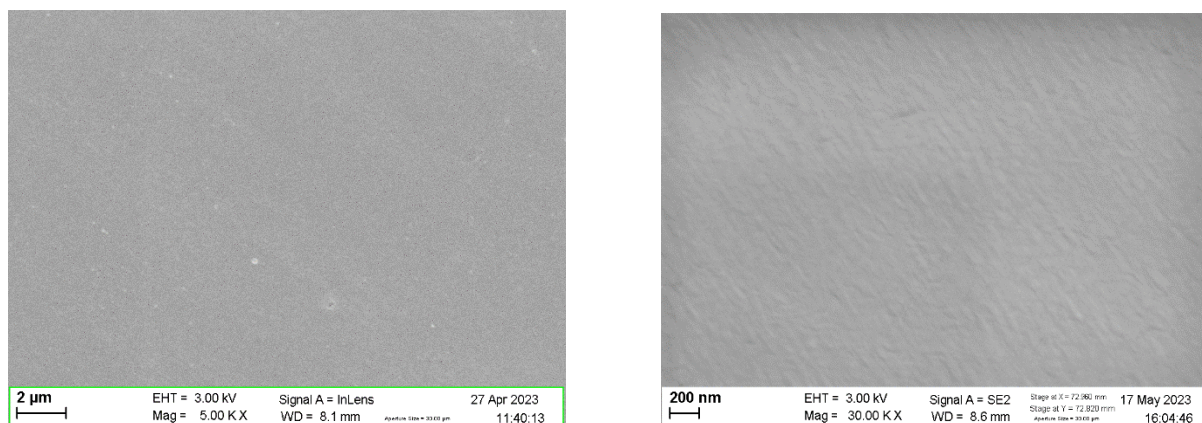


Figure 20: 20% cobalt loaded chitosan membrane surface - SEM images at 5 000x [left] and 30 000x magnification [right]

5.1.1.3 Membrane cross-section

Figure 21, below, shows the cross-section (perpendicular cut through the membrane) of the pristine CS membrane. On the image on the left, going from the bottom to the top of the image, the white section is the adhesive tape that connects the sample to the sample holder, the dark grey section is the membrane's cross-section and the black section at the top is the back of the SEM's platform. On the image on the right, we can visualize more clearly black slits within the membrane, that are parallel to the membrane's surface.

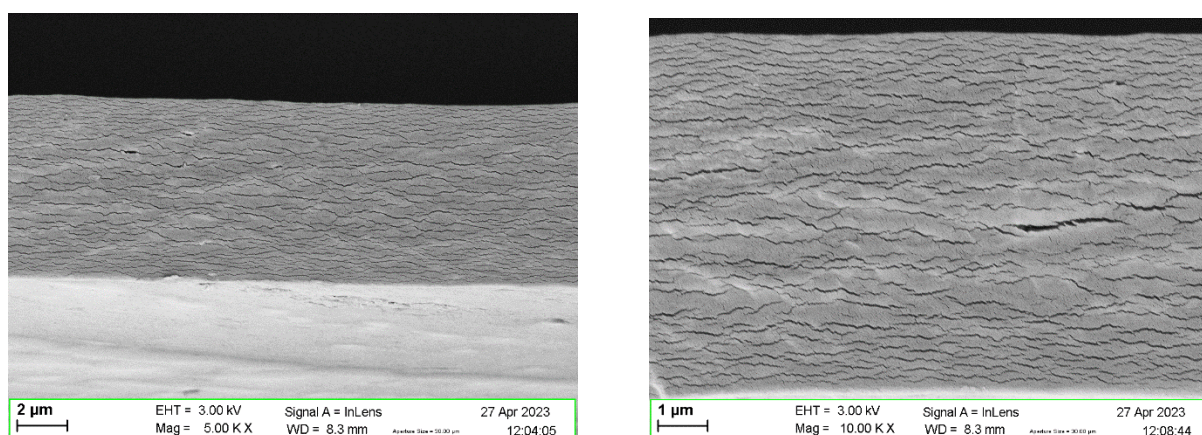


Figure 21: Pristine chitosan membrane cross-section - SEM images at 5 000x [left] and 10 000x magnification [right]

Below, on Figure 22, we can see the cross-section of the 20% cobalt loaded membrane. There are no visible differences between this 20% cobalt loaded cross section and the pristine CS cross-section. On the higher magnification image on the right, we can see, however, that the breadth and extent of these black slits is reduced as opposed to its pristine counterpart.

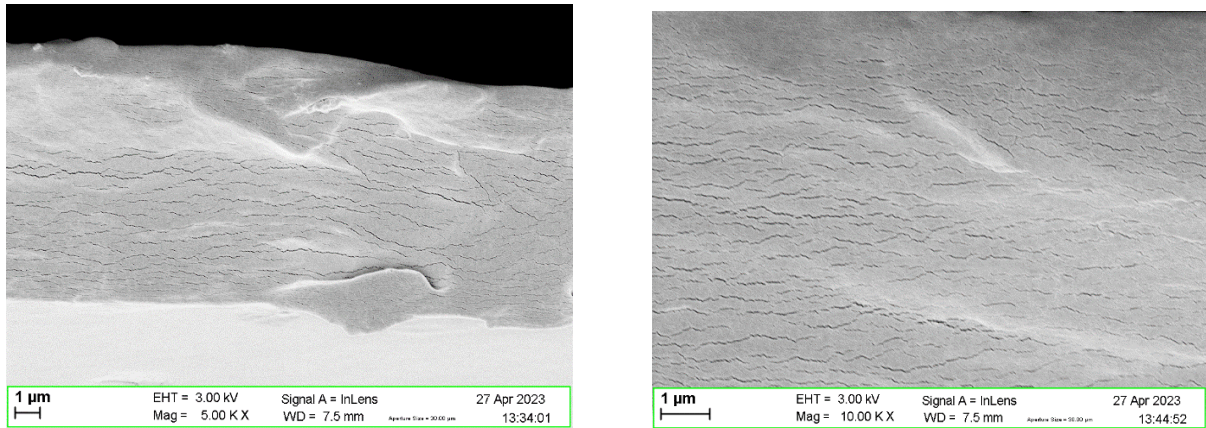


Figure 22: 20% cobalt loaded membrane cross-section - SEM images at 5 000x [left] and 10 000x magnification [right])

5.1.1.4 SEM Discussion

Based on cross-sections of CS membranes found in literature, the black slits we see on Figures 21 and 22 are defects and should not be present. Similarly to its surface, its cross-section should be equally homogeneous (dense). These cracks are most probably present because the membranes were in a dry state for too long before SEM analysis. On Figure 23 below, we can see a SEM image of a cross-section of a pristine CS membrane in a wet state (Silvestre et al., 2022). There are no cracks or slits present. It is dense. Based on the pristine and cobalt loaded CS PV separation tests which will be discussed later, we know that these cracks were not present during PV testing. As had these cracks been present during the PV separation tests, flux would have been much higher and its separation factor and selectivity much smaller. During these PV tests, the membranes were in a wet state. Moreover, we can see below the images that the intensity of the SEM electron beam is set at 10kV for the following sample, whereas the SEM electron beam intensity used for our samples was set at 3kV, which will result in lower electron penetration within our samples. The intensity of the electron beam is thus not to blame for the slit formation in the cross-sections.

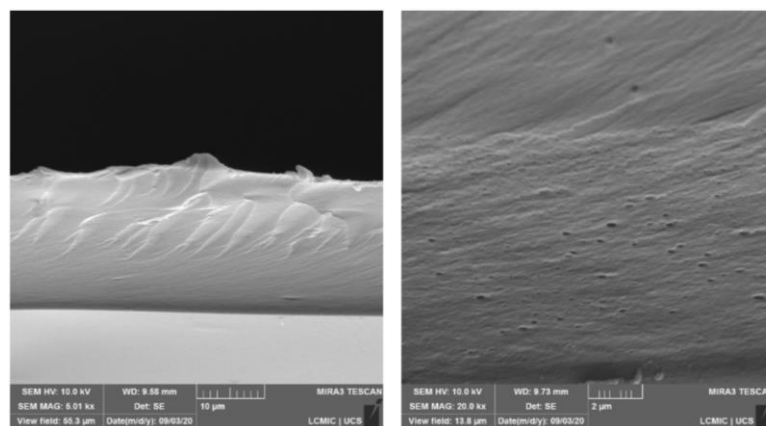


Figure 23: Pristine chitosan membrane cross-section - SEM images at 5 000x [left] and 20 000x magnification [right] (Silvestre et al., 2022)

Based on the similarity between the pristine and the cobalt loaded CS membranes ⁴, we can firstly assume good interfacial compatibility between the added filler and the CS polymer. However, if Co FA crystals were present within the biopolymer, we would expect to see a more substantial difference between the loaded and pristine surfaces and cross-sections. Indeed, as MOFs integrate a polymer, the texture of their surface usually turns rougher. Their structure becomes less dense due to the MOFs disruption in the arrangement of the polymer chains. Our cobalt loaded membranes, on the other hand, consistently have a smooth looking texture. Below, on Figure 24, we can see the rougher texture of a CS membrane once MOFs are present within its polymer chain (X. Xu et al., 2022).

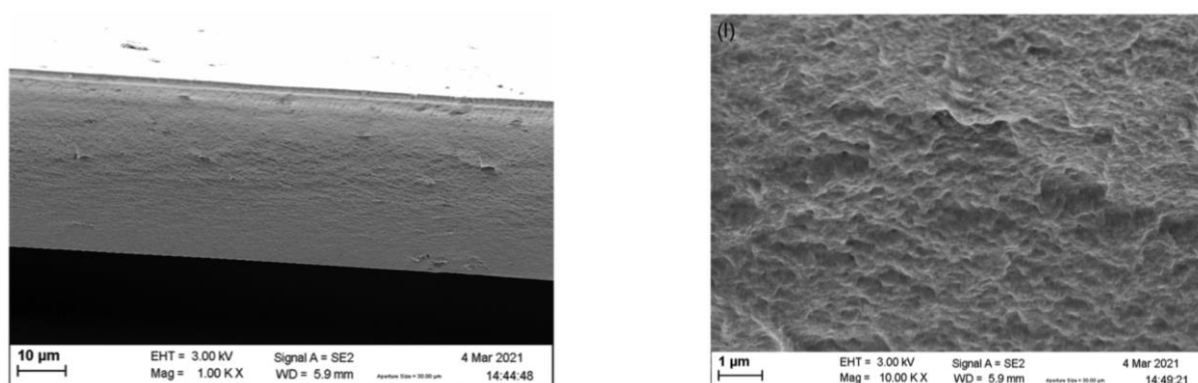


Figure 24: MOF-loaded chitosan membrane (ZIF-8) cross-section - SEM images at 1 000x [left] and 10 000x magnification [right] (X. Xu et al., 2022)

5.1.2 EDX Results

The elemental analysis which the EDX offers allows us to identify qualitatively the different elements that are present within the pristine and cobalt loaded CS membranes. It should be noted however, that its analysis is determined based on a chemical mapping system whereby points are arbitrarily selected on the membrane's cross-section. These chosen points are shown at the top right-side corner of the figures below. The elemental analysis is given as counts per second electron volt (cps/eV) as a function of kilo electron volts (keV). The intensity calculated by the cps/eV calculates the energy distribution of X-ray emissions from the sample. Based on Figure 25, below, we can see that the peak related to cobalt (light blue) for the pristine CS membrane is non-existent. Comparatively, Figure 26, shows two cobalt related peaks (dark pink) for the 20% cobalt loaded CS membrane.

⁴ SEM images of the 4%, 12% and 24% are presented in section 8.3.1. It should be noted that no visible differences were noted between these latter membranes and the pristine and 20% cobalt loaded chitosan membranes.

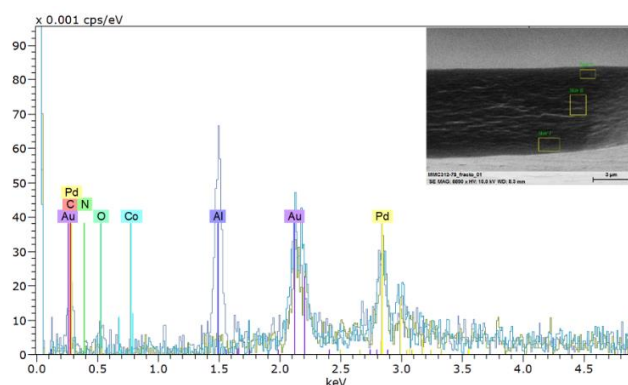


Figure 25: Pristine chitosan membrane EDX analysis [left] - chosen analysis sites on the cross-section [top right]

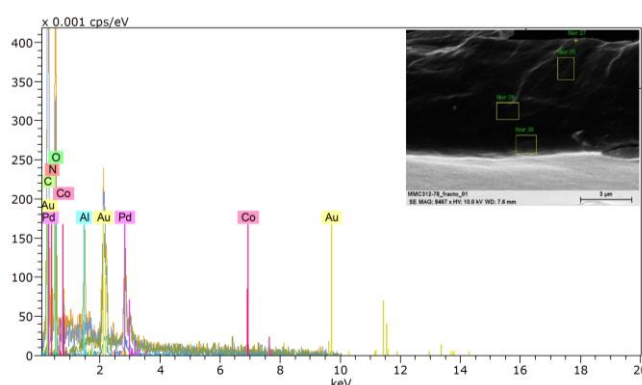


Figure 26: 20% cobalt loaded chitosan membrane EDX analysis [left] - chosen analysis sites on the cross-section [top right]

5.1.2.1 EDX Discussion

Based on the EDX results shown above, we have conclusive proof that cobalt is indeed present within the cobalt loaded membranes, however, we do not know yet under what form. The presence of gold and palladium in all analysed samples is due to the sputter coating that is done before EDX analysis so as to enhance the samples conductivities and to improve the detection efficiency. Aluminium is also detected in every sample. This is most likely a component present in the metal sample holder, which is in very close proximity to the membranes' cross-sections. The fact that no other elements are present indicates that our membranes do not possess many contaminations. The EDX results of the 4%, 12% and 24% are shown in section 8.3.2, however the cobalt related peaks do not show conclusively an increasing linear cps/eV trend based on an increasing amount of cobalt loading within the membrane. This can be due to the shortcomings related to quantitative analysis using EDX. This shortcoming is proved by the differing amounts of carbon and nitrogen which both originate from the CS polymer.

Based on the qualitative analysis of these EDX patterns, we can see that cobalt appears in all selected analysis points indicating that the cobalt filler is uniformly distributed within the membrane. The reason why we can observe two peaks for heavier components (such as palladium, gold, cobalt) is due to the fact that their electrons can reside in various energy levels or shells (Gibson, 2005). Following the EDX's electron irradiation, the resulting X-rays originating from these different levels exhibit different discrete energies. The EDX detects these different emitted X-rays which leads to multiple peaks being observed in the EDX spectrum. This could also be an indicator that cobalt is present in different chemical forms.

5.1.3 XRD Results

5.1.3.1 Crystals

The XRD spectrum of $\text{Co}(\text{Ac})_2$ is shown in section 8.3.3. The XRD analysis of the synthesized crystals confirmed that Co FA was produced. The peaks of the synthesized crystals are displayed in black on Figure 27 below, and the red lines are the indicators of the expected peaks relating to Co FA from the software's data bank. This implies that the overall homogeneity and purity of the synthesized crystals is achieved.

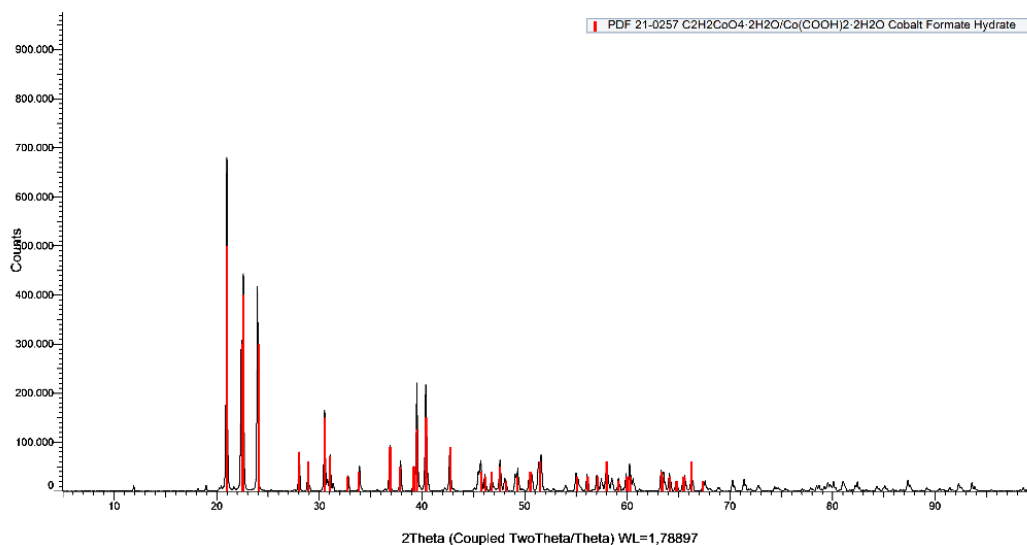


Figure 27: XRD spectrum of cobalt formate

Co FA's prominent XRD peaks can be found at the 20,9; 22,6; 24 (the three most prominent peaks to the left) 30,5; 39,5; 40,3; 42,7 and 51,6 2θ angles which corresponds to what is found in the literature (Ravi et al., 2022) further implying that highly crystalline Co FA was produced, and that impurities are scarce. The d-spacing (an indicator of interplanar spacing within a crystal lattice) for the three most prominent peaks to the left of the figure are 4,9; 4,6 and 4,3 Å which confirm how effective this MOF might be in the separation of the MeOH/DMC mixture as DMC's kinetic diameter ranges between 4,7 and 6,3 Å.

5.1.3.2 Membranes

Firstly, 1cm^2 pieces of free-standing membranes were placed on the PMMA sample holder to undergo XRD analysis. All the differently cobalt loaded membranes were subjected to this analysis. The XRD results of the sample holder (red), pristine CS (black) and 24% cobalt loaded membranes (blue) are superimposed and displayed on Figure 28, below.

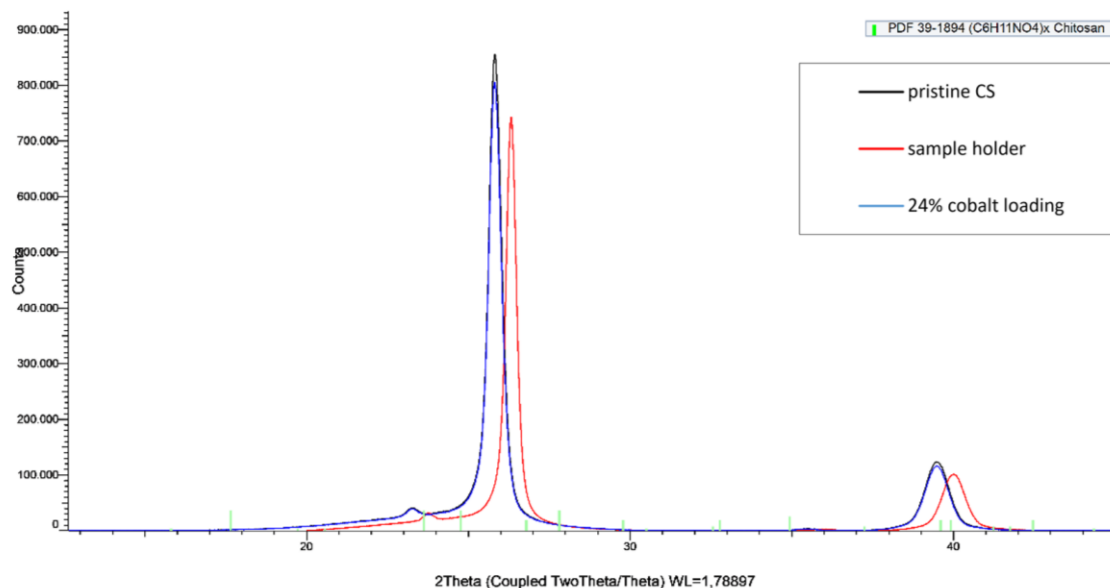


Figure 28: XRD spectra of the PMMA sample holder (red), pristine (black) and 24% cobalt loaded CS membranes (blue)

The sample holder's (red) prominent peaks can be found at the 23,77; 26,32; 40; 56,32 and 63,37 2θ angles. The CS membranes (both pristine and cobalt loaded) share very similar peaks at the 23,25; 25,82; 39,4; 55,9 and 62,95 2θ angles with varying intensities. Both the graph and the 2θ angles indicate that a translation of the PMMA peaks have occurred, as the 2θ angles corresponding to all tested CS membranes (pristine and cobalt loaded) neither coincide with CS related peaks (found in literature) nor Co FA.

The diffrac.EVA software, which uses both peak shape analysis and background subtraction, has failed to discern CS crystalline peaks within the membrane from the PMMA's amorphous phase in the background. The free-standing membranes, being very thin, seem to have increased PMMA's peak intensity and shifted the latter to the left due to the distortion and scattering caused by the "transparent" crystal-free membranes, provoking a misalignment between the planes within the crystal lattice of PMMA (Cappuccio & Letizia Terranova, 1996).

To confirm this, the free-standing membranes were ground, using a pestle and mortar, into a very fine powder to enhance signal intensity. Only the pristine CS, 8%, 16% and 24% cobalt loaded membranes were ground. To compare the pristine CS membranes to the CS powder used to make the membranes, the latter was also analysed within the XRD. The XRD results of the CS powder (black), pristine (red) and 24% cobalt loaded membranes (blue) are shown in Figure 29 below.

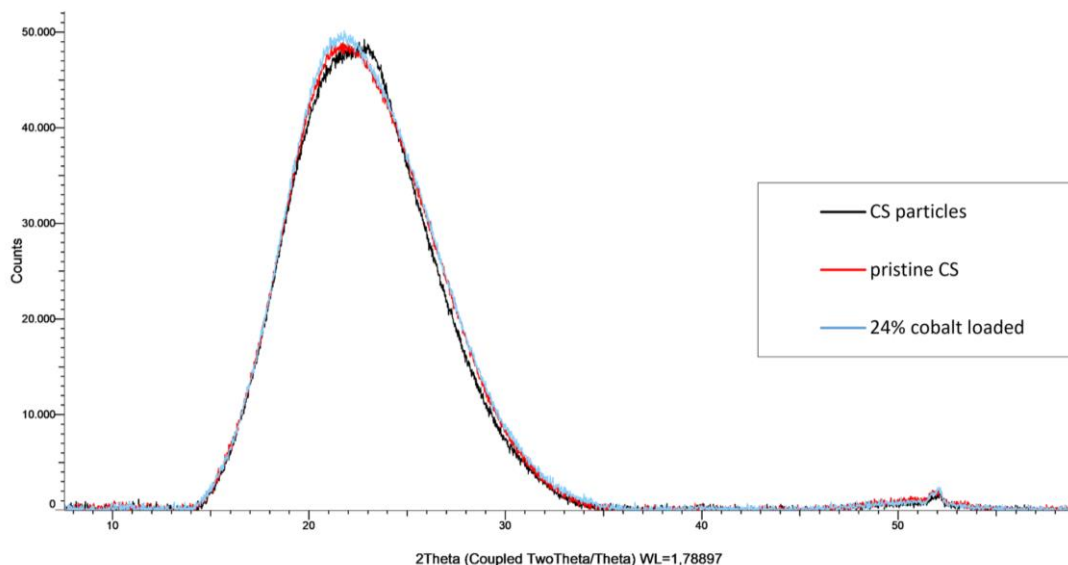


Figure 29: XRD spectra of CS powder particles (black) and grounded pristine (red) and 24% cobalt loaded membranes (blue)

Figure 29 above firstly shows that there is no background noise corresponding to the PMMA-based sample holder as the broad peaks correspond to those attributed to CS's largely amorphous nature (Fu et al., 2023). It also shows that, apart from a slight shift to the left, there is no visible difference between the CS particles used to make the membranes and the membranes themselves. There are two visible amorphous peaks centered near the 22 and 52 2θ angles respectively.

In this case however, the software can distinguish crystalline peaks that can be attributed to CS's semi-crystalline nature. Among the latter peaks, a recapitulative table of the peaks that were common and different between the powder and/or the membranes is shown below, in Table 9.

Table 9: 2θ angles and d-spacing values ($d(\text{\AA})$) of CS powder and grounded membranes (/ signifies the peak is not present)

2θ angles	$d(\text{\AA})$				
	CS powder	pristine CS	8% loading	16% loading	24% loading
11,5	8,894	8,873	/	/	/
21	4,981	4,92	4,901	/	4,902
39,9	/	/	2,618	2,625	2,624
43	/	2,429	2,441	2,421	2,405
47,5	/	/	2,22	2,2	2,229
52	/	2,043	2,037	2,039	2,04
77,2	/	1,434	1,433	/	1,426

Peaks related to 11,5 and 21 2θ angles are the most common polymorphic crystal forms found for CS (Samuels R. J., 1981). We can notice that the first crystal form (the 11,5 2θ angle) disappears once cobalt is inserted within the membrane. We can also notice that the second crystal form (the 21 2θ angle) has disappeared for the 16% cobalt loaded membrane. We can

see that new peaks have emerged at the 39,9 and 47,5 2θ angles when cobalt is inserted. Above the 40 2θ angle threshold, we can see that new peaks have formed for the membranes, however these cannot be found for the CS powder particles.

5.1.3.3 XRD Discussion

The disappearance of the 11,5 2θ angle is commonly attributed to the alteration of the hydrogen bonding between the NH_2 and OH functional groups of CS, which is often synonymous with crosslinking (Devi et al., 2005; Kanti et al., 2004).

The disappearance of the 21 2θ angle for the 16% cannot be explained as empirical data suggests that this peak is omnipresent, as cases where notable usage of glutaraldehyde (one of CS's most widely used crosslinkers) as well as zeolite or MOF insertion within CS do not affect the presence of this peak (Kachhadiya & Murthy, 2023; Sun et al., 2008; W. Zhang et al., 2010). Perhaps the powder for this sample was not ground finely enough.

Generally, comparing the 2θ angles that are only found in both the pristine CS and cobalt loaded membranes, we notice that d-value spacing values decreases. This suggests that a shrinkage has occurred within the inter-segmental space of CS and that there is a general reduction in free volume within the membranes as cobalt loading increases (Devi et al., 2005). This is another sign that crosslinking has occurred.

Only two peaks were found which were also found in Co FA's XRD pattern (at the 39,9 and 47,5 2θ angles). However, their 2,6 and 2,2 Å respective sizes indicate that these would not play any role in size selective sieving, as this is smaller than both kinetic diameters of the components within the feed mixture. The latter peak is attributed to metallic cobalt diffraction peaks which stem from metallic cobalt packed in tight cubic and hexagonal forms (Maekawa et al., 2012). Nonetheless, this added crystallinity might play a role in increasing membrane stability. All of the above suggests that cobalt coordination has occurred. Below, Figure 30 shows the superimposed XRD graphs of Co FA (black), a pristine (red) and 24% cobalt loaded CS membranes (blue). The lack of corresponding peaks related to Co FA within the CS membrane is a clear indication that no Co FA MOF was formed within the membranes.

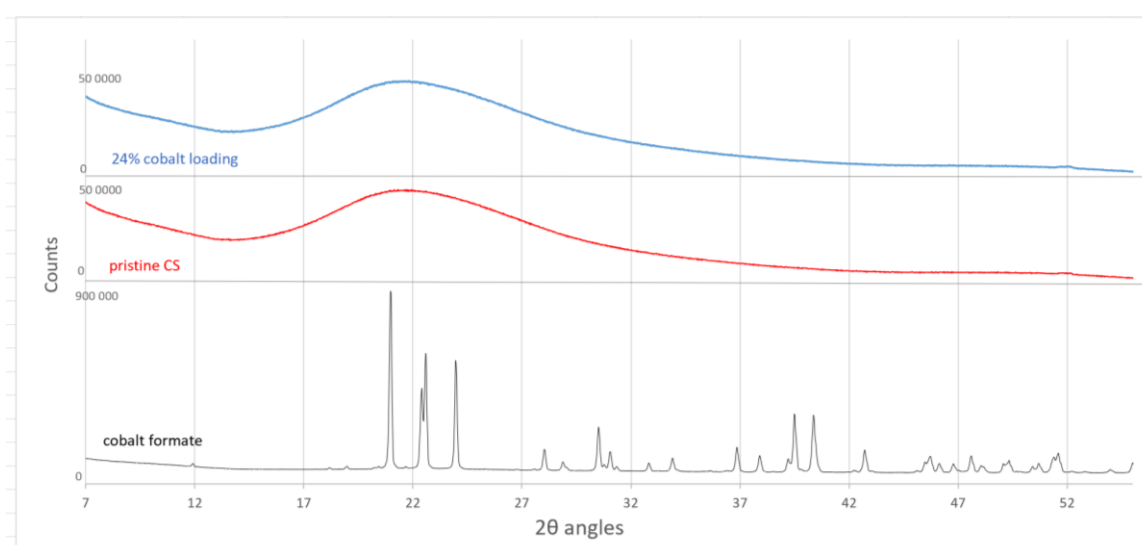


Figure 30: Superimposed XRD spectra of cobalt formate (black), and grounded pristine (red) and 24% cobalt loaded membranes (blue)

5.1.4 FTIR Results

5.1.4.1 Crystals

Below, on Figure 31, are the overlaid FTIR spectra of the Co FA synthesized crystals (above, in red) and the Co(Ac)₂ powder (below, in blue).

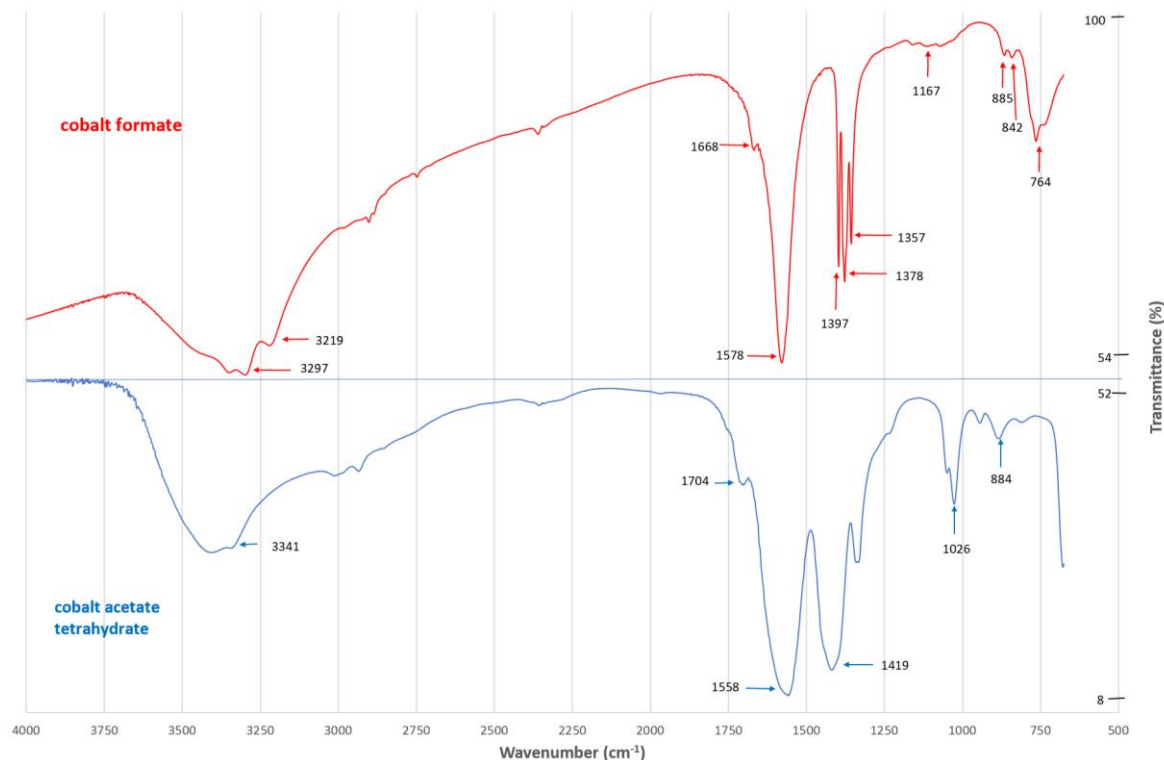


Figure 31: Overlaid FTIR spectra of cobalt formate (red) and cobalt acetate tetrahydrate (blue) powders

Firstly, we can see that the Co FA (red spectrum) FT-IR spectrum is slanted. The baseline should, ideally, be linear. This is probably due to the greater thickness of the Co FA pellet⁵ that was analysed. This results in an instrumental misalignment with the sample.

We may observe the areas that are common to the two spectra. Going from left to the right, we can see the stretching of the -OH group at 3297 and 3219 cm⁻¹ for Co FA and 3341 cm⁻¹ for Co(Ac)₂ (Marins et al., 2020; Wanjun & Donghua, 2007a). We can also see the asymmetric stretching vibration of the -C=O group at the 1668 and 1704 cm⁻¹ wavelength for Co FA and Co(Ac)₂ respectively.

It is striking to see, however, how different the right sides of the spectra are between both samples. For Co(Ac)₂, the 1558 and 1419 cm⁻¹ correspond to the -COO⁻ group adsorption band (Wanjun & Donghua, 2007b). This carboxylate group is represented between the 1397, 1378 and 1357 cm⁻¹ wavelengths for Co FA (Marins et al., 2020). These represent the asymmetric stretching, asymmetric and symmetric bending vibrations of the carboxylate group respectively. Most importantly, looking at the Co(Ac)₂ spectrum, we can see a peak at 1026 cm⁻¹ which

⁵ After having shown me the technique to construct a FT-IR pellet with the cobalt acetate powder, Ms Bebelman let me make the cobalt formate pellet. The corrected baseline version of cobalt formate FT-IR graph is shown in section 8.3.4.

corresponds to the C-C bond of the acetate group. Co FA does not possess such a peak. The 1167 cm^{-1} band most likely represents the wagging of its C-H group.

The 884 cm^{-1} band represents the twisting vibration of water of the tetrahydrate linked to $\text{Co}(\text{Ac})_2$ (Wanjuan & Donghua, 2007b). Whereas the 885 cm^{-1} band represents the twisting of -COH group for Co FA (Marins et al., 2020). It is possible that the 764 cm^{-1} band represents the vibration of the Co-O bond however, it could also be the out of plane deformation vibration of the carboxylate group.

5.1.4.2 Membranes

Below, on Figure 32, are the superimposed FT-IR spectra of a pristine CS (black), a 16% cobalt loaded membrane (green) and a 24% cobalt loaded membrane (blue).

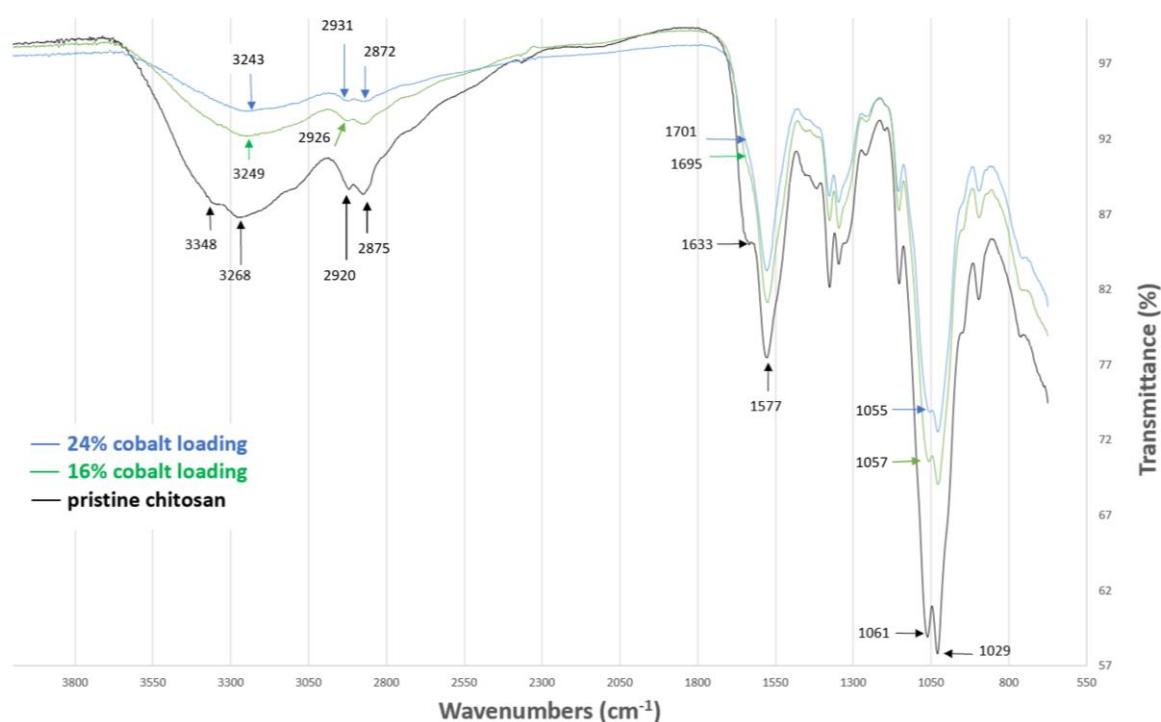


Figure 32: Superimposed FTIR spectra of a pristine chitosan (black), a 16% cobalt loaded (green) and a 24% cobalt loaded membrane (blue)

We shall proceed by analysing Figure 32 above, from left to right. We can see that there no longer exists a second (albeit smaller) peak at 3348 cm^{-1} for the cobalt loaded membranes. A wide peak at 3268 cm^{-1} is seen for the pristine CS membrane. This peak corresponds to the stretching vibration of the $-\text{NH}_2$ group and the asymmetrical stretching vibration of $-\text{OH}$ groups (Eldeeb et al., 2021). Moreover, this wide peak (3268 cm^{-1}) has shifted to the right as loading has increased. This indicates that the vibrational frequencies of these chemical bonds have increased, suggesting that these bonds have become stiffer.

The peaks between 3000 and 2800 cm^{-1} are attributed to the stretching of the C-H bond (Eldeeb et al., 2021). In this region we can see two peaks per spectrum. The 2920 cm^{-1} wavenumber peak which may be ascribed to the symmetrical stretching vibration of the C-H group seems to slightly increase as cobalt loading increases (to 2926 cm^{-1} and 2931 cm^{-1} for the 16% and 24%

cobalt loaded membranes respectively). The second peak, to its right, which can be ascribed to the asymmetrical stretching vibration of the C-H group remains approximately constant as cobalt loading increase (with their peaks being equal to 2875, 2877 and 2872 cm^{-1} for pristine CS, 16% and 24% cobalt loading respectively) (Katare et al., 2023).

Moreover, the peak at 1633 cm^{-1} for the pristine CS membrane has shifted to 1695 cm^{-1} for the 16% loaded membrane and is nearly non-existent for the 24% cobalt loaded membrane. This peak corresponds to the asymmetric stretching vibration of the -C=O group on a primary amide (Eldeeb et al., 2021; X. Wei et al., 2021).

The peak at 1061 cm^{-1} (pristine CS membrane) which is assigned to the secondary hydroxyl group gradually decreases with cobalt loading (with their peaks being equal to 1057 and 1055 cm^{-1} for the 16% and 24% cobalt loaded membranes respectively) (Kumar & Koh, 2012).

Finally, we should also note that the formation of new peaks in low wavenumbers (below 550 cm^{-1}) would be signs of “metal ion – N” and “metal ion – O” bonds (Olanipekun et al., 2021). However, our FTIR analysis does not allow us to visualize these wavenumbers.

5.1.4.3 FTIR Discussion

Firstly, the gradual disappearance of the -C=O group on the FTIR spectra of the membranes is an indication that the CS used is not fully deacetylated and secondly, that cobalt may break the acetyl bond due to its electrophilic nature. Olanipekun et al.'s (2021) study showed this, as adding nickel or copper to carboxymethyl chitosan caused decarboxymethylation.

The shift of the wide peak at 3268 cm^{-1} , corresponding to the stretching vibration of the -NH₂ and -OH peaks and the shift of the peak at 1061 cm^{-1} , assigned to the secondary hydroxyl group, are strong indicators that a compound is interacting with these groups. As per Kumar & Koh (2012); Rashid et al. (2015) and X. Wei et al. (2021), these shifts have also happened when CS coordinated with Cu(II), Ni(II) and Ca(II). This is thus convincing evidence that cobalt is interacting directly with the -NH₂ and -OH groups directly. (The absorption bands of the -NH₂ and -OH groups were found at 3273 cm^{-1} for Cu-CS, 3253 cm^{-1} for Ni-CS as opposed to 3281 cm^{-1} for pure CS). This shift seen on our spectra thus most likely represents the metal ion coordination of CS.

Lastly, were a MOF present within a membrane, characteristic MOF crystal peaks of Co FA would appear on the MOF-membrane spectrum (Jiamjirangkul et al., 2020; Kachhadiya & Murthy, 2023; Silvestre et al., 2022). This is not the case as can be seen on the superimposed spectra of Co FA, pristine CS and the 24% cobalt loaded CS membrane which is presented below on Figure 33. We also know, via the FTIR analysis of the Co FA pellets, that the equipment is responsive to this compound and that the concentration needed for detection is not an issue as the quantity inserted for the formation of the pellets was very small as compared to what was added to the membrane. Had Co FA been present as a MOF crystal, peaks corresponding to its prevalent -COO⁻ group would have appeared (as was seen in its 1397, 1378 and 1357 cm^{-1} bands in Figure 31). We would thus expect transmittance to decrease in percentage in these areas, as is seen in literature when MOFs are inserted within polymeric material, as the MOFs most notable bands appear on the MOF-membrane spectrum (F. Wu et al., 2017b; X. Xu et al., 2022). However, we do not observe this. The opposite is visible, as can be seen in Figure 34 below, where the 1322 cm^{-1} corresponds to C-N stretching vibrations, 1377

cm^{-1} and 1417 cm^{-1} are ascribed to the bending and symmetrical deformation of C-H bonds respectively, as is confirmed in Queiroz et al.'s (2014) study.

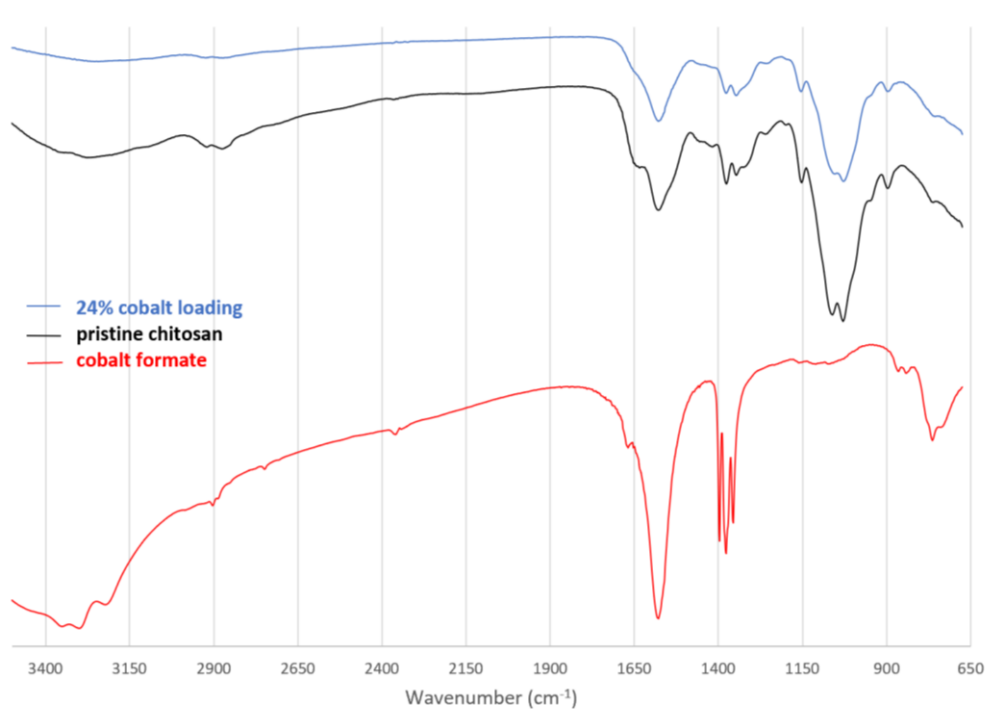


Figure 33: Superimposed FTIR spectra of cobalt formate (red), pristine CS (black) and 24% cobalt loaded chitosan membrane (blue)

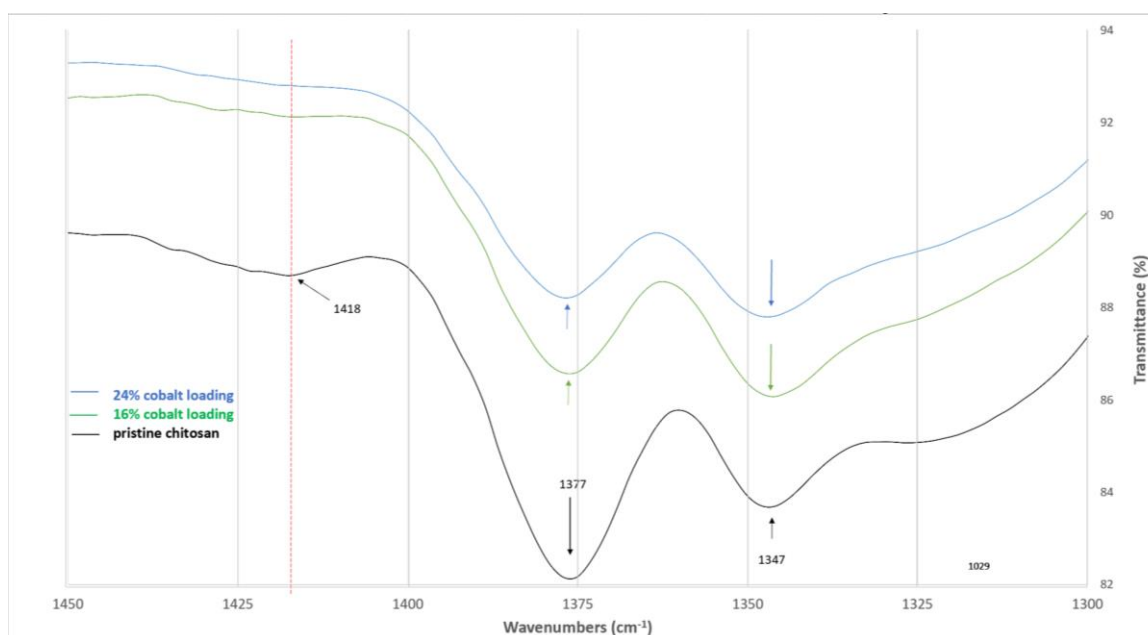


Figure 34: Superimposed FTIR spectra of the pristine and cobalt loaded membrane where bands related to cobalt formate would be present (1450 to 1300 cm^{-1})

5.1.5 General discussion

To determine whether cobalt formate MOFs have been formed within the membranes, a brief summary of the characterization results is presented below.

1. The surfaces of the cobalt loaded CS membranes cross-sections as is seen by the SEM are smooth. This is not expected as the literature states that MOF insertion within membrane yields a rougher texture due to the disruption of the polymer chains. However, the similarity between pristine and cobalt loaded CS membrane does indicate good compatibility between the polymer and the filler.
2. The EDX analysis of the cross-sections demonstrates that the cobalt filler is uniformly distributed within the membrane. No contaminations are present save for aluminium which is due to the membranes cross-sections being in close proximity to the metal sample holder. EDX was used for qualitative analysis of cobalt due to its shortcomings as a quantitative analysis tool for membranes.
3. The XRD analysis proves that Co FA crystals were indeed synthesized. However, the XRD analysis also shows that no peaks related to the Co FA MOF can be found within cobalt loaded CS membranes. The XRD analysis of the membranes reveals the amorphous nature of CS and how cobalt insertion leads to both crystalline peak removal and addition. The disappearance of the 11,5 2θ angle when cobalt was present within the CS membranes is an indication of alteration of the hydrogen bonding between CS's NH_2 and OH groups. The general decrease in d-spacing values for identical 2θ angles as cobalt increases within the membranes are indicators of coordination. Lastly, two peaks found in Co FA's XRD pattern were found within the cobalt loaded CS membranes, however, these were not indicative of the Co FA crystals as the attributed d-spacing values were much smaller than those corresponding to Co FA's MOF.
4. Lastly, FTIR proves that the cobalt filler is definitely interacting with CS's NH_2 and OH groups. Their attributed wavenumbers' progression as cobalt filler increases within the membrane is similar to what has been noticed beforehand when CS is coordinated with metal cations. Bands that are exclusive to Co FA would also be present in the cobalt loaded membranes' FTIR spectra had the MOF been present within the membrane. However, this cannot be seen in our case.

Through the prior characterization analyses, the evidence strongly suggests that Co FA MOFs have not formed within the CS membranes, but that cobalt has coordinated with the CS polymer, acting as a crosslinker.

5.2 SOLVENT UPTAKE RESULTS AND MASS LOSS RESULTS

In membrane science, solvent uptake and mass loss tests are realized to determine and evaluate the affinity and compatibility between the membrane material and the solvents it will separate (Bapat et al., 2021). Through these tests, it is also possible to determine whether a solvent exhibits threats to a membrane, such as its dissolution. Solvent uptake and mass loss will enable us to assess how the gradual increase of cobalt loading within CS will affect its behaviour and affinity towards MeOH and DMC.

The use of Hansen Solubility Parameters (HSP) is widely used and helps predict these interactions (W. J. Lee et al., 2021). It is thus a powerful tool in forecasting and explaining the adsorption and transport of the solvents on and through the membrane respectively. Via the HSP, the solubility interactions can be described using three main parameters: a dispersion component (δ_D), a polar component (δ_P) and a hydrogen bonding component (δ_H) (S. Abbott, 2017). These components are expressed in molar volume and the units used are $\text{MPa}^{1/2}$ ⁶. The distance (R_a) that is calculated is an indicator of the compatibility and solubility between two components (more information is available in section 8.3.5). The lower the R_a value, the more affinity there is between the polymer and the solvent.

In the literature, no HSP for $\text{Co}(\text{Ac})_2$, Co FA and cobalt cations can be found, unfortunately. HSP parameters for ions and other charged species are not conventionally found as their main interaction stems from their electrostatic behaviour, rather than dispersion, polar and hydrogen bonding forces (Kobayashi et al., 2020). The HSP values needed for a better understanding of the solvent uptake and mass loss tests to come are given in Table 10 below. The data within the latter stems from X. Xu et al. (2022).

Table 10: Hansen solubility parameters for pure CS, MeOH, DMC, our feed and their interaction with CS (X. Xu et al., 2022).

	δ_D [$\text{MPa}^{1/2}$]	δ_P [$\text{MPa}^{1/2}$]	δ_H [$\text{MPa}^{1/2}$]	R_a (-CS)
CS	17,8	14,2	24,1	0,0
MeOH	14,7	12,3	22,3	6,7
DMC	15,5	8,6	9,7	16,1
Feed solution	15,5	8,8	10,4	15,5

Finally, temperature is known to strongly affect component affinity toward a membrane, that is why all the following tests were realized at 50°C, the temperature at which the pervaporation separation tests were realized (W. Li et al., 2019).

⁶ The use of $\text{MPa}^{1/2}$ allows to quantitatively assess the strength of the intermolecular forces associated with each parameter in the Hansen solubility parameter system (Abbott, 2017).

5.2.1 Solvent uptake results

The pristine CS and different cobalt loaded CS membranes were immersed into pure MeOH and pure DMC, in sealed bottles in an oven at 50°C for 48 hours. The membranes were dried using tissue paper to wipe off all residual solvent on the membrane's surface. They were then weighed using an analytical balance and their weight is noted as w_1 . The solvent from their bottles was discarded. Thereafter, they were put back into their empty bottles and in the oven for 72 hours at 50°C. The bottle caps were placed upon the bottles but not sealed to let the solvents evaporate. They were then weighed again using the analytical balance, this weight is noted as w_2 .

The solvent uptake ratio is then calculated as follows, as per (X. Xu et al., 2022):

$$\text{solvent uptake (\%)} = \frac{w_1 - w_2}{w_2} \times 100 \quad (8).$$

The results are represented on Figure 35, below. The membranes having been immersed in pure MeOH are displayed in red, whereas the membranes immersed in pure DMC are displayed in green. The error bars represent the standard deviations of each membrane as the test was done twice.

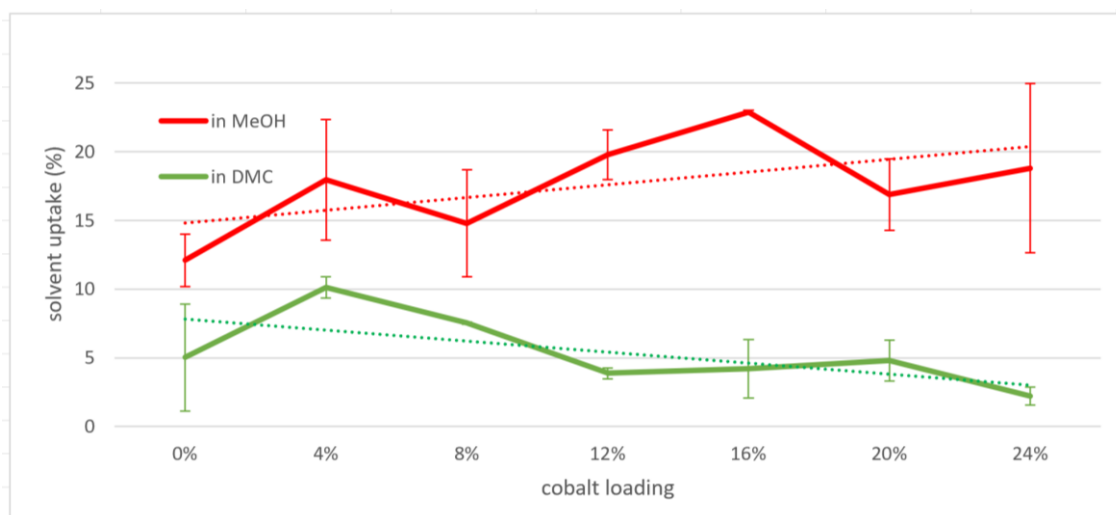


Figure 35: Solvent uptake results for MeOH immersion (red) and DMC immersion (green) (dotted lines indicate the corresponding trendlines)

Firstly, we can observe that the solvent uptake ratio for all the membranes having been immersed within MeOH is consistently greater than those having been immersed into DMC. This can be attributed to the HSP shown in Table 11, where the R_a for CS in MeOH is nearly three times smaller than for CS in DMC.

We can also see that for the membranes immersed into MeOH, their solvent uptake generally increases (however not consistently) as cobalt loading increases. The slope of the trendline, represented as a dotted red line, is positive. The opposite of this is true for the membranes having been immersed in DMC. The cobalt-loaded CS matrix thus shows preferential sorption to MeOH than DMC. Effective pervaporation separation is very much reliant on the membranes showing preferential affinity towards MeOH.

5.2.2 Mass loss results

Before having been immersed into pure solvents at 50°C for 48 hours, the (dry) membranes were weighed with an analytical balance. Their weight is noted as w_0 . Their weight after having been dried for 72 hours at 50°C is noted as w_2 .

The mass loss ratio is then calculated as follows:

$$\text{mass loss (\%)} = \frac{w_0 - w_2}{w_2} \times 100 \quad (9).$$

The results are represented on Figure 36, below. The membranes that were immersed in pure MeOH in between these two weighing measurements are displayed in red, whereas the membranes that were immersed in pure DMC are displayed in green. The error bars represent the standard deviations of each membrane as the test was done twice.

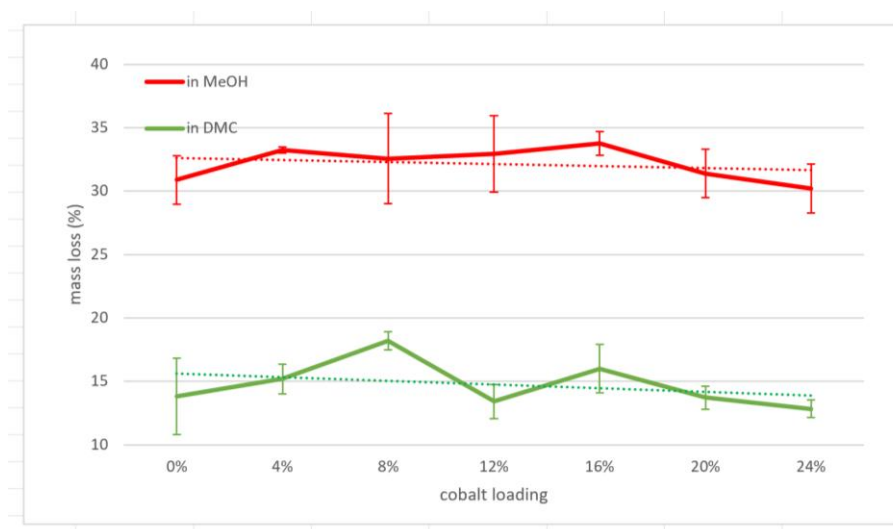


Figure 36: Mass loss results for MeOH immersion (red) and DMC immersion (green) (dotted lines indicate the corresponding trendlines)

Subjecting the membranes to this drying process allows to assess whether the solvents cause membrane degradation or dissolution. If so, this would lead to a potential decrease in pervaporation separation efficiency due to the structural damage caused by the solvent. The mass loss ratio can be an indicator in determining whether a solvent is compatible with the membrane for long-term use and/or the proportion at which the solvent may become problematic for the membrane's chemical integrity.

On Figure 36 above, we can firstly see that when the membranes are in contact with MeOH, its mass loss ratio is significantly and consistently superior to that of DMC. Secondly, we see that as cobalt loading increases for the membranes having been immersed in MeOH, there is no significant fluctuation in mass loss. The slope of its trendline is only marginally negative, but not significantly so. Supplementary increases in cobalt loading could however lead to decreased mass loss, as we see that mass continually decreases when the 16% cobalt loading is reached. Finally, we can see that as cobalt loading increases, mass loss concerning the membranes immersed in DMC shows a bit more oscillation in its mass loss results. The slope of its trend line is slightly negative, and continually decreases when the 16% cobalt loading threshold is reached.

5.2.3 General discussion

As per the solvent uptake results, we can see that there is increased sorption of MeOH and decreased sorption of DMC as cobalt loading increases. Knowing that cobalt has coordinated with CS, the cobalt atom will have an electron-withdrawing effect which will enhance the possibility of the nitrogens' lone pairs to induce the polarization of MeOH (Anggarini et al., 2021). The crosslinking of cobalt has effectively rendered the CS-based membranes more hydrophilic. As for DMC, due its relatively non-polar nature, it becomes more reluctant to pass through the increasing hydrophilic membrane (as cobalt loading increases). Kachhadiya & Murthy (2023) show that increasing MeOH concentration within the liquid feed leads to increased membrane swelling. The membrane thus becomes less efficient and durable in time. Figure 10 (p.19) demonstrates how flux increases through a CS membrane when MeOH's concentration increases in the feed mixture. In tandem, the separation factor decreased.

We may also observe a decrease in solvent uptake and mass loss for the 20 and 24% cobalt loaded membranes immersed in MeOH. This could be due to the gradual increase in cross-linking which results in a decrease in membrane swelling and reduced permeability for MeOH (Ravishankar & Dhamodharan, 2020). The crosslinker also acts as a barrier and makes the membrane less flexible through its more rigid structure, which would reduce MeOH sorption (Beppu et al., 2007).

As per the mass loss results, we can see that when immersed in MeOH, its mass loss ratio is significantly superior to when it is immersed in DMC. This can be explained via the HSP where we can see that CS has a stronger affinity for MeOH. The latter, being polar, will interact with CS's hydroxyl and amine groups through hydrogen bonding. Moreover, high concentrations of MeOH can cause solvation of CS, effectively dispersing and dissolving its polymer chains (Bahlakeh et al., 2017; Roy et al., 2017). However, chemical crosslinking of CS usually results in increased durability and a decrease in mass loss (Gu et al., 2021; Kachhadiya & Murthy, 2023). We see however that mass loss for the membranes immersed in MeOH remains approximately constant as the crosslinking degree (cobalt loading) increases. This can be attributed to the membrane's crosslinker also increasing its hydrophilicity (which is not often the case) and, simultaneously, linking CS's polymeric chains together, making the membrane more robust, and MeOH's sorption onto it more difficult.

Looking at the 4% and 8% cobalt loaded membranes immersed in DMC, we can see that both show a marginal increase solvent uptake and mass loss which is not consistent with a membrane that has been crosslinked and is more hydrophilic. It is possible that these membranes are thinner than the others (due to inhomogeneous spreading of the polymer solution when it was produced), leading to increased swelling. This would have to be checked using a micrometre.

Lastly, we can notice the fact that the solvent uptake trendline decreases for pure DMC as cobalt loading increases. This is an indicator that cobalt particles have not agglomerated as cobalt loading increased. Indeed, as we saw for nickel-coordinated APTES (section 2.7.3), the metal ions had less affinity to its less basic primary amine group as compared to the other membranes' secondary amines (Anggarini et al., 2022b). As nickel loading increased, and as a result of this lessened affinity, nickel agglomerated and formed larger interparticle pores leading to non-selective sorption and diffusion. Had cobalt agglomerated, it is likely that DMC's solvent uptake would have increased. This is a promising indicator that cobalt loading could still be increased (beyond 24%) within CS membranes.

5.3 PERVAPORATION SEPARATION RESULTS

The pervaporation separation tests will allow us to determine whether the developed cobalt-coordinated CS membranes show promising results in the separation of the MeOH/DMC mixture. These tests will establish whether this coordination will prove successful in improving pristine CS's permeability and selectivity towards MeOH.

Firstly, a pristine CS membrane was tested. Cobalt loading within the membranes was then progressively increased by a 4% increment. Batches of 4 to 8 replicas of every membrane type were produced. This allowed for replacements to be available had any faulty membranes been developed. Additionally, this allows experiment repeatability as two to six same type membranes were tested within the PV setup. Two to three permeates were collected per membrane. The operating conditions during the following experiments are given in Table 9. The calibration curves used to convert GC peak areas to weight fraction are given in sections 8.2.4 & 8.2.5.

As was stated in section 4.4.5, a 10/90 mol% (or 4/96 weight%) MeOH/DMC feed mixture was used to assess whether the cobalt loading in a CS membrane had a meaningful effect on the separation process. The reasons for using a mixture with such a low concentration of methanol are twofold: it enables the coupling of fluxes to be discarded and it allows us to better identify the membrane's efficiency in separating the compounds (Lipnizki & Trägårdh, 2001).

X. Xu et al. (2022) show that for a 10/90 mol% MeOH/DMC feed mixture, MeOH's permeance decreases as temperature increases (in the 30 to 50°C range). However, DMC's permeance decreased more rapidly with the same increase in temperature, consequently increasing the selectivity. In the 50 to 60°C range, DMC's permeance increased whereas MeOH's permeance remained approximately constant. Moreover, flux was maximal at 50°C. For these reasons, our feed was heated at 50°C.

5.3.1 Influence of cobalt loading in the membrane

5.3.1.1 *Effect on flux and separation factor*

On Figure 37 below, we can see how the flux and the separation factor are affected by cobalt loading. The blue rectangles represent the mass flux of MeOH, the green rectangles represent the mass flux of DMC, and the marked red X spots represent the separation factor ($\beta_{\text{MeOH/DMC}}$) of the membrane. The sum of both rectangles represents the total mass flux of the membrane. The error bars represent the standard variations between the measures. The raw data of the experiments (membrane loading, time, permeate weight, relative MeOH and DMC mass fractions in the feed and permeate) can be found in section 8.3.7.

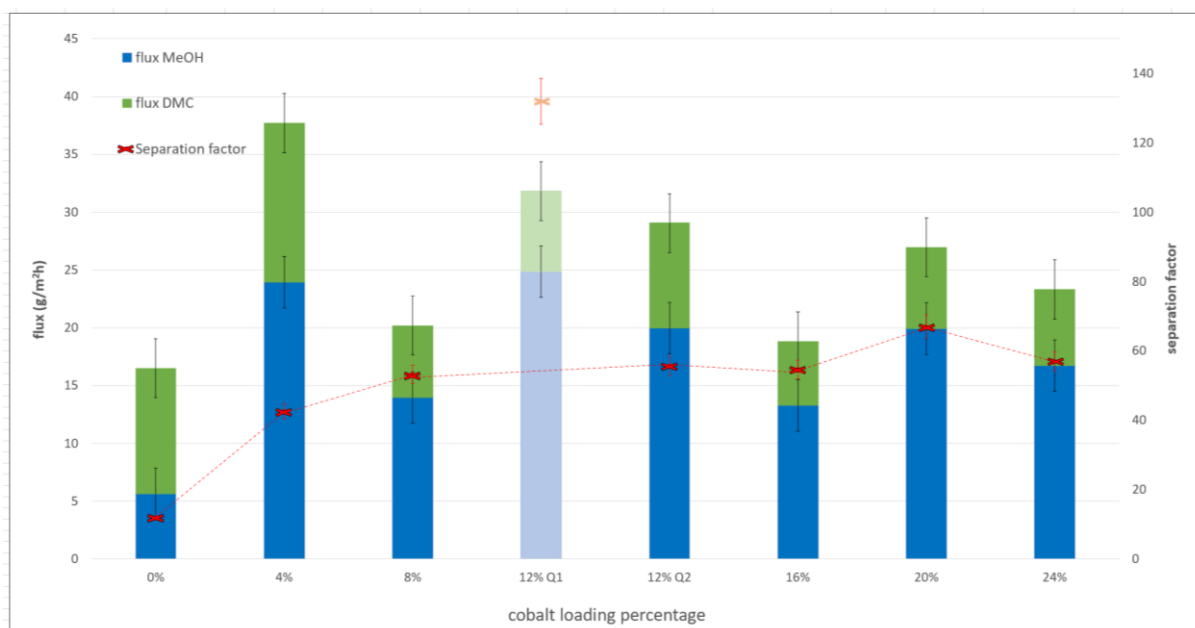


Figure 37: MeOH flux (blue), DMC flux (green) and separation factors for pristine and cobalt loaded CS membranes (4 wt% MeOH feed; feed heated at 50°C; $\beta = \theta_{\text{MeOH/DMC}}$)

Based on the Figure 37 above, we can see (on the far left) that the overall flux of pristine CS (0% cobalt loading) is the lowest of all the membranes that were produced. Its mean total flux reached 16,5 g/m²h. The proportion of DMC within that total flux ($\approx 65\%$) explains its low separation factor of 11,8. As cobalt loading increases, we can see that both flux and the separation factor increase. Its flux greatly increases (by $\approx 130\%$) with a 4% cobalt increase. When more cobalt is loaded into the membrane, its flux then decreases to values that show an approximately 50% increase in comparison to pristine CS. Disregarding the results from the first semester's 12% cobalt loaded membrane (shown in lighter colours and noted "12% Q1") for reasons explained in the discussion section below, the separation factor increases almost linearly as cobalt loading increases. It plateaus around the 12% Q2 – 16% cobalt loading mark. It then increases to its highest value of 67 (a 475% increase from the pristine CS membrane) and a flux of 27 g/m²h then both the flux and separation factor decrease to 23 g/m²h and 57 respectively, when a 24% cobalt loading was reached.

5.3.1.2 Effect on permeance and selectivity

Figure 38 below, shows how the permeances and selectivity are affected by cobalt loading. The blue rectangles represent the permeance of MeOH, the green rectangles represent the permeance of DMC, and the marked red X spots represent the selectivity ($\alpha_{\text{MeOH/DMC}}$) of the membrane. The sum of both rectangles represents the total permeance of the membrane. The error bars represent the standard variations between the measures.

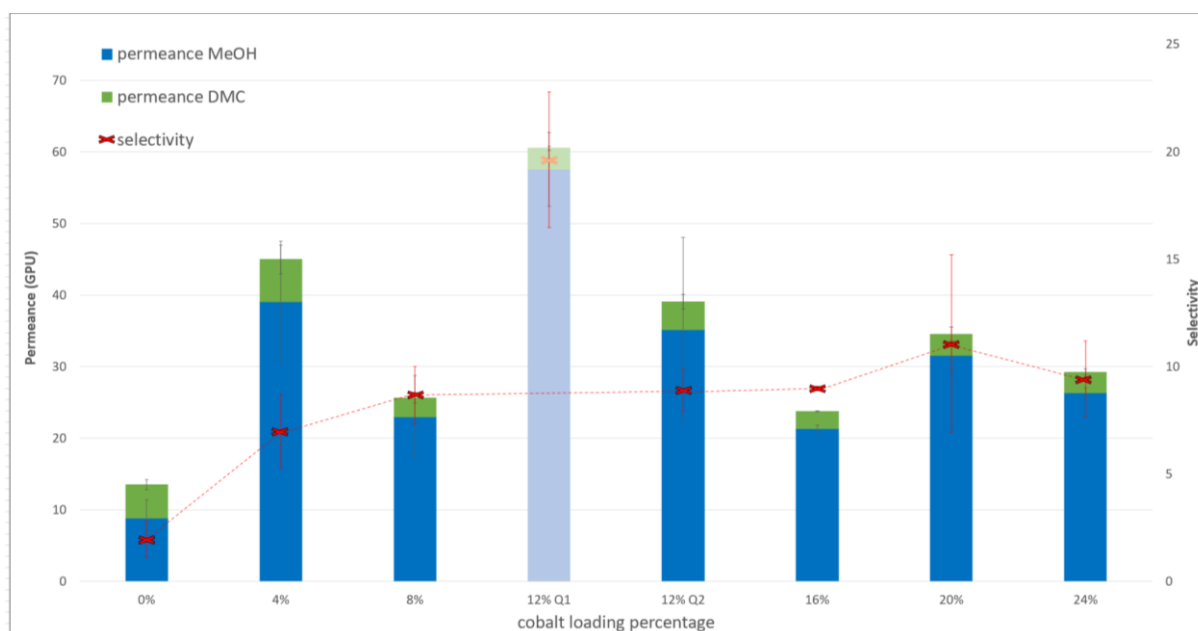


Figure 38: MeOH permeance (blue), DMC permeance (green) and selectivity for pristine and cobalt loaded CS membranes (4 wt% MeOH feed; feed heated at 50°C; $\alpha = \alpha_{\text{MeOH/DMC}}$)

The first thing that is noticeable is how similar this Figure (38) and Figure 37 are. Both permeance and selectivity evolve in a similar fashion to flux and the separation factor respectively. However the permeance of MeOH takes a greater proportion of total permeance as opposed to flux. Measuring the ease at which a compound passes through the membrane instead of the mass transfer, the permeance shows how preferentially permeable CS is to MeOH. As per the results on the figure above, cobalt loading only increases CS's permeability to MeOH. Similarly to flux however, the proportion of DMC permeance on total permeance decreases as cobalt is added to the membrane. The pristine CS membrane has a permeance of 8,9 and 4,7 GPUs for MeOH and DMC respectively and has a selectivity of 2. This selectivity continuously increases as cobalt loading increases and reaches its maximum value for the 20% cobalt loaded membrane. The latter membrane has a selectivity of 11,1 , with MeOH and DMC permeances being equal to 31,5 and 3 GPUs respectively. This latter membrane has effectively shifted the molar fraction of the feed (11%MeOH : 89% DMC) to an 89:11 (MeOH/DMC) molar fraction permeate. Both permeances and selectivity then decrease slightly for the 24% cobalt loaded membrane.

5.3.2 Discussion

Once a membrane has gone through a PV cycle, the feed is collected from the feed tank to be re-used for the following experiment. After a cycle, the feed's concentration in MeOH has thus decreased as the membranes have more affinity to this polar compound. Therefore, it is necessary to readjust the feed's MeOH concentration by adding pure MeOH to it (to preserve a 10 molar %, or 4 weight % MeOH feed). Between the testing of the 8% and 12% Q1 cobalt loaded membranes during the first semester, this step had unfortunately been neglected. The feed's MeOH concentration had gone down to an 8% molar weight (or 2,7 weight %). This is why the 12% Q1 pervaporation results are discarded.

Consequently, its separation factor had increased to a mean value of 132 (a 1019% increase from the pristine CS membranes) and its selectivity increased to a value of 19,6 as opposed to 2 (for pristine CS).

Most likely this is the result of the coupling effect, which stems from the interaction between the two components within the feed mixture. As per the HSP and solvent uptake tests, we know that the membranes have more affinity for MeOH than DMC. The amount of MeOH within the feed will thus affect DMC's transport rate. Indeed, as MeOH will preferentially (and more rapidly) permeate through the membrane, it will drag DMC through the membrane with it (W. Li et al., 2018). The concentration of MeOH in the membrane alters DMC's diffusivity through the coupling effect. The higher the concentration of the feed is in MeOH, the more MeOH is available to drag DMC with it on the membrane. Inversely, as MeOH concentration decreases, the less influence it will have on DMC's transport behaviour. This can also be seen on Figure 10, where we can see that with a higher MeOH concentration within the feed, comes a smaller separation factor as a consequence.

To analyse the relationship between selectivity (dependant variable) and the cobalt loading percentage (independent variable), a linear regression using all PV separation results from all the membranes plus the 12% Q1 results was compared to a linear regression using the same results plus the 12% Q2 results. (The entire regression statistics and ANOVAs can be found in sections 8.3.6.1 & 8.3.6.2 for the 12% Q1 results and 12% Q2 results respectively). The main data⁷ is shown below, in Table 11.

Table 11: Regression statistics and ANOVAs justifying the dismissal of the 12% Q1 results

<i>Regression statistics of the data set with</i>	<i>12% Q1</i>	<i>12% Q2</i>
Multiple R	0,450	0,817
R square	0,202	0,667
Adjusted R square	0,043	0,600
Standard Error	5,194	1,849
Observations	7	7

<i>ANOVA</i>	<i>12% Q1</i>	<i>12% Q2</i>
F-value	0,311	0,025

Firstly, we can see that the correlation (*Multiple R*) between selectivity and cobalt loading percentage within the membranes goes from being moderately positive ($R=0,450$) for the data set which comprises the 12% Q1 results to strongly positive for the one comprising the 12% Q2 results ($R= 0,817$). Via the R^2 , we can see how different the variance in selectivity can be attributed to the cobalt loading percentage between the two data sets. It is much bigger for data set that possesses the 12% Q2 results. We can also see how big the average distance is between the values and the regression line via the *Standard Error* measure. This distance being much bigger for the data set possessing the 12% Q1 results.

⁷ A more complete comparison and analysis of these two data sets is given in section 8.3.6.3.

Lastly, the F -value from the ANOVA, suggests that there is no linear relationship between selectivity and cobalt loading percentage (this being the null hypothesis) for the 12% Q1 data set, however this relationship does exist for the second data set, as its value is below $p < 0,05$.

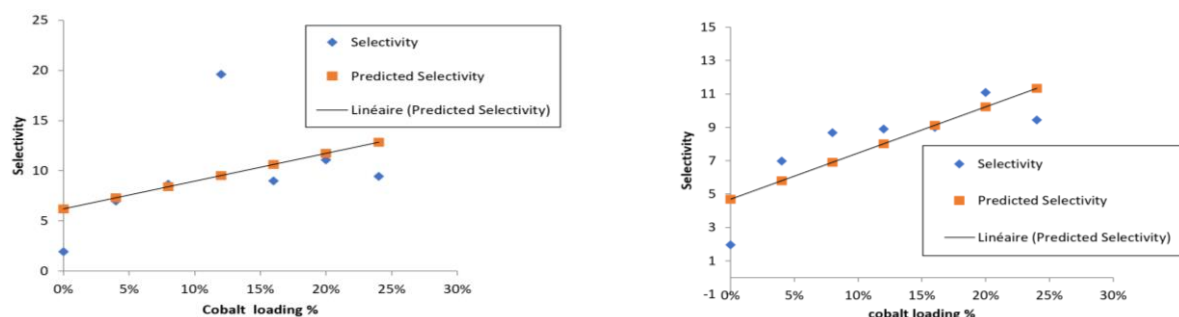


Figure 39: Line fit plot of the linear regression with the 12% Q1 (left) and the 12% Q2 results (right)

The line fit plots shown above on Figure 39 demonstrate how aberrant the 12% Q1 results are as opposed to the predicted selectivity values based on the other cobalt loaded membranes. The 12% Q1 results are thus discarded as they hold an unfair advantage over the other membranes. As opposed to the other membranes, the 12% Q1 results cannot be judged based on their cobalt loading percentage alone but also on the decreased MeOH concentration within the feed. These results are indicative however of the membranes' separation capabilities in feeds containing smaller amounts of MeOH.

The obtained pervaporation separation results also serve as proof that the cracks that are visible on the SEM images are due to the membrane being in a dry state and were indeed not present during the pervaporation separation tests. Had they been present, these large gaps would have yielded much poorer results.

It is also interesting to notice that the 4% cobalt loaded membrane holds the maximal flux. It is, by far, the membrane that allows the biggest mass transport of MeOH however it is also the least selective of all the cobalt loaded membranes. It is difficult to conceive that the reason behind this impressive flux could be due to the fact that it is less coordinated than the other cobalt loaded membranes. Indeed, it being less coordinated signifies that the CS polymer matrix is wider and thus less selective. However, if that were the case, the pristine CS membrane would possess the highest flux. Rare are the cases found in literature where both flux and selectivity increase. The most probable cause would be that a small number of cobalt particles within the polymer matrix clustered due to inhomogeneous mixing. This is one of the most common issues that arise when developing MMMs (X. Xu et al., 2022). The wider gap resulting within the membrane's matrix would allow flux to increase, to the detriment of its separation factor.

We can also note that the error bars for the 16% cobalt loaded membranes are smaller as compared to the others. Only two membranes for the 16% cobalt loaded membranes were tested within the PV set-up. The other loading percentages were tested with a greater number of membranes. The results for two 16% cobalt loaded membranes showed great reproducibility leading to very small error bars.

It is interesting to see that the separation factor, flux and selectivity decrease for the 24% cobalt loaded membrane as compared to the 20% cobalt loaded membrane. As per the solvent uptake ratio results, this could be due to the membrane's inherent decreased affinity for the feed mixture due to increased crosslinking. Abundant crosslinking generates more fragile and brittle membranes, decreasing their free volume (reducing permeability) and dimensional stability leading to a declined separation performance (J. Chen et al., 2009; Smitha et al., 2004; N. Wang et al., 2017). This hypothesis could be proved or disproved by further increasing cobalt loading.

Finally, it is a difficult task to qualitatively compare the cobalt loaded membranes to other CS membranes that are found in literature as conditions such as the concentration of MeOH in the feed and temperature vary and have a role that is paramount within the process. Moreover, most of the literature only discusses flux and separation factor, meaning that the driving force is not taken into account.

As far as crosslinked CS membranes are concerned, results from Won et al 2003 demonstrated that using H_2SO_4 as a CS crosslinker yields a flux of $215 \text{ g/m}^2\text{h}$ and a separation factor of 19 at 50°C , however the weight % of MeOH within the feed was 29% (Table 5). The 20% cobalt loaded membranes presented above yielded a flux of $27 \text{ g/m}^2\text{h}$ and a separation factor of 81, with a MeOH weight % of 4. When comparing our 20% cobalt loaded membrane to other types of CS membranes in the literature, it often yields a much smaller flux but a better separation (Table 5). Only GA and PEEK crosslinked MMM CS membranes with a silica-based filler possess both higher separation factors (90,5 and 120,3 respectively) and higher fluxes (1030 and $910 \text{ g/m}^2\text{h}$ respectively) (J. H. Chen et al., 2016).

It is interesting to notice however that cobalt loaded membranes yield a separation factor that is similar to a MOF CS membrane with a feed containing a similar wt% of MeOH. A ZIF-8 filled CS membrane yielded a flux that reached $45 \text{ g/m}^2\text{h}$ and a separation factor of 71,2 (X. Xu et al., 2022). However, this MOF CS membrane possesses both a higher MeOH permeance ($97,2 \text{ GPU}$ s) and selectivity (11,2) as compared to our 20% cobalt loaded membrane that has a MeOH permeance of $31,5 \text{ GPU}$ s and a selectivity of 11,1. This considerable difference in permeance could be due to advantages linked to the usage of MOFs. If the latter are compatible with the polymer and show decent affinity for the feed's targeted component, their size-selective window allows for a smoother flow of MeOH through the membrane as compared to crosslinking which effectively renders the polymer denser and more rigid.

5.4 EXTERNAL INFLUENCE

To substantiate the PV separation results from the first semester (that included the 12% Q1 results discussed above), developing membranes anew and repeating the PV separation process was necessary. However, as is shown on Figure 40 below, the beginning of the second semester yielded PV separation results that were perplexingly inferior to that of the first semester.

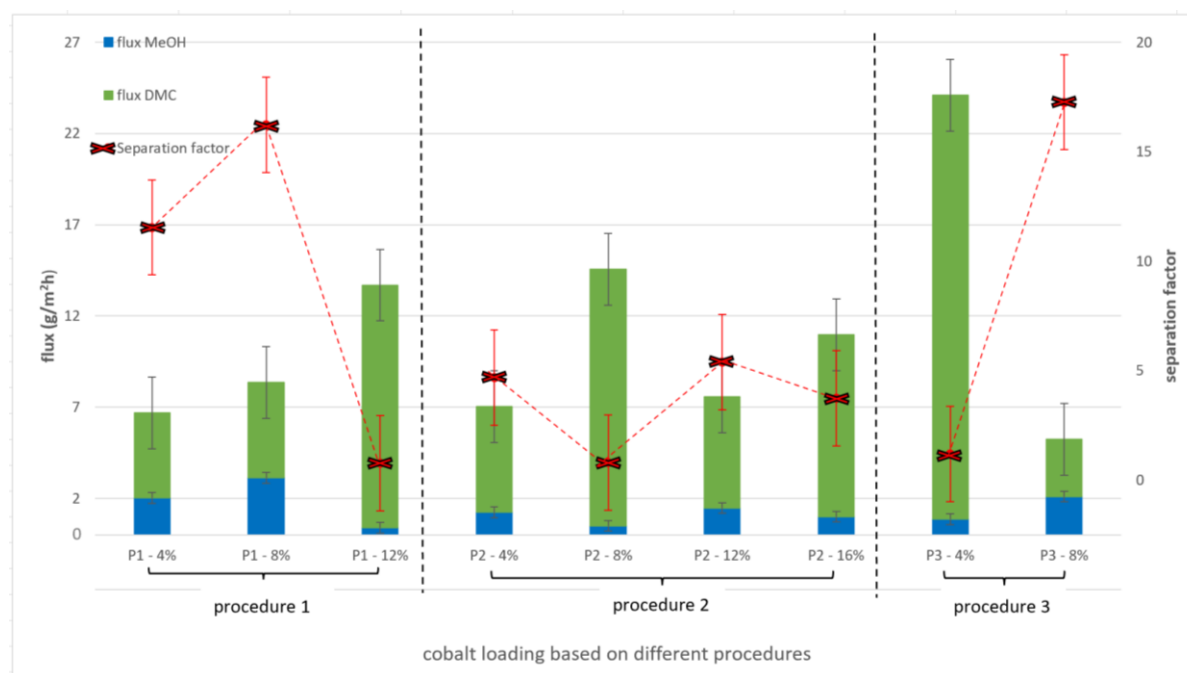


Figure 40: MeOH flux (blue), DMC flux (green) and separation flux for pristine and cobalt loaded CS membranes (polluted feed, feed heated at 50°C; $\beta = \beta_{MeOH/DMC}$)

The first sign was the time it took to gather one permeate. Instead of taking 90 to 120 minutes, a sufficient amount of permeate would take 180 to 240 minutes to condense within the cold bath. Once these permeates were analyzed, their separation factors ($\beta_{MeOH/DMC}$) had decreased from 42, 53 and 132 for the 4%, 8% and 12% cobalt loaded CS membranes to 11, 16 and 0,78 respectively. This is shown on the left of Figure 40 above, named “procedure 1”, which is the procedure explained in the Materials & Methods section. Procedure 1 aims to develop the MOFs within the solvent, then adding the polymer to the solvent. In this case, the solvent used to disperse and dissolve the inorganic precursor also holds the organic linker, formate anions. MeOH is directly present within the solution as the organic solvent will help reduce the solvation effect and thus increase the chances of crystal nucleation and growth. However, as this was not working, different in situ MOF synthesis techniques were attempted.

Procedure 2 consisted of dissolving the CS in a 2% formic acid solution. The protonation of CS would lead to the formation of formate ions. The $Co(Ac)_2$ powder was then added and mixed into the solution. MeOH was subsequently added. Procedure 3 consisted of dissolving the CS in a MeOH/2% formic acid mixture. Another solution consisted of mixed $Co(Ac)_2$ in a MeOH/2% formic acid mixture. The two suspensions were subsequently mixed.

However, all the membranes originating from the different procedures generated the same, exceedingly inferior, results. No relationship between cobalt loading and the separation factor can be deduced, for all three procedures. The raw data of these experiments (membrane loading, time, permeate weight, relative MeOH and DMC mass fractions in the feed and permeate for every procedure) can be found in section 8.3.8.

Following these experiments, we decided to violently shake the permeate holder, and the transparent permeate within it turned cloudy. This was a clear indication that another compound was present within the system. The most obvious candidate was water, as the latter forms a ternary azeotropy with MeOH and DMC, it also turns the mixture opaque when its concentration within the mixture becomes significant. Moreover, water is invisible on the FID GC spectra, the latter being more sensitive to organic compounds (Shellie, 2013). Furthermore, its hydrophilic affinity with CS would be greater than that of MeOH, signifying that it would preferentially sorb and diffuse through the membrane. This leads to CS hydration, whereby polymer chains would surround water molecules, causing the membrane to swell profusely (Mengatto et al., 2013). The MeOH would then have less space within which to diffuse, leading to a decrease in flux, separation factor and selectivity.

Based on Won et al.'s (2003b) work, that investigated the effect of small amounts of water in MeOH/DMC mixtures, it was observed that water had an increased and pronounced negative effect on pervaporation when the initial mixture had greater concentrations of DMC, the results are shown below on Figure 41 for a feed solution heated at 45°C containing 10 wt% MeOH.

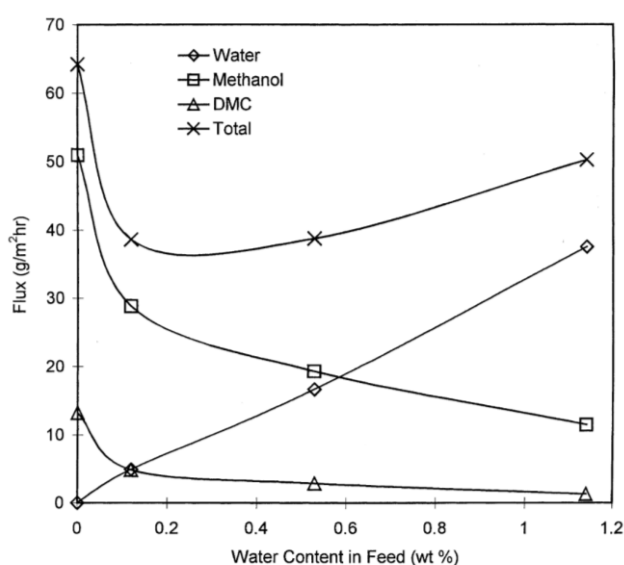


Figure 41: total and partial flux for the separation of 90 wt% DMC/ 10 wt% Methanol/water mixtures with a varying weight% of water (45°C) (Won et al., 2003b)

On the far left of the Figure above, between the 0 and 0,1 wt% marks, we can see the marked negative effect that even the slightest increase in water concentration within the feed provokes, as compared to a pure MeOH/DMC mixture.

A Karl-Fischer titration was done to test the water content within the pure MeOH and DMC solvents as well as the first semester's feed solution (named feed Q1) and a newly made feed solution (named feed Q2). The results are shown in Table 12 below.

Table 12: Karl Fischer titration results for the pure solvents and different feeds (water content given in ppm)

Solvent	Water content [ppm]
DMC (99%)	301,8
CH ₃ OH (100%)	878
Feed Q2	900,1
Feed Q1	1402,4

We can see that feed Q1 possesses 50% more water than feed Q2. Feed Q2 possesses $\approx 0,9\text{g}$ of water per liter of feed (0,09 wt% of the feed) whereas feed Q1 possesses $\approx 1,4\text{g}$ of water per liter (0,14 wt% of the feed). Looking at Figure 41 above, around the 0,1 wt% marker (on the x-axis), even the slightest addition in water content leads to a strong decrease in overall, MeOH and DMC flux, and an increase in water flux. The Karl-Fischer titration tests were made after a cumulated 6,32g of permeates were collected throughout the procedure 1-3 experiments. We can thus expect that Feed Q1 had a greater concentration of water at the beginning of the tests. Moreover, as our feed solution contains a higher wt% of DMC within it, it would be expected that the decrease in flux be even more pronounced than what is presented on Figure 10, as per Won et al.'s (2003b) findings.

As we do not use water in our laboratory, save for washing our beakers and jars, it remains a total mystery as to how water appeared within the feed solution between the end of the first and the beginning of the second semester. Following the observation of the cloudy permeate, the entire PV set up was washed and dried. The experiments could then be repeated with the newly made feed solution (feed Q2) and tests relating to further cobalt loading (16 – 24%) ensued.

Lastly, we should notice that the solvents we mix to produce our feed solution possess a non-negligible amount of water that can considerably affect our PV separation tests. As is seen on Figure 41, even 900 ppms of water within the feed is enough to decrease overall flux by over 30%. It would be interesting to dehydrate the feed solution using drying agents such as anhydrous salts. The use of $\text{Mg}(\text{SO}_4)$ salt, for example, will adsorb the water present within our feed. The salt can then be recuperated via filtration. The feed solution would thereafter yield better PV separation results.

6 CONCLUSION AND PERSPECTIVES

The goal of this thesis was to address the separation of MeOH/DMC mixtures by pervaporation using cobalt loaded chitosan membranes and to assess their separation efficiency. Via the membrane characterization, solvent affinity, and pervaporation separation tests, we can now address the objectives that were initially defined.

- *Will cobalt crystals form within CS?*
If so, will homogenous cobalt formate MOFs develop within CS membranes?
If not, what will be the architecture of the filler within the CS membrane?

The membrane characterization tests indicate that no Co FA MOFs are present within the cobalt loaded CS membranes. As per the XRD, we saw that the addition of cobalt triggers a shrinkage in inter-segmental space of CS (indicating a reduction in the polymer's free volume). Moreover, no peaks related to the would be MeOH size-selective Co FA MOF are present on the cobalt loaded membranes' XRD spectra. Both XRD and FTIR reveal notable modifications to both -NH₂ and -OH groups on CS, which is common for metal ion coordinated CS. The architecture of the filler within the membrane is thus quite assuredly a cobalt divalent cation that coordinates with the amine and hydroxyl groups of the two CS units that surround it.

- *Will the resulting membrane show more affinity towards MeOH or DMC?*

As per the solvent uptake tests, we can see that cobalt-coordinated CS membranes have more affinity to MeOH and, generally, less affinity towards DMC as compared to pure CS membranes. The cobalt has not only crosslinked the membrane but has also made its surface more hydrophilic, facilitating MeOH adsorption due to cobalt electron withdrawing atoms making the nitrogen on CS's amine groups more likely to polarize other compounds. This increase in hydrophilicity results in a decreased affinity between DMC and the membranes.

- *Will the cobalt loaded membranes improve upon a pure CS membrane's performance regarding the separation of the MeOH/DMC mixture through pervaporation?*

When compared to a pristine CS membrane, cobalt-coordinated CS membranes exhibited significant increases in flux, permeance, separation factor and selectivity.

- *How will an increase in cobalt loading affect all these prior questions?*

The increase in cobalt loading did not seem to affect the cobalt loaded membranes' architectures. Its affinity to MeOH increased and its affinity to DMC decreased as cobalt loading within the membrane increases. The solvent uptake tests also indicate that cobalt particles have not agglomerated, suggesting that cobalt loading could be further increased.

A 4% cobalt loading caused a sharp increase in flux, permeance and selectivity. Additional increases in cobalt loading led to slightly reduced fluxes and permeances but lead to a relatively consistent increase in selectivity. The 20% cobalt loaded CS membrane managed to invert the molar fraction found in the feed, a 11:89 MeOH:DMC molar ratio in the feed resulted in a 89:11 ratio in the permeate. These results are comparable to that of MOF insertion within CS membranes.

We also saw how effective the cobalt-coordinated CS membranes are when less methanol is present within the feed, due to the coupling effect. This led to a selectivity of 19,6 for the 12% cobalt loaded membranes.

This work demonstrates that cobalt-coordinated CS membranes can be used for PV processes and will be more selective towards polar components. Developed using very modest amounts of solvents and producing very little waste, these novel membranes can be an easy, effective and more sustainable solution for the separation of MeOH/DMC mixtures that are rich in DMC.

6.1 PERSPECTIVES

Firstly, it would also be interesting to repeat the tests that have been done in this thesis using a dehydrated feed solution. We saw that our feed solution possesses a small amount of water which can, nonetheless, be very detrimental to the results we obtain. It may then be interesting to further increase cobalt loading within the CS membrane to see whether this yields improved selectivity.

In-situ synthesis of Co FA MOFs did not occur. Due to the high concentration of water within the formic acidic solution, water's strong dipole-dipole interactions have probably stabilized the divalent cation's positive charge, leading to the solvation of cobalt and rendering crystal nucleation and growth impossible.

In our procedure, we used a 50/50 wt% acidic solution/MeOH ratio to dissolve the $\text{Co}(\text{Ac})_2$ powder. Increasing the amount of $\text{Co}(\text{Ac})_2$ powder and the percentage of MeOH within this solution might reduce this solvation effect, due to the organic liquid's weaker intermolecular forces. However, MeOH solvation of CS must then be considered (Bahlakeh et al., 2017). Increasing the concentration of acid within the acidic solution might also allow for more formate anions to react with the cobalt, however we should note that this might have a detrimental effect on CS's structure, as an excess of acid will affect the packing of polymer chains and the membrane will ultimately be weaker and more brittle (Melro et al., 2020).

The blending method showed promising results for Co FA MOF presence in a PEBA membrane (Y. Zhang et al., 2016). This polymer however is not as hydrophilic as CS. Pre-emptively crosslinking the CS with glutaraldehyde to block amine groups and then inserting (pre-made) Co FA crystals within it would increase the chances of Co FA MOF preservation within the membrane. However, we should note that GA does decrease the overall hydrophilicity of CS membrane (leading to less affinity with MeOH) and would also decrease the number of available adsorption sites for MOFs within the membrane (Benavente & Thesis, 2008; Beppu et al., 2007).

Lastly, it may be interesting to develop cobalt-coordinated CS membranes in an acid solution and neglecting the use of MeOH. Knowing that the latter can cause CS solvation, the resulting membranes may benefit from extra crystallinity within the CS polymer.

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8 APPENDICES

8.1 STATE OF THE ART

8.1.1 DMC production evolution

As DMC's applications are steadily growing, so is its production. It is interesting to note that its production process has changed over the years. Up until the 1980's, DMC used **phosgene** as one of its precursors and was formed through phosgene alcoholysis (top left of Figure 5, below). Due to its environmental and toxic concerns, the latter process has been phased-out (S. Huang et al., 2015). Since then, the main process for its production processes has been the following: **direct oxidative carbonylation of alcohol** (middle left of Figure 5) through the gas-phase method. Originally, the process was done through a liquid-phase method, which used CuCl as its main catalyst, however catalyst separation, corrosion and high operating pressures resulted in the development of the gas-phase method which operates at lower pressures. However, water production negatively affects catalyst conservation (composed of CuCl₂ on activated carbon and PdCl₂) and creates a ternary azeotrope with DMC and methanol (MeOH). Thermodynamically, it is the most favourable production process, and works on an industrial scale. Moreover, it uses CO as a raw material, so it is interesting for areas with resources in syngas. The **methylnitrite carbonylation** (bottom left of Figure 5), also called the UBE process, has also been proven to work on an industrial scale. The use of alkyl nitrites is chosen as an oxidative agent for safety concerns, as too much oxygen within the system incurs the risk of explosions. In this process, water isn't produced, prolonging the catalyst's usage and avoids the formation of a ternary azeotrope. This process has thus gained traction however the formation of toxic gases such as NO_x and RONO conflicts with the principles of "green chemistry" (S. Huang et al., 2015).

By using CO₂ for the direct synthesis of DMC (on the right of Figure 5), three main routes exist: direct carbonylation (top right), urea alcoholysis (middle right) and transesterification of cyclic carbonates with alcohol (bottom right of Figure 5) (S. Huang et al., 2015). Although **direct carbonylation** is the simplest of all processes, its yields are far too low which are preventing it from gaining more traction. The CO₂ within this process makes it safer, countering the risk of explosions between CO and O₂, but its kinetic inertness is also its main drawback. The reaction is also thermodynamically limited (and reversible) and DMC hydrolysis and catalyst deactivation are also recurring problems (Deng et al., 2019). **Urea alcoholysis** on the other hand is gaining popularity and is expected to be a viable production process in the coming years. Both urea and methanol are abundant materials, the limiting factor remains the liberated ammonia. However, if the latter is recycled within the production of urea, only CO₂ and water will have been consumed. This process also shows signs of easier product separation and purification as well as safer general operations. Lastly, the **transesterification of cyclic carbonates** is the most mature of all process using CO₂ for direct synthesis. It does however rely on the production of epoxides which are costly, hazardous materials and aren't deemed as safe due to the risks of explosions. Firstly, epoxides react with CO₂ to produce cyclic carbonates, mainly propylene carbonate (but also ethylene carbonate). The latter then produces DMC through an ester exchange reaction with methanol, also creating propylene glycol as a high value-added by-product. Presently, 90% of the DMC produced in China uses this process.

8.1.2 VLE data

Data used to compute the “Isobaric vapor-liquid equilibrium of MeOH/DMC binary mixture” that is relayed on Figure 6, comes from Z. Zhang et al. (2016).

T(°C)	x_i	y_i
81,3	0,06	0,287
78,8	0,085	0,353
75,05	0,134	0,455
69,85	0,251	0,59
67,7	0,337	0,654
66,05	0,443	0,706
64,85	0,57	0,74
64	0,719	0,794
63,85	0,772	0,81
63,7	0,845	0,844
63,7	0,868	0,868
63,8	0,912	0,895
63,95	0,946	0,928
64,1	0,967	0,958

Where x_i is the vapor mole fractions of MeOH and y_i is the liquid mole fractions of MeOH.

8.1.3 Mixed Matrix Chitosan Membranes used in PV

Table A.1: MMMs, MOFs and polymer blends-based CS membranes in PV

				without the filler		with the filler		
polymer	filler	feed composition	T (°C)	flux (g/m ² *h)	separation factor (β _{MeOH/DMC})	flux (g/m ² *h)	separation factor (β _{MeOH/DMC})	Referenc e
Pure CS MMMs								
CS	TiCl ₄ 14wt%	10wt% water - Ethanol	77	1500	200	1403	730	(Zhao et al., 2013)
CS	NaY 40%wt	10wt% water - Isopropanol	30	50	2000	113	11000	(Premakshi et al., 2015)
CS	ETS-10 5wt% (titanosilicate)	50wt% water - Ethanol	50	450	47	550	30	(Casado- Coterillo et al., 2014)
CS	tetraethoxysilane (TEOS) 10wt%	50wt% water - Ethanol	30	/	/	720	450	(Asghari et al., 2017)
CS	K ⁺ MMT 10wt% (potassium montmorillonite)	5wt% water - Acetone	70	1500	800	1700	2200	(Gao et al., 2014)
CS	SiO ₂ xerogel 0,25wt%	10wt% water - Butanol	25	400	500	500	1900	(Lin et al., 2018)
CS	Mxene 3wt% (2-D Ti ₃ C ₂ T _x MXene nanosheets)	2wt% water- DMC	50	1000	400	1400	900	(Z. Xu et al., 2018)
CS	r-GO 1wt%	10wt% water - MeOH	30	230	/	690	/	(Hung et al., 2017)
CS	S-CMS 2wt%	5wt% water - Acetone	50	1100	480	1810	832	(Gao et al., 2016)
CS	Ag ⁺ MWNT 1,5wt% (multiwalled carbon nanotube pervaporation)	50wt% benzene - Cyclohexane	20	100	4,5	357	7,89	(Shen et al., 2014)

Pure CS MOFs								
CS	ZIF-7 5%wt	10wt% water - Ethanol	25	600	148	322	2812	(Kang et al., 2013)
CS	ZIF-8 2,5%wt	15wt% water - Isopropanol	25	325	800	280	800	(Fazlifard et al., 2017b)
CS	MOF-801 4,8wt% Zr ₆ O ₄ (OH) ₄ (-CO)	10wt% water- Ethanol	70	1000	7000	1100	2156	(Q. Li et al., 2017)
CS	Al-MOF 5wt%	10wt%water – Ethanol	25	383	240	458	2741	(Vinu et al., 2018)
CS	Al-MOF 0.15wt% (DUT-5)	10wt%water – Ethanol	25	315	347	378	3429	(Vinu et al., 2019)
Polymer blends								
CS/PVP	TEOS 28,4wt%	6wt% MeOH - Ethylene glycol	60	150	500	60	6000	(Q. G. Zhang, Hu, et al., 2013)
CS/PVP	BTEE 10,4wt%	6wt % MeOH - EG	60	40	900	50	6129	(Q. G. Zhang, Han, et al., 2013)
CS/PV A	NH ₂ -MWNTs 10wt%	30wt% water - Isopropanol	25	1800	5	800	99,5	(Langari et al., 2018)

This table shows the wide array of different materials that can be inserted within CS and the mixtures these membranes have separated. Their fluxes and separation factors with and without the filler are listed. Pure CS MMMs, CS MOFs and CS blended with other polymers are listed. This table aims to show how effective these techniques are as the difference in flux and separation factors are quite remarkable.

8.1.4 Additional mechanisms enabling MOF separation

Additional (but weaker) mechanisms enable MOFs to separate compounds in a liquid mixture via pervaporation. Hendon et al. (2017) discuss the physisorption phenomena, whereby the electric field produced by the framework can interact in favour of one the components within the liquid mixture. This interaction's strength (E_{int}) between the MOF's surface and the feed's individual compounds is reliant on the electric field produced by the framework ($E_{x,y,z}$) (which is dependent of its local spatial charge density) and the permanent dipole moment of the “guest” molecule (μ) and can be noted as:

$$E_{int} = \mu E_{x,y,z}. \quad (A1).$$

For molecules that do not possess permanent dipole moments, an instantaneous or induced dipole moment (μ_i) can be generated as the molecules approach the framework's electric field. As per Hendon et al. (2017), This instantaneous dipole moment can be found by multiplying the guest molecule's polarizability (α) by the framework's electric field ($E_{x,y,z}$) and can therefore be noted as:

$$\mu_i = \alpha E_{x,y,z} \quad (A2).$$

The authors do state however that this interaction is much weaker than the preceding one.

Below is Table A2 displaying the physical parameters of the used liquid solvents in this thesis:

Table A.2: Kinetic diameter, dipole moment and polarizability of MeOH and DMC.

Solvent	Kinetic diameter [$\text{\AA}$]	Dipole moment μ [D]	Polarizability α [$\cdot 10^{-25} \text{ cm}^3$]
MeOH	3,6 (Edlund, 2016)	2,8 (X. Xu et al., 2022)	32,3-33,2 (X. Xu et al., 2022)
DMC	4,7-6,3 (X. Xu et al., 2022)	0,18-0,3 (Danielson et al., 2012)	77 (Danielson et al., 2012)

From Table A2, we can deduce that the physisorption effect between a MOF and methanol will generally be greater than DMC as its dipole moment is much more important. As DMC's dipole moment is close to being null, its polarizability parameters are given.

8.2 MATERIALS AND METHODS

8.2.1 Mathematical description of the solution-diffusion model

8.2.1.1 Solution-diffusion model

The solution-diffusion has been proven to be a good approximation and simple to use for the modelling of mass transport for pervaporation through polymeric membranes (Bettens et al., 2007). This model describes the mass transport in three steps (Lipnizki & Trägårdh, 2001):

- 4- Sorption of the permeating compound(s) into the polymer.
- 5- Diffusion through the polymer along the gradient of the chemical potential.
- 6- Desorption at the permeate side.

The main assumptions for this model are the following: constant pressure across the membrane is assumed. As opposed to the pore-flow model, the phase change occurs on the membrane-permeate intersection, where the liquid-vapor equilibrium exists. It is also assumed that an equilibrium state exists on the retentate-membrane intersection. The membrane is considered to be a homogeneous medium, there are no coupling effects⁸ and that Fick laws are valid (as the flux is considered to be only diffusive) (Wijmans & Baker, 1995; Crespo & Brazinha, 2015). The general steps of the solution-diffusion model and the concentration gradient of component i (from the feed C_i^f to the permeate C_i^p) are shown on Figure A1. Chemical potential, pressure and activity gradients along the membrane during this mass transfer are schematised in Figure A2 below.

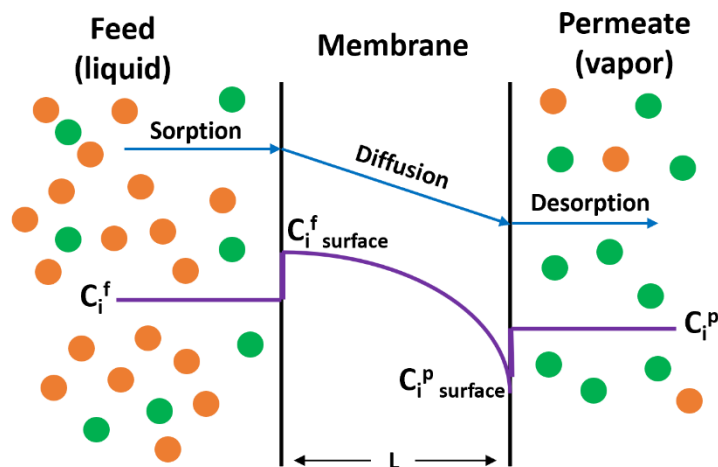


Figure A.1: solution-diffusion model steps and concentration gradient of component i

⁸ The coupling effect is the process whereby components within the liquid feed can permeate faster or slower with a change in the feed's composition or with the addition of other components to the feed. Coupling can be either thermodynamic (caused by the interactions between the feed and the added components, the change of concentration in the feed or the interaction between the added components and the membrane) or kinetic (caused by a change in the diffusion coefficients of the components) (Luis, 2018).

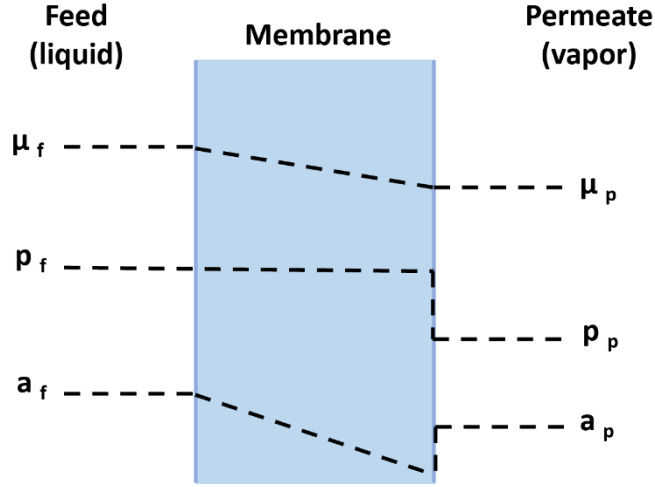


Figure A.2: chemical potential μ , pressure p , and activity gradients across the membrane

The solution diffusion model can be described mathematically⁹ as follows:

The flux J_i is proportional to the product of the concentration (c_i), the mobility (B_i) and the gradient in the chemical potential ($\frac{d\mu_i}{dx}$) which acts as the driving force:

$$J_i = -c_i B_i \frac{d\mu_i}{dx} \quad (A3).$$

Knowing that the chemical potentials in the feed and on the membrane's surface are in an equilibrium state, we can write the chemical potential of i as follows:

$$\mu_i = \mu_i^0 + RT \ln(\gamma_i x_i) + V_i(p - p_i^{SAT}) \quad (A4).$$

Where γ_i is the activity coefficient that links activity and concentration, V_i is the molar volume p is the pressure, p_i^{sat} is the saturation pressure and x_i is the mole fraction of the i component. We can thus rewrite equation (A3) as follows:

$$J_i = -c_i B_i \left(RT \frac{d \ln a_i}{dx} + V_i \frac{dp}{dx} \right)_T \quad (A5).$$

Where a_i is the activity of the i component. However, as the pressure gradient is considered constant throughout the membrane, $\frac{dp}{dx}$ is null.

D_i is the diffusion coefficient of the i component, also known as the Fickian diffusion constant, and is described as:

$$D_i = B_i RT \quad (A6).$$

Thus, equation (A5) is rewritten as:

$$J_i = -c_i D_i \frac{d \ln a_i}{dx} \quad (A7).$$

⁹ All equations in this section come from the following sources: Luis (2018), Lipnizki & Trägårdh (2001), Luis & van der Bruggen (2015) & Wijmans & Baker (1995).

As the last step of the solution-diffusion model (the desorption at the permeate side) is often discarded mathematically as it is not the limiting step in the mass transport. Equation (A7) is thus integrated from the feed side to the permeate side of the membrane. The whole process can be surmised as:

$$J_i = \frac{D_i C_i}{a_i} \frac{1}{l} (a_{F_i} - a_{P_i}) \quad (\text{A8}).$$

Where a_{F_i} and a_{P_i} are the activity of the i component on the feed side and on the permeate side respectively and l is the thickness of the membrane. However, obtaining the majority of the terms within this previous equation is quite challenging, therefore the permeability (P_i) equation is written as:

$$P_i = \frac{D_i C_i}{a_i} \quad (\text{A9}).$$

The final flux equation used is thus expressed as, :

$$J_i = P_i \frac{1}{l} (a_{F_i} - a_{P_i}) \quad (2)$$

As was seen in section 2.5. This is not to be confused with equation (1) which empirically describes the flux of the entire permeate.

$$J_{\text{permeate}} = \frac{w}{A \Delta t} \quad (1)$$

To find J_i , the flux of component i in equation (2), simplifying the driving force ($a_{F_i} - a_{P_i}$) is done through substitution. They are substituted for the relative partial pressure on either side of the membrane, which can be calculated using Raoult's laws:

$$p_{i_{\text{feed}}} = x_i \gamma_i P_i^0 \quad (\text{A10}) \quad \text{and} \quad p_{i_{\text{perm}}} = y_i P_p \quad (\text{A11}).$$

Where y_i and x_i are the vapour and liquid molar fractions of component i respectively. γ_i is the activity coefficient of component i (which measures the nonideality of the mixture) and P_i^0 is the saturated vapour pressure of i , at the corresponding temperature (section 8.2.6). These can be found using the activity coefficient γ_i equations depending on the MeOH mole fraction at 50°C (sections 8.2.2 & 8.2.3). The driving force [Pa] can thus be rewritten as:

$$(a_{F_i} - a_{P_i}) = (p_{i_{\text{feed}}} - p_{i_{\text{perm}}}) = x_i \gamma_i P_i^0 - y_i P_p \quad (\text{A12}).$$

Experimentally J_i , the mass flux of component i , is determined using by the following equation:

$$J_i = J y_i \quad (\text{A13}).$$

Where J is the flux found in equation (1) and y_i is the mass fraction of i in the permeate given by the gas chromatographer. Once this is done, J_i is converted from an hourly mass flux to a molar per second flux (j_i). The molar flux can then be divided by the driving force (equation (A9)) to obtain the membrane's permeance ($\frac{P_i}{l}$) such as:

$$\frac{P_i}{l} = \frac{j_i}{x_i \gamma_i P_i^0 - y_i P_p} \quad (\text{A14}).$$

The permeance can then be converted from the following units $\left[\frac{\text{mol}}{\text{m}^2 \text{ s Pa}} \right]$ to the more conventionally used Gas Permeation Unit (GPU) $\left[\frac{10^{-6} \text{ cm}^3 (\text{STP})}{\text{cm}^2 \text{ s cmHg}} = 1 \text{ GPU} \right]$. We can then also determine a membrane's permeability, by multiplying the permeance by the membrane's

thickness l . Regarding the description of a membrane's performance, the flux of the entire permeate (equation (1)) is often used in literature to describe a membrane's productivity. As we have seen above, permeance or permeability would be more pertinent indicators of a membrane's performance in seeing how productive it is in separating only the desired component in the mixture.

8.2.2 Activity coefficient γ equations - MeOH mole fraction at 50°C

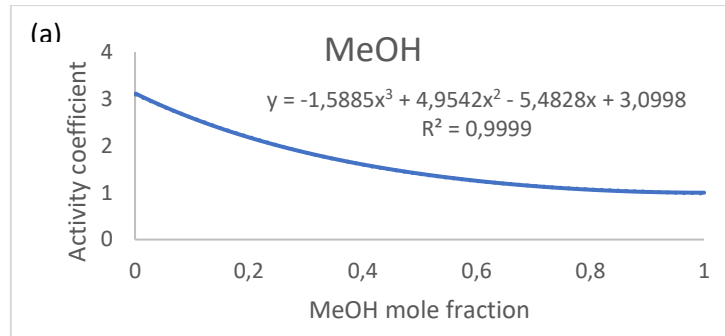


Figure A.3: activity coefficient equation for MeOH mole fraction at 50°C

The gamma coefficient is estimated by an equation $ax^3 + bx^2 + cx + d$ where the x-axis represents the MeOH mole fraction and the y-axis corresponds to the activity coefficient. The equation is built based on the results obtained in Aspen Plus. This data was provided in X. Xu et al.'s (2022) Supplementary Information.

8.2.3 Activity coefficient γ equations - DMC mole fraction at 50°C

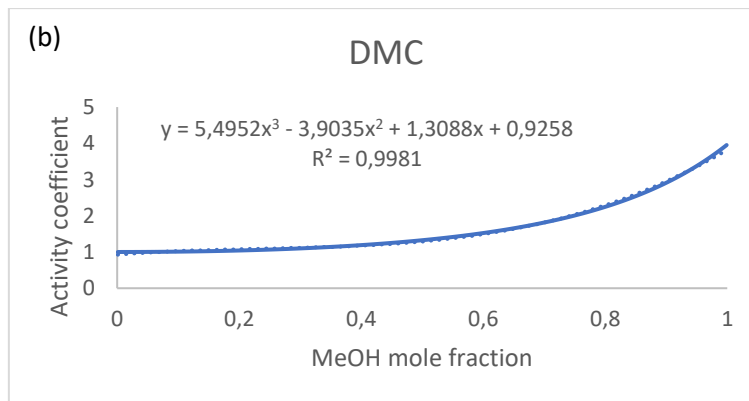


Figure A.4: activity coefficient equation for DMC mole fraction at 50°C

The gamma coefficient is estimated by an equation $ax^3 + bx^2 + cx + d$ where the x-axis represents the DMC mole fraction and the y-axis corresponds to the activity coefficient. The equation is built based on the results obtained in Aspen Plus. This data was provided in X. Xu et al.'s (2022) Supplementary Information.

8.2.4 MeOH gas chromatography calibration curve

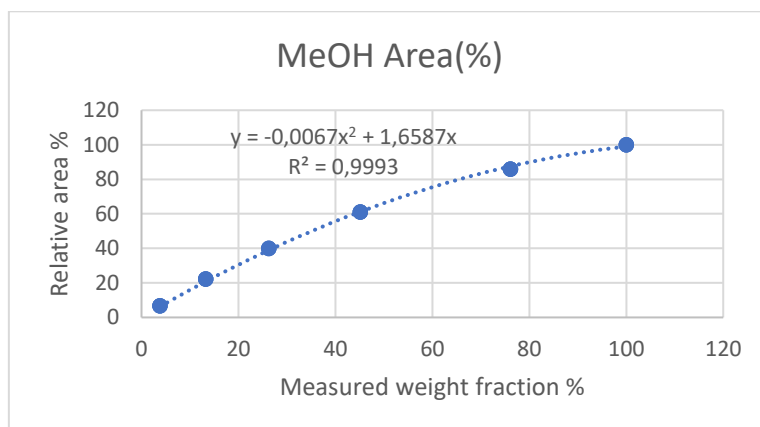


Figure A.5: MeOH calibration curve corresponding relative area % to weight fraction %

The graph correlating the relative area % (y-axis) to the measured weight fraction (x-axis) of MeOH within the feed and permeate samples was constructed by analysing a series of samples of known concentrations within the gas chromatography system. The data of these tests is shown below on Table A3.

Table A3: Data used to make MeOH's calibration curve

MeOH												
parameter	Mole fraction	Real mole fraction	Area signal 1	Area signal 2	Area signal 3	AVR Area	SD Area	Relative Area 1	Relative Area 2	Relative Area 3	AVR Relative Area	SD Relative Area
unit	%	%	pA*min	pA*min	pA*min	pA*min	pA*min	%	%	%	%	%
1	100,000	100,000	410,201	319,973	396,294	375,489	48,579	99,940	99,950	99,83	99,907	0,067
2	90,000	90,005	330,953	304,481	312,187	315,874	13,616	85,930	86,000	86,040	85,990	0,056
3	70,000	69,909	196,703	224,209	213,901	211,604	13,896	60,890	60,740	60,870	60,833	0,081
4	50,000	50,061	133,093	137,546	138,138	136,259	2,758	39,790	39,870	39,540	39,733	0,172
5	30,000	30,004	67,587	67,621	71,868	69,025	2,462	21,940	21,910	21,900	21,917	0,021
6	10,000	10,176	21,038	21,732	20,856	21,209	0,462	6,810	6,940	6,860	6,870	0,066
7-blank	0,000	0,000	0,070	0,058	0,055	0,061	0,008	0,020	0,020	0,020	0,020	0,000

8.2.5 DMC gas chromatography calibration curve

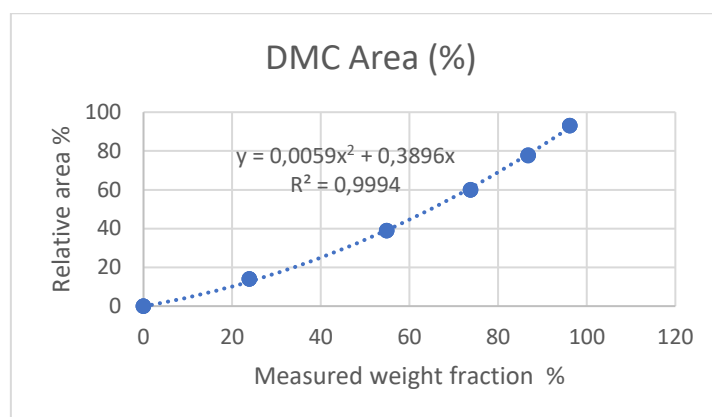


Figure A.6: DMC calibration curve corresponding relative area % to weight fraction %

The graph correlating the relative area % (y-axis) to the measured weight fraction (x-axis) of MeOH within the feed and permeate samples was constructed by analysing a series of samples of known concentrations within the gas chromatography system. The data of these tests is shown below on Table A4.

Table A4: Data used to make DMC's calibration curve

DMC												
parameter	Mole fraction	Real mole fraction	Area signal 1	Area signal 2	Area signal 3	AVR Area	SD Area	Relative Area 1	Relative Area 2	Relative Area 3	AVR Relative Area	SD Relative Area
unit	%	%	pA*min	pA*min	pA*min	pA*min	pA*min	%	%	%	%	%
1	100,000	100,000	296,169	307,662	306,247	303,359	6,267	99,940	99,94	99,94	99,940	0,000
2	90,000	90,005	287,712	291,206	283,006	287,308	4,115	93,100	93,100	93,100	93,100	0,000
3	70,000	69,909	240,337	240,933	256,220	245,830	9,003	78,020	78,050	78,060	78,043	0,021
4	50,000	50,061	201,333	207,418	211,119	206,623	4,941	60,190	60,120	60,430	60,247	0,163
5	30,000	30,004			137,438	137,438				39,110	39,110	#DIV/0!

8.2.6 Vapour pressure of MeOH and DMC at 50°C

Table A5: Saturated vapour pressure of MeOH and DMC at 50°C

	T (°C)	P _i ⁰ [Pa]
MeOH	50	55526,8599
DMC	50	23302,5209

In Table A5 above, P_i⁰ corresponds to the saturated vapour pressure of the component at 50°C

8.3 RESULTS & DISCUSSION

8.3.1 SEM images

8.3.1.1 4% cobalt loaded membrane

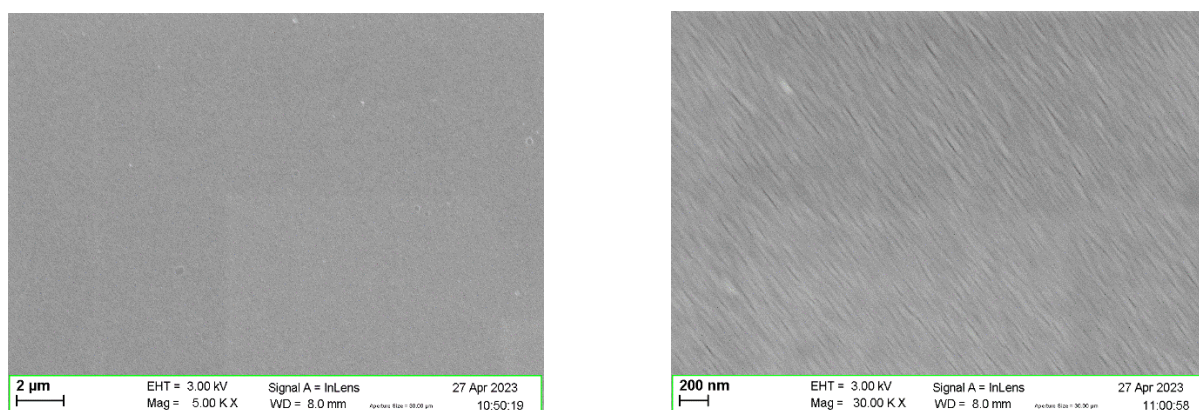


Figure A.7: Surface images 4% cobalt loaded membranes at 5 000x [left] and 30 000x magnification [right]

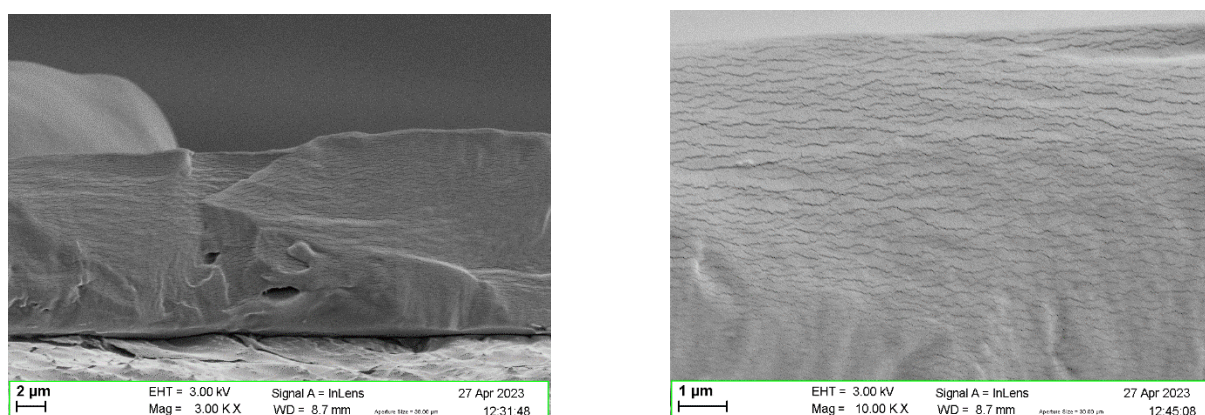


Figure A.8: Cross section images 4% cobalt loaded membranes at 3 000x [left] and 10 000x magnification [right]

8.3.1.2 12% cobalt loaded membrane

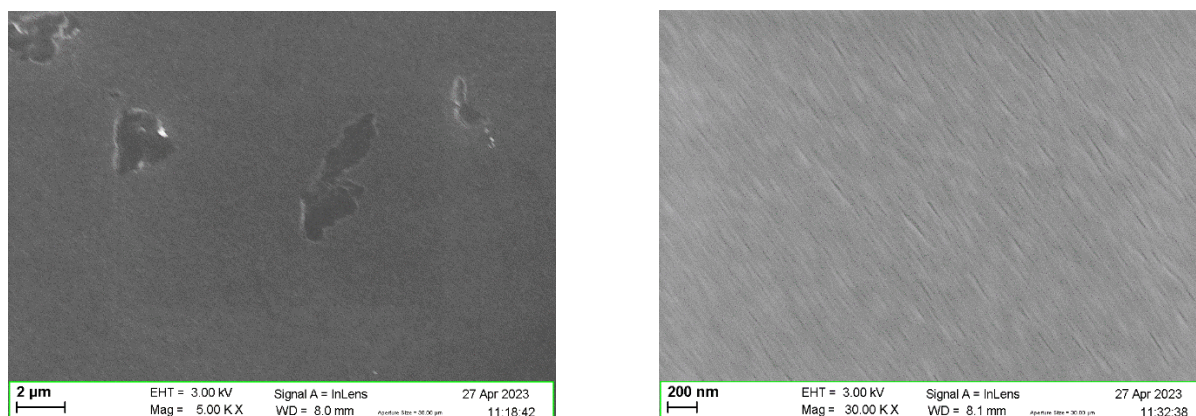


Figure A.9: Surface images 12% cobalt loaded membranes at 5 000x [left] and 30 000x magnification [right]

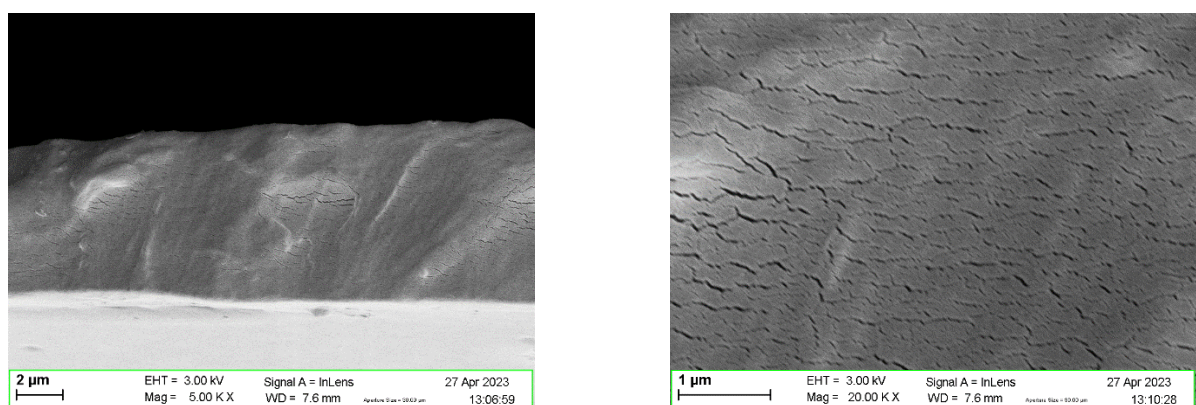


Figure A.10: Cross section images 12% cobalt loaded membranes at 5 000x [left] and 10 000x magnification [right]

8.3.1.3 24% cobalt loaded membrane

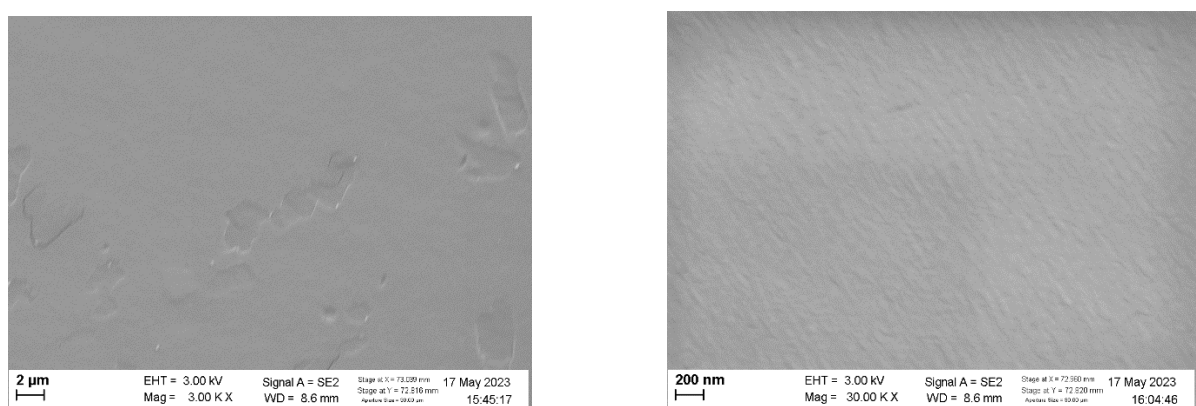


Figure A.11: Surface images 24% cobalt loaded membranes at 3 000x [left] and 30 000x magnification

These images demonstrate that there is no visible difference between the different cobalt loaded membranes. The cracks within the cross sections do not seem as wide on the cobalt loaded membranes as opposed to the pristine CS membrane. This is the only discernible difference we can find on the SEM images. The cross-section images for the 24% cobalt loaded membranes are not shown as they are blurry.

8.3.2 EDX results

8.3.2.1 EDX results of the 4% cobalt loaded membrane

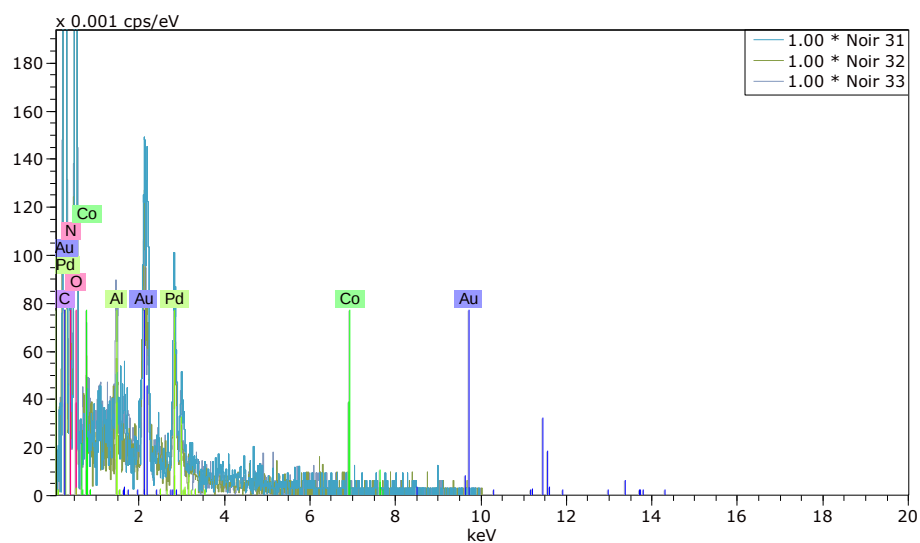


Figure A.12: EDX spectrum for the 4% cobalt loaded membranes

8.3.2.2 EDX results of the 12% cobalt loaded membrane

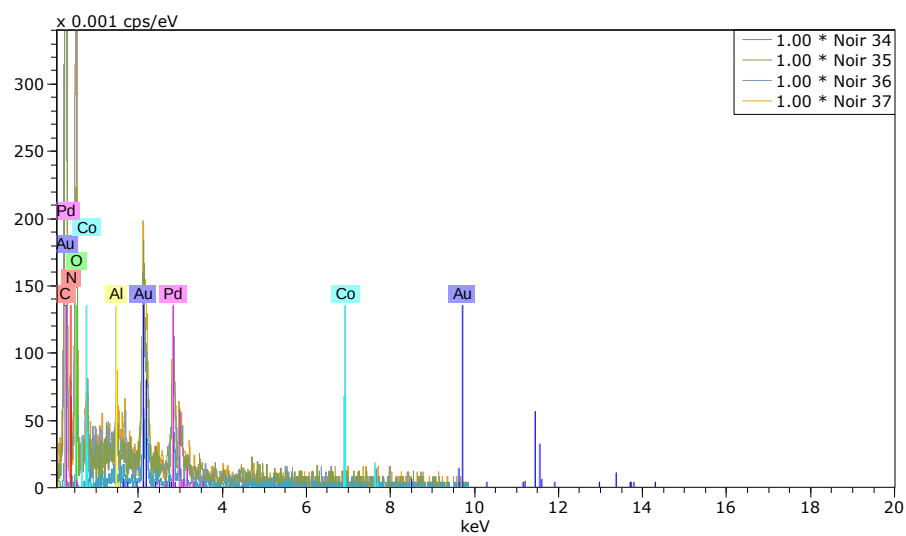


Figure A.13: EDX spectrum for the 12% cobalt loaded membranes

8.3.2.3 EDX results of the 24% cobalt loaded membrane

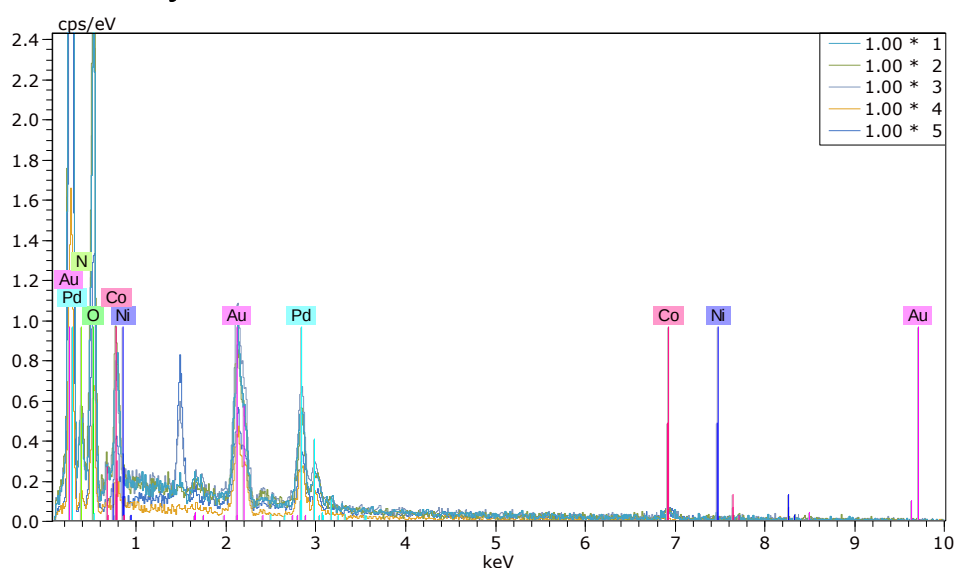


Figure A.14: EDX spectrum for the 24% cobalt loaded membranes

These results show us the EDX peak related to cobalt for the 4%, 12% and 24% cobalt loaded membranes. There is no linear relationship between cobalt peak intensity and cobalt loading. This is due to EDX's shortcomings in quantitative analysis. It is better used for its qualitative analysis. The presence of gold and palladium are due to the sputter coating. Aluminium is present due to the close proximity of the cross-sections with the metal sample holder. The source of nickel on the 24% cobalt loaded membrane EDX spectrum remains however unknown. The fact that no other elements are present on our EDX spectra is indicative that our membranes do not have any (or many) contaminations.

8.3.3 XRD spectrum of cobalt acetate tetrahydrate

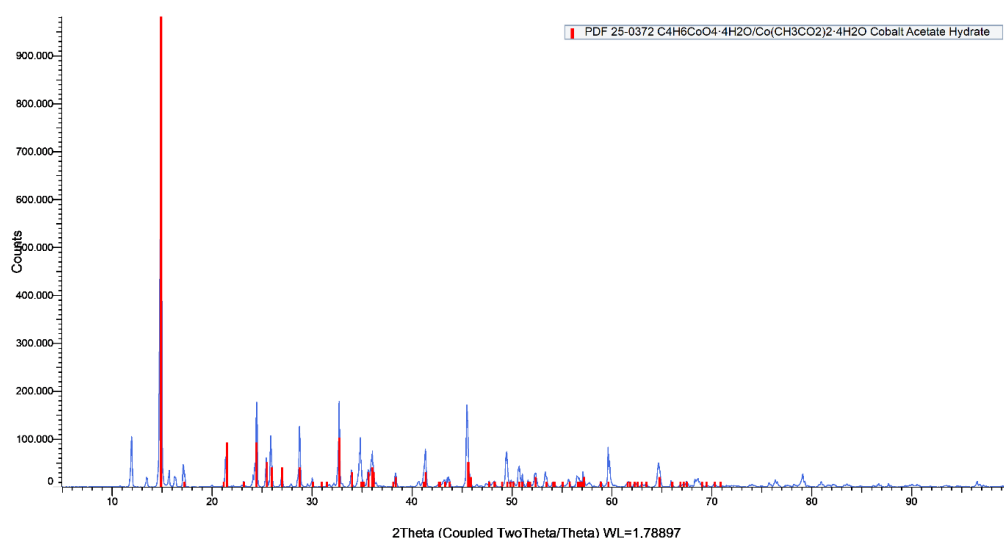


Figure A.15: XRD spectrum for the cobalt acetate tetrahydrate powder

The XRD spectrum of $\text{Co}(\text{Ac})_2$ is shown here above. As we can see, its peaks (blue) are crystalline. The red vertical lines are the peaks most commonly found in the software's data bank when analysing $\text{Co}(\text{Ac})_2$.

8.3.4 FTIR spectrum cobalt formate – corrected baseline

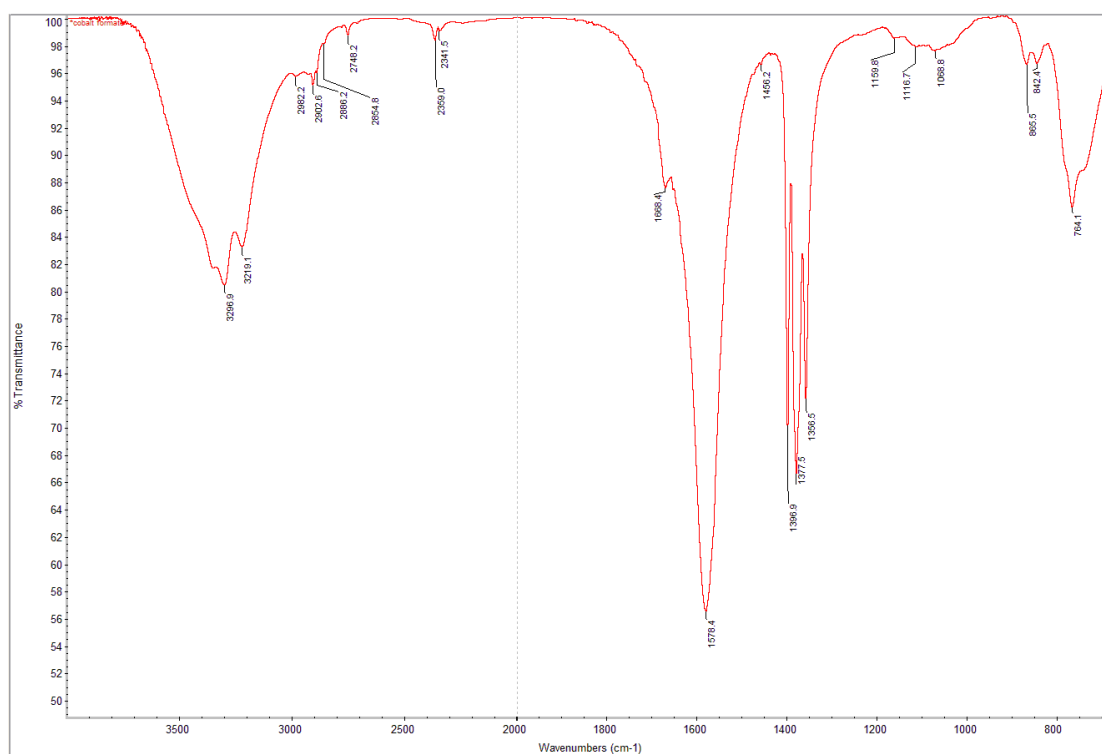


Figure A.16: FTIR spectrum of cobalt formate powder – corrected baseline version

Here above, on Figure A.16, lies Co FA's corrected baseline FTIR. This correction was done using the Omnic Picta software.

8.3.5 Hansen solubility

Via the HSP, the solubility interactions can be described using three main parameters: a dispersion component (δ_D), a polar component (δ_P) and a hydrogen bonding component (δ_H). These components are expressed in molar volume and the units used are $\text{MPa}^{1/2}$ ¹⁰. It is possible to represent this visually as the aforementioned parameters correspond to the three axes of a three-dimensional space (Hansen space) in which it is possible to represent the solvent as a point (with the following coordinates: (δ_{D2} ; δ_{P2} ; δ_{H2})) and the solute as a sphere (Hansen sphere). The polymer is represented by a sphere whose centre's coordinates (δ_{D1} ; δ_{P1} ; δ_{H1}) and radius are determined by HSP parameters (found in literature). This sphere represents the polymer's solubility region (Bapat et al., 2021; W. J. Lee et al., 2021). The distance (R_a) between the solvent's point and the centre of the Hansen sphere is determined as follows, as per W. J. Lee et al. (2021):

$$R_a = \sqrt{(\delta_{D1} - \delta_{D2})^2 + (\delta_{P1} - \delta_{P2})^2 + (\delta_{H1} - \delta_{H2})^2} \quad (\text{A15}).$$

The result being the lower the R_a value, the more affinity there is between the polymer and the solvent. The Hansen solubility sphere is schematised below, on Figure A.17.

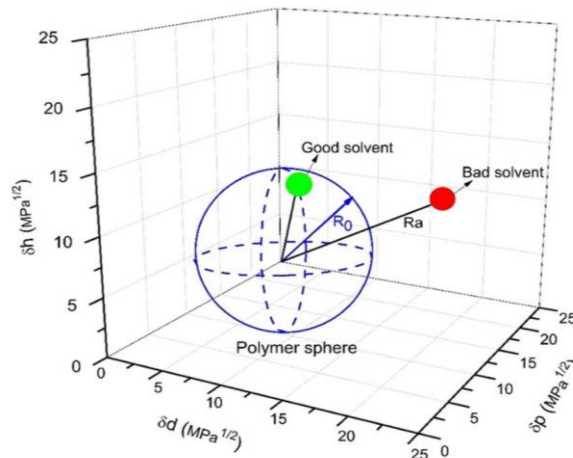


Figure A.17: Hansen solubility sphere schematised (W. J. Lee et al., 2021)

As our feed is a mixture of two solvents, its HSP can be estimated using Hildebrand solubility parameters, via the following formula, as per Barton (1975):

$$\overline{\delta K} = \sum \phi_i \delta K_i \quad (\text{A13}).$$

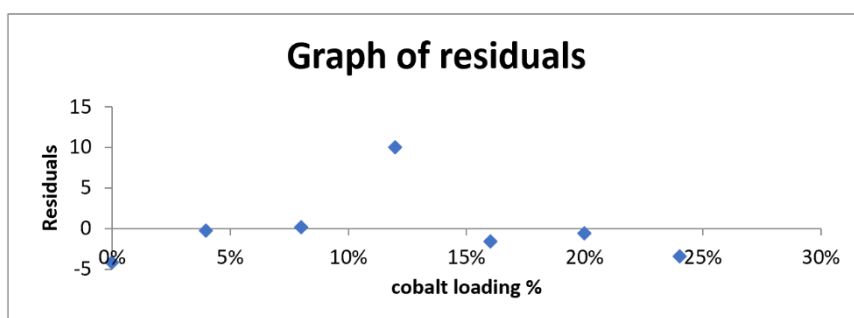
Where the K component encompasses the dispersion, polar and hydrogen bonding components and ϕ_i represents the volume fraction of pure MeOH and DMC in the mixture.

¹⁰ The use of $\text{MPa}^{1/2}$ allows to quantitatively assess the strength of the intermolecular forces associated with each parameter in the Hansen solubility parameter system (Abbott, 2017).

8.3.6 Regression statistics

8.3.6.1 12% Q1: Regression, ANOVA and Residuals analysis

<i>Regression statistics</i>	<i>12% Q1</i>
Multiple R	0,450
R square	0,202
Adjusted R square	0,043
Standard Error	5,194
Observations	7,000



ANOVA

	<i>Degree of freedom</i>	<i>Somme des carrés</i>	<i>Moyenne des carrés</i>	<i>F</i>	<i>Valeur critique de F</i>
					0,31123187
Regression	1	34,209664	34,20966404	1,2682118	p>0,05
Residual	5	134,873623	26,97472453		
Total	6	169,083287			

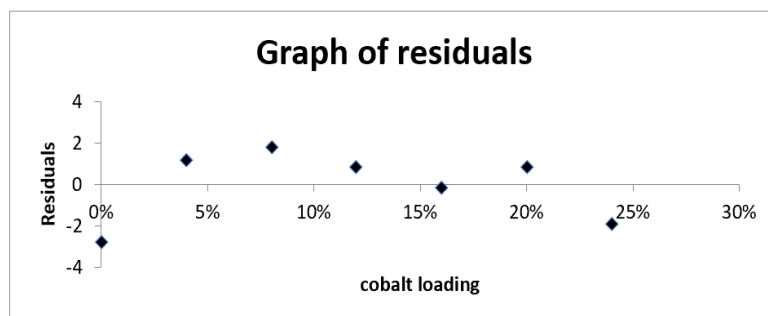
	<i>Coefficients</i>	<i>Std Error</i>	<i>T - Statistic</i>	<i>P-value</i>
Intercept	6,222301476	3,53892346	1,758246978	0,13903701
% cobalt loading	27,63346834	24,5380192	1,126149103	0,31123187

RESIDUALS Analysis

<i>Observation</i>		<i>Predicted Selectivity</i>	<i>Residuals</i>	<i>Standardized Residuals</i>
0% cobalt loading	→ 1	6,222301476	-4,2589486	-0,898285765
4% cobalt loading	→ 2	7,327640209	-0,3434719	-0,07244416
8% cobalt loading	→ 3	8,432978943	0,24385894	0,051434059
Residual > +/- 3 12% Q1	→ 4	9,538317676	10,0866811	2,127455109
16% cobalt loading	→ 5	10,64365641	-1,6498857	-0,347989366
20% cobalt loading	→ 6	11,74899514	-0,6646561	-0,140187443
24% cobalt loading	→ 7	12,85433388	-3,4135777	-0,719982434

8.3.6.2 12% Q2: Regression statistics, ANOVA and Residuals analysis

<i>Regression statistics</i>	<i>12% Q2</i>
Multiple R	0,81657097
R square	0,66678814
Adjusted R square	0,60014577
Standard Error	1,84907995
Observations	7



ANOVA

	<i>Degré de liberté</i>	<i>Somme des carrés</i>	<i>Moyenne des carrés</i>	<i>F</i>	<i>Valeur critique de F</i>
Regression	1	34,209664	34,209664	10,0054685	0,02500672
Residual	5	17,0954833	3,41909667		
Total	6	51,3051474			

	<i>Coefficients</i>	<i>Std Error</i>	<i>T Statistic</i>	<i>P-value</i>
Intercept	4,68917867	1,25993561	3,72176057	0,01368714
% cobalt loading	27,6334683	8,73608162	3,16314219	0,02500672

RESIDUALS Analysis

<i>Observation</i>		<i>Predicted Selectivity</i>	<i>Residuals</i>	<i>Standardized Residuals</i>
0% cobalt loading	→ 1	4,68917867	-2,7258258	-1,6148532
4% cobalt loading	→ 2	5,79451741	1,18965086	0,70478144
8% cobalt loading	→ 3	6,89985614	1,77698175	1,05273218
12% Q2 cobalt loading	→ 4	8,00519487	0,8879443	0,52604229
16% cobalt loading	→ 5	9,11053361	-0,1167629	-0,0691735
20% cobalt loading	→ 6	10,2158723	0,86846669	0,51450322
24% cobalt loading	→ 7	11,3212111	-1,8804549	-1,1140325

8.3.6.3 Regression statistics discussion

Regression statics

Comparing both sets of regressions statistic, we can see that R^2 , which determines the variance in selectivity which can be attributed to the loading percentage of cobalt is much smaller for 12% Q1 than for 12% Q2 (0,20 vs 0,67 respectively).

The **adjusted R^2** , which takes into account the number of independent variables in the analysis to correct for bias only further proves this.

The average distance that is seen between observed values and the regression line are given by the **Standard Error**, which shows that the 12% Q1 data set has far less a precise regression line than the 12% Q2 data set.

ANOVA

We can see via the critical **F-value** test of the ANOVA that there is no linear relationship between selectivity and cobalt loading for the 12%Q1 data set. This being the null hypothesis and its F-value being superior to 0,05 for 12%Q1, we assume this null hypothesis to be true. The opposite is true for the 12% Q2 data set.

The **P-value** of the % cobalt loading being superior to 0,05 for the 12% Q1 data set proves that cobalt loading percentage has no significant impact on selectivity.

Residuals analysis

The **residuals** (indicators of the distance between the actual data point and the line of best fit) for the data point holding the 12% Q1 is an outlier in the first case, whereas it is not in the second data set. As a rule of thumb, residuals that are superior to +/- 3 are considered to be outliers.

Graph of residuals

A perfect line of best fit would find its data points on the graph points being on the x-axis. The more distanced a data point is from it, the more chances they are that that data point is an outlier. The fourth point of the Y-axis corresponds to the 12% data point. We can see looking at these graphs how farther away this point is from the x-axis for the first data set (12% Q1) as compared to the second.

We thus have sufficient proof to reject the 12% Q1 results and to accept the 12% Q2 results.

8.3.7 Pervaporation separation results

Table A6: PV experiments - data

loading %	h:m	h:m	g	h:m	decimals	g/m ² *h	feed weight %		permeate weight %	
	start time	finish time	permeate weight	time	time	flux (j)	xi MeOH	xj DMC	yi MeOH	yj DMC
0	13:00	15:03	0,13	02:03	2,05	16,48	4,39	96,66	14,14	37,87
0	15:05	18:48	0,236	03:43	3,72	16,50	4,39	96,66	35,07	49,91
0	15:16	18:06	0,22	02:50	2,83	20,18	4,38	96,68	58,49	30,72
0	18:08	19:15	0,35	01:07	1,12	81,45	4,38	96,68	53,88	43,67
0	14:03	16:17	0,202	02:14	2,23	23,51	4,32	96,72	26,12	52,17
4	11:50	13:57	0,35	02:07	2,12	42,97	4,13	96,19	43,64	39,35
4	14:00	16:27	0,399	02:27	2,45	42,32	4,13	96,19	60,7	35,86
4	11:53	13:00	0,24	01:07	1,12	55,85	4,05	97,02	69,82	12,94
4	13:05	14:23	0,187	01:18	1,30	37,38	4,05	97,02	73,46	21,26
4	14:25	15:56	0,261	01:31	1,52	44,72	4,05	97,02	67	30,54
4	13:58	15:31	0,18	01:33	1,55	30,18	4,29	96,7	66,95	32,11
4	15:35	17:23	0,196	01:48	1,80	28,30	4,29	96,7	67,71	31,54
8	15:15	16:27	0,11	01:12	1,20	23,82	3,42	97,42	37,1	52,26
8	16:28	17:38	0,124	01:10	1,17	27,62	3,42	97,42	37,65	56,03
8	10:35	11:59	0,167	01:24	1,40	31,00	4,69	96,36	50,56	48,63
8	12:03	13:33	0,179	01:30	1,50	31,01	4,69	96,36	52,44	46,85
8	12:02	13:25	0,107	01:23	1,38	20,10	4,107	96,98	69,19	29,63
8	13:28	14:53	0,095	01:25	1,42	17,43	4,107	96,98	68,47	30,12
8	15:19	16:46	0,054	01:27	1,45	9,68	4,06	97,02	63,98	34,55
8	14:20	16:39	0,231	02:19	2,32	25,91	4,21	96,61	40,7	22,9
8	16:45	18:18	0,133	01:33	1,55	22,30	4,21	96,61	70,95	25,64
8	14:01	16:20	0,2	02:19	2,32	22,44	4,17	96,69	65,74	31,41
8	16:24	19:10	0,298	02:46	2,77	27,99	4,17	96,69	57,45	40,97
8	12:54	14:47	0,174	01:53	1,88	24,01	4,03	96,86	70,63	27,35
8	14:54	16:57	0,154	02:03	2,05	19,52	4,03	96,86	69,05	28,77
12	12:10	13:28	0,169	01:18	1,30	33,78	2,68	98,12	77,86	20,24
12	13:30	14:40	0,135	01:10	1,17	30,07	2,68	98,12	72,97	24,78
12	14:42	15:55	0,148	01:13	1,22	31,61	2,68	98,12	78,85	19,61
12	15:41	18:36	0,145	02:55	2,92	12,92	3,35	97,41	36,42	60,96
12	11:07	14:12	0,102	03:05	3,08	8,60	4	97,08	34,59	62,97
12	14:50	16:33	0,078	01:43	1,72	11,81	4,3	96,78	33,38	39,36
12	16:40	18:34	0,08	01:54	1,90	10,94	4,3	96,78	50,59	47,33
12	12:09	14:04	0,264	01:55	1,92	35,79	3,82	97,29	36,54	37,09
12	14:12	15:35	0,119	01:23	1,38	22,36	3,82	97,29	65,68	32,65

12	15:39	17:13	0,247	01:34	1,57	40,97	3,82	97,29	30,73	32,92
12	12:10	13:35	0,195	01:25	1,42	35,77	3,75	97,36	69,13	29,86
12	10:12	12:32	0,138	02:20	2,33	15,37	3,69	97,42	9,99	22,57
12	12:37	15:21	0,141	02:44	2,73	13,41	3,69	97,42	35,31	60,4
16	11:11	12:52	0,12	01:41	1,68	18,53	4,26	96,82	69,99	28,87
16	12:57	14:25	0,108	01:28	1,47	19,14	4,26	96,82	57,23	23,97
16	10:35	12:20	0,132	01:45	1,75	19,60	4,21	96,89	67,13	26,31
16	15:00	18:18	0,099	03:18	3,30	7,80	4,21	96,89	36,66	58,15
20	14:25	16:18	0,201	01:53	1,88	27,74	4,35	96,72	67,73	30,46
20	16:23	18:09	0,178	01:46	1,77	26,18	4,35	96,72	78,96	20,75
20	16:36	17:30	0,231	00:54	0,90	66,70	4,12	96,97	46,72	52
20	17:34	18:09	0,125	00:35	0,58	55,69	4,12	96,97	52,3	47,21
20	18:13	18:59	0,185	00:46	0,77	62,71	4,12	96,97	45,97	53,07
20	14:15	16:37	0,221	02:22	2,37	24,27	4,05	96,91	65,35	32,18
24	14:47	18:17	0,107	03:30	3,50	7,94	4,23	96,91	23,03	73,79
24	12:45	14:50	0,593	02:05	2,08	73,97	4,207	96,88	6	94,95
24	14:54	16:08	0,122	01:14	1,23	25,71	4,207	96,88	9,35	91,31
24	16:12	17:23	0,134	01:11	1,18	29,43	4,207	96,88	14,75	85,68
24	12:10	14:08	0,173	01:58	1,97	22,86	4,37	96,66	73,01	25,03
24	14:14	15:36	0,125	01:22	1,37	23,77	4,37	96,66	68,77	30,72
24	15:40	17:08	0,148	01:28	1,47	26,22	4,37	96,66	63,2	35,4

On Table A6 above, we can find the data attributed to the PV separation tests. The time it took to gather the corresponding permeate weight is given for every differently cobalt loaded membrane. Flux is calculated following equation (1), the feed and permeate weight percentages were converted using into mass fractions using the calibration curves in sections 8.2.4 and 8.2.5.

8.3.8 Pervaporation separation results with external factor

Table A7: PV experiments with external factor- data (/ signifies that there was too little permeate for GC analysis)

	loading %	h:m start time	h:m finish time	g permeate weight	h:m time	decimals time	g/m ² *h flux (j)	feed weight %		permeate weight %	
								xi MeOH	xj DMC	yi MeOH	yj DMC
procedure 1	4	10:38	13:34	0,059	02:56	0,933333352	5,22703614	3,75	96,93	32,73	67,26
		14:41	17:51	0,089	03:10	0,16666667	7,30386249	3,77	96,91	33,97	64,19
		10:40	13:45	0,089	03:05	0,083333335	7,50126422	3,67	97,04	23,27	72,84
	8	08:25	12:02	0,091	03:37	3,61666679	6,53879664	3,7	96,99	40,94	57,38
		12:53	17:32	0,182	04:39	4,65000013	10,1714615	3,72	96,98	34,03	64,48
	12	10:15	13:32	0,23	03:17	3,283333339	18,2044595	3,73	96,96	2,64	98,15
procedure 2		14:05	16:55	0,1	02:50	2,83333335	9,17206746	3,71	96,99	2,59	98,19
	4	11:15	12:45	0,022	01:30	1,5000001	3,81150356	/	/	/	/
		12:46	14:51	0,036	02:05	2,083333335	4,49064445	/	/	/	/
		14:23	18:04	3,107	03:41	3,683333347	219,212417	4,38	96,15	24,99	67,02
		09:50	13:32	0,1	03:42	3,70000014	7,02365541	4,34	96,2	17,15	81,06
	8	14:04	17:34	0,196	03:30	3,5000001	14,5530141	4,27	96,28	3,4	97,25
		12:50	15:58	0,063	03:08	3,13333336	5,22515146	/	/	/	/
	12	12:00	15:05	0,069	03:05	3,083333335	5,81558687	4,09	96,47	13,17	85,38
		15:53	18:52	0,107	02:59	2,983333353	9,32066513	4,04	96,53	22,49	75,13
	16	09:37	12:30	0,09	02:53	2,883333351	8,11171282	3,93	96,644	22,29	76,06
		13:01	16:21	0,177	03:20	3,33333334	13,799376	3,9	96,68	1,12	99,91
procedure 3	4	10:30	13:17	0,097	02:47	2,783333349	9,0567301	3,78	96,82	5,84	95,18
		13:47	16:38	0,429	02:51	2,85000017	39,1180631	3,78	96,91	3,06	97,75
	8	10:18	14:43	0,089	04:25	4,41666675	5,23673155	3,75	96,93	39,36	58,93

On Table A7 above, we can find the data attributed to the PV separation tests when water was present within the feed. The time it took to gather the corresponding permeate weight is given for every differently cobalt loaded membrane. Flux is calculated following equation (1), the feed and permeate weight percentages were converted using into mass fractions using the calibration curves in sections 8.2.4 and 8.2.5.

Cobalt-coordinated chitosan membranes to separate a dimethyl carbonate and methanol mixture by pervaporation

Author: **Alexander Cosslett**

Dimethyl carbonate, an eco-friendly organic component, has gained much attention in the chemical sector due to its wide range of applications. However, its separation from its precursor in its production process, methanol, can be challenging as it forms an azeotrope. Pervaporation offers an energy efficient solution for separating azeotropes and was used within this thesis with the aim to separate the dimethyl carbonate/methanol mixture using a chitosan-based membrane.

Chitosan is a biopolymer derived from biowaste that has shown to be effective in the separation of the aforementioned mixture. However, with growing interest in this field, it has been demonstrated that inserting inorganic material within the biopolymer membrane can significantly enhance its separation performance. The aim of this thesis was to develop a cobalt formate metallic organic framework within the chitosan membranes, as this crystalline framework could act as a size-selective sieve for methanol. Unfortunately, in-situ crystal nucleation and growth did not occur. The evidence gathered in this work demonstrates that cobalt-coordinated chitosan membranes were formed.

Metal ion coordinated chitosan had never been used in pervaporation. However, our new aim was to investigate the separation performances of these novel membranes. Our work shows that the presence of cobalt ions within the biopolymer served as a crosslinker, increasing the membrane's stability. The presence of cobalt also enhanced the membrane's hydrophilicity, increasing its selectivity towards methanol. The 20% cobalt loaded membranes that were developed managed to invert the molar fraction ratio found in the feed. A 11:89 methanol:dimethyl carbonate molar ratio in the feed resulted in a 89:11 ratio in the permeate. These results are similar to what has been found when metal organic frameworks are present within chitosan membranes to separate this mixture. Nonetheless, the production process of the cobalt-coordinated chitosan membranes is more facile and generates less waste, resulting in an effective and more sustainable solution for the separation of dimethyl carbonate/methanol mixtures that are rich in dimethyl carbonate.