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Elaboration of macrocyclic membranes based β-cyclodextrin by physical mixing and these application to dialysis organic molecules.

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Abstract

The purpose of this study is to demonstrate a process facilitated transport of molecules of different natures through a plasticized polymer membrane (MPP). This membrane was obtained by the intercalation of an extractant, the β-cyclodextrin macrocycle (β-CD). A cellulose triacetate membrane were proposed and tested as a dialysis membranes. The cellulose triacetate polymer (TAC) not only provides the elasticity of the membrane but also acts as a plasticized through which the extracted molecule can diffuse easily because of the double functionality of the TCA. The flux and permeability coefficients of different chemical species were calculated in aqueous solution. To carry out the measurements, the method requires that samples of various solutions must be performed when the diffusion quasi-steady state has been established. The obtained membranes were characterized by (FTIR, DSC, AFM, AC) was conducted to obtain a better understanding of the transport properties in the membrane and to acquire information's concerning the composition and interactions which may exist between the components of the membrane. The β – CD macrocycle membranes were tested as a dialysis membrane for separation of molecules. The experimental results showed the improved selectivity of the newly processed membranes for number molecules carboxylic acid, phenol. The possibility of studying the separation of carboxylic acids by the neutral membrane based on β-CD macrocycle or by increasing the thickness or by modifying the accessibility of the cavity of the macrocycle. Generally the calculated P and J confirm the influence of the size of the molecules for the three membranes employed glucose and ammoniac.

1.Introduction

A membrane is a selective barrier of a few hundreds nanometers to a few millimeters thickness and selective which under the gradient effect will allow or prevent the passage of certain components between two separated media. The membrane treatment of industrial water took is widely applied particularly in the field of agri-food and pharmaceutical industries. In fact, there are two major categories of membranes. Porous membranes used primarily in the filtration procedures methods and the non-porous. The later, may be homogeneous, composite solids, liquids, ionic or neutral.

The development and application of membranes demand for a multi-disciplinary research. Several studies were directed in the membrane development and their application in different fields.

Current trends are more oriented to the development of molecular recognition membranes which are permeable only to the species recognized by molecular targets incorporated in the membrane. Considerable attention, is focused on plasticized polymers membranes PPM, also called inclusion polymers membranes IPM [1-8]. The ease of transport of different organic and inorganic molecules and in particular the transition metal extraction were of practical interest in many research's fields. In the study, Aliquate 336 was used as a plasticizer in a IPM system containing D2EHPA as a support for the elimination of Cr (III) [19-28]. The effect of different parameters on the efficiency of transport through the membranes was investigated.

This study focuses on the use of a β-CD macrocycle as a support, the cellulose triacetate polymer that as a plasticizer and a polymer. In addition, for a better understanding the transport phenomenon and membrane

properties, the membranes were characterized by AFM, DSC, FTIR and AC. The obtained membranes were tested as dialysis membranes for separation of several organic and inorganic molecules.

2.Experimental details

2.1. Chemical reagents

The Cellulose triacetate polymer (TAC) was purchased from Fluka, it is a thermoplastic polymer base to promote the mechanical strength of the membrane, to provide a degree of elasticity for the diaphragm and to ensure mobility of the molecules during transport. Chloroform was from Fluka. Folin Ciocaleux pure was obtained from Aldrich.

2.2 Preparation of plasticized polymers membranes

The studied membranes were prepared according to the phase inversion process and more specifically precipitation by solvent evaporation [20-27]. In this method, 130 mg of methylated-allylated β-CD or methylated β-CD and 100 mg of cellulose triacetate polymer are dissolved of chloroform by magnetic stirring. The resulting solution was poured into a petri dish of 9 cm diameter. It is partially covered to allow the evaporation of the chloroform and let to rest overnight. A homogeneous film which covers the surface of the impregnated area was obtained. For retrieving the film, deionized water was added and allowed to rest two hours.

2.3 *Characterization of* plasticized polymers membrane

2.3.1 *FTIR analysis*

IR spectra of membranes in the range from 500 to 4000 cm^{-1} were acquised by Perkin Elmer FTIR spectrophotometer 100. The assays were carried out directly on the membrane film (TAC, β-CDMe-ally and β-CDMe).

2.3.2 AFM *analysis*

The images of atomic force microscopy (AFM) were obtained using a microscope Nano-Scope III-a-home Veeco driven by a μ-computer.

2.3.3. *DSC analysis*

The thermal images are made with a device to differential scanning calorimetry (DSC). The analyzes were carried out from 25°C to 500°C with a heating rate of 10°C.min^{-1}. The wettability or the contact angle is achieved by GB.X device (Romain-France).

2.3.4. *Contact angle measurement*

The surface energy of the functionalized electrodes was assessed from contact angle measurements carried out by deposition of drops of three different liquids (water, formamide and diiodomethane) on the electrode surface. A contact angle instrument from GBX Scientific Instruments was used. A sequence of successive images of the drops was taken as they spread with a CCD camera connected to a graphics board. The digital images were analyzed for their profile and the contact angle was extracted at both sides of the drops by the tangent method. The equilibrium contact angle was the mean of the right-side and left-side angles taken once equilibrium shape had been reached.

2.3.5**.** *Dialysis*

We have adopted the following experimental protocol: The membrane is placed between the two compartments, each filled with 180 ml of water is balanced over a magnetic stirring overnight .Then, after clean the cell, we introduce simultaneously 180 ml of a solution of species i to study C_0 concentration in the compartment (I) and 180 ml in the compartment (II). The diffusion time is counted from that point. The solutions of the two compartments are agitated for a sufficiently long time ($t \geq 8$ hours) so that the quasi steady state is established. The initial and final concentration of studied substances were determined by titrimetrically or visible detection of equivalence. We assayed by pH-meter two families one monoacid: acetic acid (AA) and lactic acid (LA) and other diacid acetic: oxalic acid (OA) and tartaric acid (TA). The adopted experimental method was used based on the unidirectional diffusion to the quasi-steady state [29-36]. The two compartments are separated by the obtained membrane (Fig.1). The parameters are as follow:

A_0 membrane active surface is 19.6 cm^2, thickness l = 0.005 cm for a β-CDMe-ally membrane and l = 0.003 cm for a β-CDMe membrane.

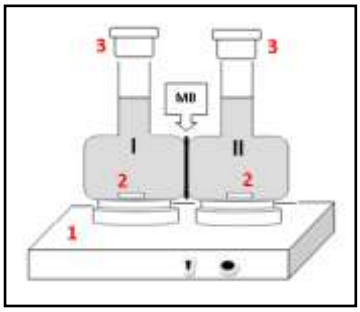


Figure 1: Schematic representation of the dialysis cell.

(I and II) donor and receiver compartments; (1) magnetic stirrers; (2) magnetic bars; (3) diffusion cell; Mb: membrane.

The used method is based on the following principal :

The donor compartment (I) contains initially (t = 0) a solution of know concentration (C_0) of the species. While the receiving compartment (II) contains pure water. At time t concentrations in both compartments are expressed by C_I (t) and C_{II} (t). To exploit the results obtained, the transport flux (J) was determined using the first Fick's law [10]:

$$\frac{P.C_0}{l}$$

Where P is the permeability of the different species in the aqueous feed phase. P is calculated by using the equation P coupled to the volume V of the solution, a is the slope, l is thickness, S is the surface of the membrane C_F is the residual concentration in the membrane, C_A is the concentration in the donor phase, C_R is the concentration of the receptor phase .

$$\frac{a.l.V}{2.S}$$

This relation is obtained by combining equations 1, 2, and 3 and the integration of equation 4.

$$\frac{dC_R}{dt} = \frac{j.S}{V} \quad (1)$$

$$J = \frac{P.\Delta C}{l} \quad (2)$$

$C_F = C_0 - C_R$ et $\Delta C = C_A - C_R = C_0 - 2C$ (3)

$$P.dt = \frac{\frac{l.V}{S}.dC_R}{C_0 - 2C_R} \quad (4)$$

$$P(t - C_L) = \frac{l.V}{S} Ln(C_0 - 2C_R) \quad (5)$$

2.3.6**.** Transport mechanism of plasticized polymers membrane

The flux and selectivity of a membrane are established by the carrier selection. The latter is implied by its concentration, hydrophobicity and its kinetic characteristics, such as complexing and decomplexing speed.

The transport mechanism through a plasticized polymer membrane from a source phase and to a receiving phase can be described as a combination of four simultaneous processes based on the diffusion of species through the membrane [11, 12]:

a) The Complexing step is carried out in the first interface separating the donor phase and the membrane. At this level the chemical species are complexed by the membrane carrier according to a reversible reaction having an equilibrium constant K of about 10^3. Indeed, a high K value of the complexing reaction may prevent the decomplexation step in the second interface and consequently slow down the transport operation.
b) The distribution of the complex formed through the membrane, which mainly depends on the viscosity of the organic phase.
c) The decomplexation step is performed at the second interface between the membrane phase and the aqueous receiving phase. Indeed this step can be difficult if the complex is very stable.

d) The retro-diffusion of the carrier in the membrane from the second interface to the first interface which is then available for a second transmission cycle.

3.Resulats and Discussion

3.1. Characterization of MPP

3.1.1. *FTIR analysis*

IR obtained spectra showed that the major bands are those characterizing the individual components of the membrane (Fig 2). An existence of weak interactions between the various components of the plasticized polymer membranes could be suggested. These interactions are primarily static type Van Der Walls or hydrogen bonds. The FTIR spectra of our membranes are appear a band around 3500 cm^{-1} that can be attributed to OH bonds stretching vibrations in membranes TAC and β-CDMe respectively. Bands around 1748 cm^{-1} and 1215 cm^{-1} refer to the groups C = O and C-O and affirm the presence of carboxylate groups in respective membranes β-CDMe-ally + TAC and β-CDMe.

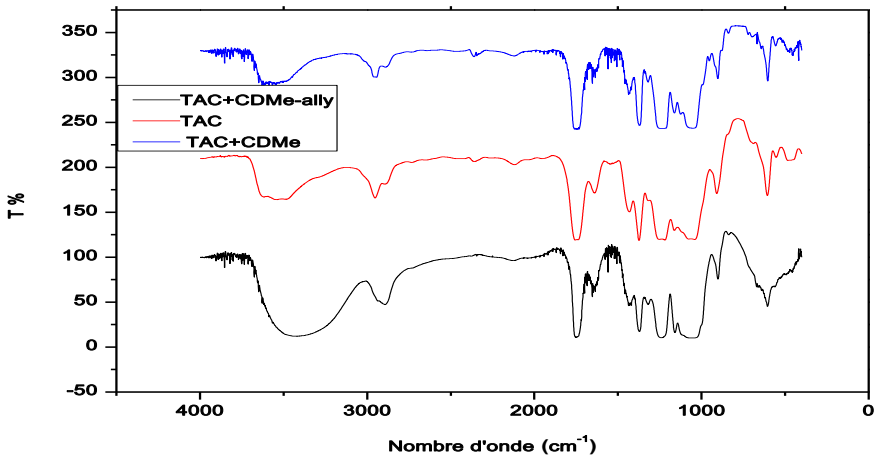


Figure 2: FT-IR spectrum of membranes.

3.1.2. *AFM analysis*

The AFM surface images obtained in Tapping Mode (Figure I) showed. The film obtained is composed of a formulation (mixture of TAC and β-cyclodextrins .The methylated cyclodextrin menbranes has a smooth, uniform surface and appear dense and without apparent porosity (Fig.3, a). In contrast the methylated -allylated membranes remained was observed o AFM image (Fig.3, b) on the AFM image as different grain size was observed.

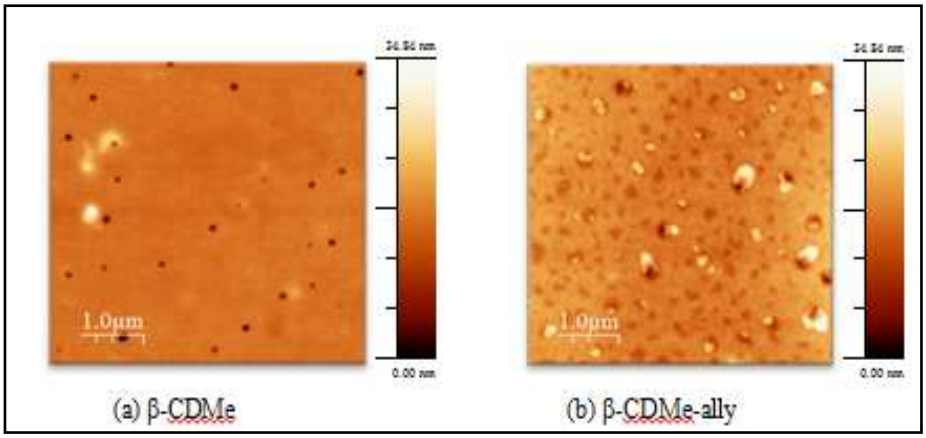
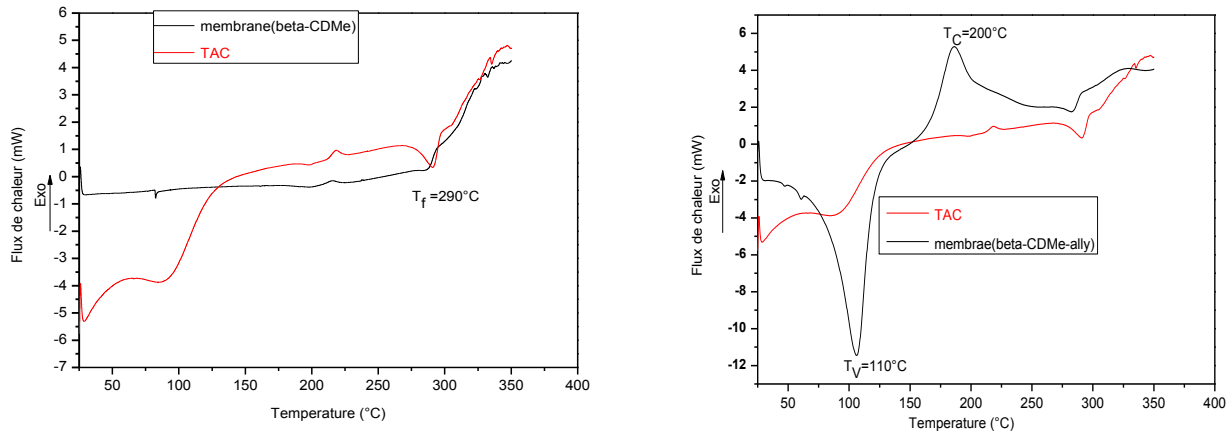


Figure 3: AFM Image of β-CD macrocycle membrane

3.1.3. *DSC analysis*

Thermal analysis (DSC) was carried out to better elucidate the thermal anomalies of the sample relative to an inert control during heating or cooling. In fact we observe in case of β-CD macrocyle and thermogram only two endothermic events TAC for each successively corresponds to the boiling temperature of the water molecules and the melting temperature of the tow polymer. The thermogram of a β-CD-Me membrane shows that there is not a

melting temperature but there is a single endothermic event at about 300° C which corresponds to the membrane degradation temperature. The latter coincides with the melting cellulose triacetate polymer temperature and therefore thermal deterioration of the main chain of the cellulose triacetate polymer. For the β-CDMe-ally membrane we observe an endothermic event at 110 ° C corresponding to molecule water loss and another event to 200 ° C which can be attributed to the crystallization temperature (Fig 4). Based on the results of thermal analysis (DSC) we could conclude that the interactions between the various components of the MPP are weak.



(a) (b)

Figure 4: β-CDMe (a) and β-CDMe-ally membranes (b)

3.1.4. *Contact angle measurement*

The surface energy of the coating and its components were determined from the contact angles of three liquid drops using the Owens–Wendt method. This method provides the total surface energy, its dispersive and polar components (s, d and p) are also calculated by the van Oss method that provides the total surface energy, its dispersive, acid and basic components (γ_s, γ_d, γ_p, γ_+ and γ_-). The obtained results showed (table 1) the surface of membrane based on β-CDMe appears relatively more hydrophilic than the β-CDMe-ally membrane. These results were confirmed by the values of dispersive and polar components.

Table 1: Contact angle of the membranes

Angle (θ°)				Surface energies (mJ.m^{-2})				
Membrane Surface	Water	Formamide	Diiodomethane	γ_s	γ_d	γ_p	γ_+	γ_-
β -CDMe	54	14.7	33	53.1	49	4.1	0.2	19.9
β -CDMe-ally	59	25	48.6	48.6	46.1	2.5	0.1	23.8

3.2. Study of the Transport

3.2.1. Passive Transport

Passive transport involves only the physical characteristics of the membrane; the latter is governed by the concentration gradient of chemical species between the two compartments. This part was carried out with membrane formed by the base polymer only (TAC). Dialysis application has shown that there are no molecules transported through the membrane. In fact, the molecule's concentration in the donor phase remains almost constant.

3.2.2. Active Transport

The active transport processes of different types of molecules by incorporating a transport agent which provides molecular recognition. The obtained membranes β-CDMe$_1$, β-CDMe$_2$ and β-CDMe-ally was studied. The concentration profiles of acetic acid, phenol, ammoniac, and glucose were obtained.

3.3. The concentration profiles

3.3.1. Carboxylic Acid

In Part one we studied two families carboxylic acids. Testing of these acids is applied on the neutral membrane β-CDMe-ally, the concentration profiles are shown in the figures presented in below.

The satisfactory description from what profile it is easy transport itself. Based on the molecular size we notice that the accessibility of acetic acid through the β-CDMe-ally is stronger as tartaric acid and oxalic acid. Indeed, a first observation tells us clearly that the size of any molecule that is very important to study the transport phenomenon facilitated almost steady and even steady with ion exchange membranes [13,15]. In Table 2 we increased the concentration of the initial solution of each acid diffused through the membrane β-CDMe-ally and its concentration in both donor and recipient compartments. We calculated the coefficient of permeability and flux of each acid. The experimental acid used was determined using an automatic titrator Melter TOLEDO LD50.

Table 2: Acid Transport through the membrane β-CDMe-ally.

Species	Molar mass (g.mol^{-1})	C_0 (molL^{-1})	$C_I(t)$ (molL^{-1})	$C_{II}(t)$ (molL^{-1})	J(mmol cm^{-2}.s^{-1})	P(cm^{-2}.s^{-1})
AA	60.05	$7.87.10^{-3}$	$4.23.10^{-3}$	$3.75.10^{-3}$	$3.74.10^{-7}$	$2.33.10^{-6}$
LA	90.08	0.0139	$7.80.10^{-3}$	$5.81.10^{-3}$	$9.17.10^{-7}$	$1.38.10^{-6}$
TA	150.08	0.0104	$5.31.10^{-3}$	$5.05.10^{-3}$	$2.23.10^{-7}$	$2.57.10^{-6}$
OA	90.03	0.0116	$7.05.10^{-3}$	$4.51.10^{-3}$	$9.66.10^{-7}$	$1.14.10^{-6}$

3.3.2. Organic molecules

In the second part we studied a series dialysis organic molecules such as phenol, glucose, indigo and disodium ethylene diamine tetraacetic molecular size, ethylenediamine (EDA) and inorganic molecule except ammonia low size. First dialyses applied on indigo and the disodium salt of ethylene diamine tetra acetic show that these molecules are retained by the membrane and their initial concentrations in the donor phase is practically unchangeable. For molecules outlined above other than indigo, and the disodium salt of ethylene diamine tetra acetic we tested their dialyzed through three types of membranes rated respectively, β-$CDMe_1$ β-$CDMe_2$ and β-CDMe-ally (Fig 5, 6, 7, 8, 9) . The solutions of phenol and glucose are analyzed by spectrophotometry. The following two curves give another justification on the diffusion of molecular species through our membranes. For example, the time affiliation of a quasi-steady state can be assessed in terms of the diffusion time lag value (t_L) given by (-Ln (C_0-C_R)) over time (Fig 5). In the case of our system t_L = 4000s for phenol and t_L = 3000s for glucose.

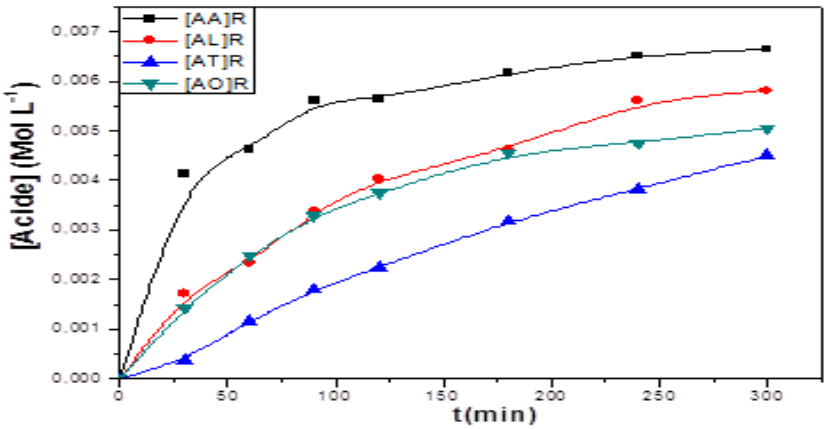
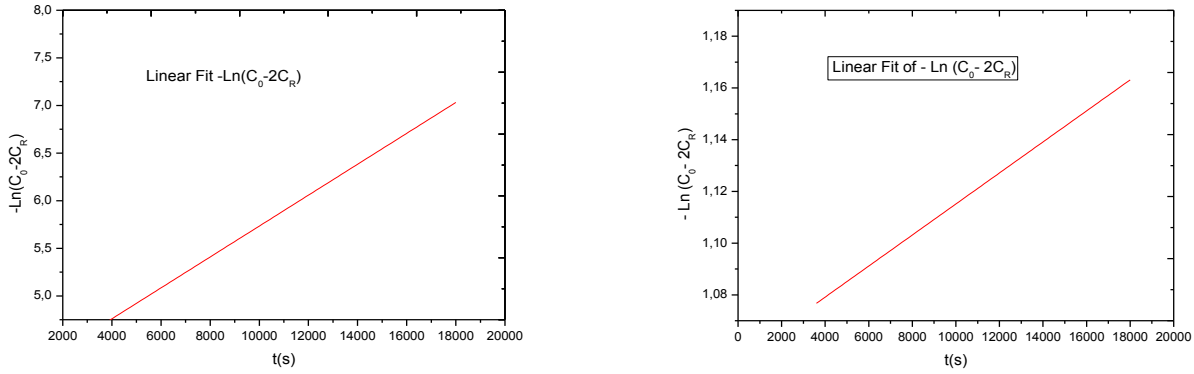
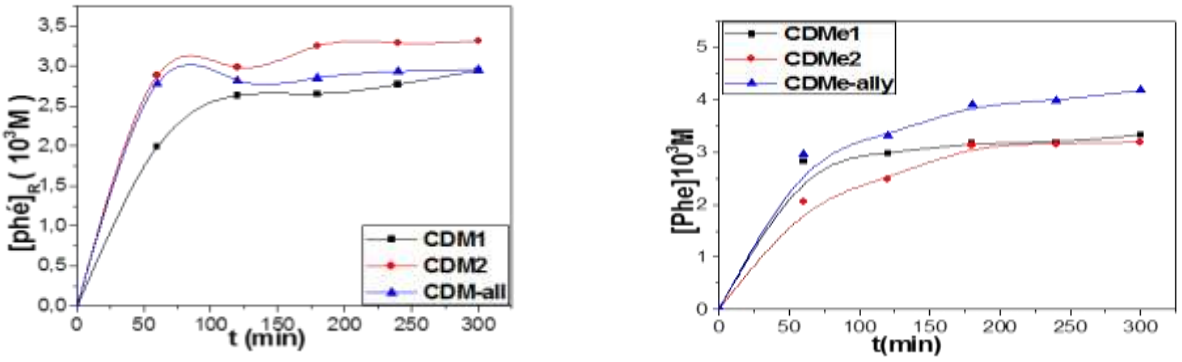


Figure 5: Concentrations profiles over time carboxylic acids.



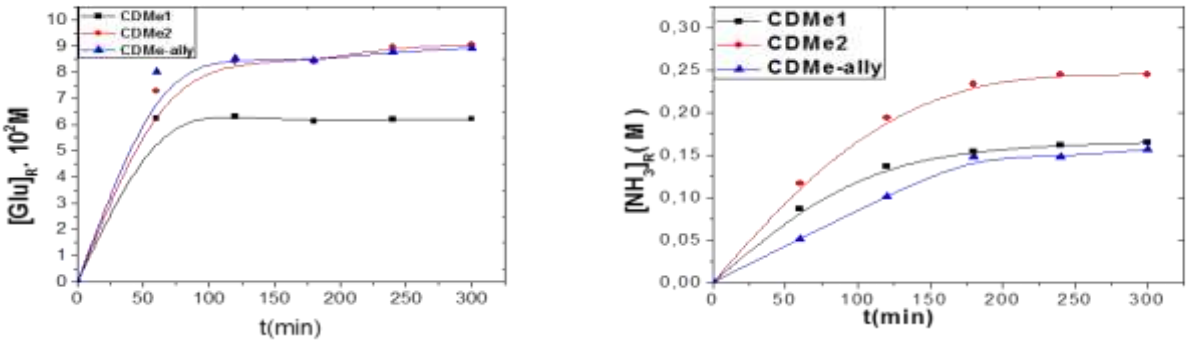
(a) (b)

Figure 6: Evaluation of the time lag for the quasi-stationary state : Phenol (a) and Glucose (b).



(a) **(b)**

Figure 7: Dialysis of phenol (a) and (b).



(c) (d)

Figure 8: Dialysis of Glucose (c) and Dialysis of NH_3 (d)

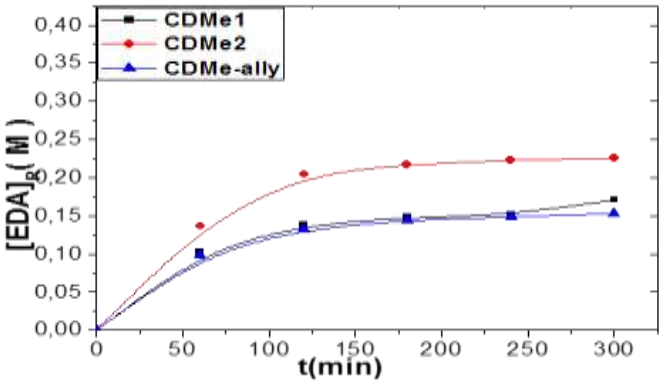


Figure 9: Dialysis of EDA

The obtained results (Table 3) allow use to offer a growing classification of the diffusion of organic molecules, while a geometric point of view, the inclusion will depend on the relative size of the cavity of the cyclodextrin from the size of the diffused molecule [16]. For if the molecule is too large in size, it can not penetrate inside the cavity of the cage molecule, against if its size is too small, it will have little interaction with the macrocyle cyclodextrin.

Table 3: Permeability coefficient P molecular species studied in aqueous solution

Molecule	Molar mass ($g.mol^{-1}$)	C_0 ($molL^{-1}$)	P ($cm^{-2}.s^{-1}$)	J ($mmol\ cm^{-2}.s^{-1}$)
$C_2H_4O_2$	60.05	$7.87.10^{-3}$	$2.33.10^{-6}$	$3.74.10^{-7}$
$C_3H_6O_3$	90.08	0.0139	$1.38.\ 10^{-6}$	$9.17.10^{-7}$
$C_4H_6O_6$	150.08	0.0104	$2.57.\ 10^{-6}$	$2.23.10^{-7}$
$C_2H_2O_4$	90.03	0.0116	$1\ .14.\ 10^{-6}$	$9.66.10^{-7}$
NH_3	17	0.672	$1.06\ 10^{-9}$	$1.42\ 10^{-7}$
EDA	60.1	0.925	$1.07\ 10^{-9}$	$1.97\ 10^{-7}$
C_6H_6O	94.11	8.10^{-2}	$7.255\ 10^{-10}$	$1.160\ 10^{-9}$
$C_6H_{12}O_6$	180	5.10^{-1}	$3.83\ 10^{-10}$	$3.83\ 10^{-9}$

Due to the non-polarity of the cavity of the cyclodextrin macrocyle, one can provide inclusion complexes with these molecules used in dialysis but these complexes are not stable, they can form and dissociate readily to recover the organic molecule studied [17]. In aqueous solution the cavity is occupied by water molecules therefore complexation of the guest molecule is accompanied by desolvation of the molecule and the cavity of the β-cyclodextrin macrocyle and thereafter the water molecules retained in the cavity are transferred in an aqueous medium while the guest comes into interaction with the interior of the cyclodextrin macrocyle. With the molecules used in the dialysis is found that only the smaller molecular weight molecules are faster through the membranes by counters in the case of phenol and glycose their permeability coefficients are smaller and in the case of molecules too large size that the phenol and the glucose diffusion is zero and therefore this type of molecules can not penetrate inside the cavity of the cage molecule β-cyclodextrin.
This is due to the creation of weak interactions of electrostatic type, Van der Waals, hydrophobic-hydrophobic and especially hydrogen bonds between these molecules and the cavity of cyclodextrin macrocyle. This phenomenon explains that the main force governing inclusion in the complexation in aqueous solution is the replacement of the water molecules retained in the cavity of the cyclodextrin macrocyle with the guest molecule [18].The conclusion to be titrated is that the ability of the macrocycle to form a β-CD inclusion complex with the guest molecule is mainly explained by two factors:

- The steric factor:
  Depend on the relative size of CDs macrocycle and the size of the guest or some key functional groups in the guest molecule. If the guest is of large size, it will not fit properly in the CD macrocycle cavity.
- The thermodynamic factor:

- This can be explained by the set of interactions that can be held between the various system components (CD, guest and solvent), but on the other hand the effects that lead to complexation are not yet well known.
- It appears that the most important diffusion rate is the lowest molecular weight of the acid where studied so we confirmed the influence of the size on the results of dialysis.
-

Conclusions

The film obtained is composed of a formulation (mixture of TAC and β-cyclodextrins macrocycle were developed for the study of the transport of organic molecules in an aqueous medium. We tested three β-CD macrocyle membranes by different methods. We go find each time the calculated flow and permeability give a better understanding to understand the phenomenon of facilitated transport. Indeed more the molecule is its biggest proportion of high retention is therefore generally confirm the influence of the size of the molecule that must be present in the diffusion. The Use of methods of surface characterization, thermal and structural (AFM; DSC, FTIR and AC) to study the morphology of the membrane surface, chemical resistance and stability suggests that the constituents of the plasticized polymer membranes we are maintained assembly inside the membrane by relatively low interactions. Indeed, the synthesis of polymer membranes plasticized by mixing β-CD macrocycle and the cellulose triacetate polymer. Also, the possibility of studying the separation of carboxylic acids by the neutral membrane based on β-CD macrocycle or by increasing the thickness or by modifying the accessibility of the cavity of the macromolecule. Generally the calculated P and J confirm the influence of the size of the molecules for the three membranes employed.

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