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New Polymer Inclusion Membrane Containing Modified B-Cyclodextrin: Application to Molecular Facilitated Transport

Fathia Ibn El Haj Amor[1], Imen Iben Nasser[1], Zeineb Baatout[1], Safa Teka[1], Nejmeddine Jaballah[1], Laura Donato[2], Mustapha Majdoub[1] and Chedly Ahmed[1]*

1. Laboratoire des Interfaces et Matériaux Avancés (LIMA), Université de Monastir, Faculté des Sciences de Monastir, Bd. de l'Environnement, 5019 Monastir, **TUNISIA**
2. Research Institute on Membrane Technology, ITM-CNR, c/o University of Calabria, Via P. Bucci, Cubo 17/C, 87030 Rende (CS), **ITALY**

Email: ahmedchedly10@gmail.com

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ABSTRACT

The current study presents the results concerning the first use of a polymer inclusion membrane (PIM) containing the modified β-cyclodextrin. The effectives PIMs containing the Methyl-Beta-Cyclodextrin (β-CDMe) or Benzyl-Beta-cyclodextrin (β-CDBn) as the carrier, cellulose triacetate (CTA) as the base polymer and 2-Nitrophenyl octyl ether (2-NPOE) as a plasticizer were synthesized and characterized by different techniques. Several factors on the transport efficient have been studied. These factors include the nature and the concentration of the carrier, the type of plasticizer and the initial concentration on the feed phase. In order to acquire an efficient transport, the new β-Cyclodextrin-based membranes were investigated by ethylenediamine (EDA) and ammonia (NH_3).

Keywords: Polymer inclusion membrane, beta cyclodextrin modified, facilitated transport, Separation.

INTRODUCTION

Liquid membranes have received considerable attention by many researchers because of their high selectivity accomplished by carriers incorporated in the membranes. Many efforts have been done to investigate the use of liquid membranes for various separation and purification or analytical application in various areas, such as biomedicine, ion selective electrodes, effluent treatment and hydrometallurgy [1,2], metal ions [3,4], etc. This category of membranes include bulk liquid membranes (BLMs), emulsion liquid membranes (ELMs), supported liquid membranes (SLMs), and polymer inclusion membrane (PIMs) [5-7]. Recently, Polymer Inclusion Membrane (PIM), a novel type of liquid membrane system, has developed. These kinds of membranes are suitable for the facilitated transport of ions and molecules [8, 9]. PIMs are formed by casting a base polymer cellulose triacetate (CTA) or polyvinyl chloride (PVC) from an organic solution containing a carrier and plasticizer to form a thin stable film [8, 10]. The resulting membrane is used to separate source and receiving aqueous phases, but it does not contain an organic solvent to allow the transport of ions or molecules through PIMs. Polymer inclusion membranes preserve a greatest of benefit by exhibiting excellent stability and versatility as compared by SLMs [11]. The main compound in

PIMs is the carrier known by the complexing agent. In fact, the inclusion of complexing sites in membranes leads to the facilitation of species transport and improvement of membrane performance [12]. Several works are devoted to the studies of separation using the polymer inclusion membrane and particularly the metallic ions separation [10, 13a, 14]. This is because of the capacity of the membranes to work in continuous processes, its modularity and efficient energy and environmentally. Various carrier or complexing agents were used in PIMs technology covering macrocycle and macromolecular compounds, i.e. crown ethers, calixarenes, calix crowns, as well as cyclodextrins [10, 13a, 13b]. Cyclodextrins (CDs) are torus-shaped molecules composed of cyclic 1, 4 oligoglucopyranosides possessing a hydrophobic cavity and hydrophilic external surface. CDs are able to include different organic molecules in the central hydrophobic cavity and forms inclusion complexes [8, 15-17]. Due to their inclusion complex formation, cyclodextrins have been extensively studied in separation field [18-22].

Over modification, cyclodextrins applications are developed. The chemical modifications of cyclodextrins have been concerned with influencing their solubility as well as with modifying their binding behaviours [23]. Due to the availability of multiple reactive hydroxyl groups, the functionality of β-cyclodextrins is greatly increased by chemical modification [24].

In this work, we studied the efficient transport of EDA and NH_3 and their separation possibility through CTA membrane based on modified β-cyclodextrine as a carrier. The facilitated extraction of EDA through cation exchange membrane is studied in our previous work [25]. For this reason, we synthesized a novel membrane containing CTA as a support, modified beta cyclodextrin as a carrier and a plasticizer. CTA provides the mechanical strength of the membrane, both carriers used are methyl-beta-cyclodextrin (β-CDMe) and benzyl-beta-cyclodextrin (β-CDBn) which bind and transport EDA and NH3 molecules. The plasticizer bis (2-ethylhexyl) sebacate (BEHS) or 2-Nitrophenyl octyl ether (2-NPOE) provides elasticity and acts as solvent in which the carrier molecule can diffuse. The type of carrier and plasticizer are the factors that influence on the flux transport of EDA [26] and NH_3. PIMs have been characterized using chemical techniques as well as Fourier Transform Infra-Red (FTIR), contact angle, scanning electron microscopy (SEM).

MATERIALS AND METHODS

The chemical reagents used for the preparation of PIMs are: Methyl-β-cyclodextrin (β-CDMe); average methylation degree of 12 and Mn =1305 $g.mol^{-1}$, as determined by MALDI-TOF; the ^{1}HNMR spectral data were obtained on a Bruker AV200 spectrometer and the chemical shifts were referenced to the $CHCl_3$ signal at 7.26 ppm.) [27]. Benzyl-β-cyclodextrin (β-CDB_n was synthesized using a previously described procedure [24]; number-average molecular weight Mn = 1568 $g.mol^{-1}$, as determined by MALDI-TOF. The ^{1}HNMR spectral data were obtained on a Bruker AV200 spectrometer: 7.5–7.1 (m, aromatic protons of benzyl groups), 5.2–4.2 (m), 4.1–3.2 (m). FT-IR (KBr, cm^{-1}): 3063, 3032 (w, aromatic C–H stretching), 1634 (s, C≡C stretching), 1051 (s, C–O–C symmetric stretching) [24].

Cellulose triacetate (CTA), di-(2-ethylhexyl) sebacate (DEHS) and 2-Nitrophenyl octyl ether (2-NPOE) were purchased from Fluka and chloroform from Merck (Germany), ethylenediamine (EDA) (97%, Fluka) and standard HCl solution (CDM). Laboratory grade ultrapure water (Millipore, Australia) was used for the preparation of all solutions. Chemical structure of PIMs compounds are illustrated in Fig. 1.

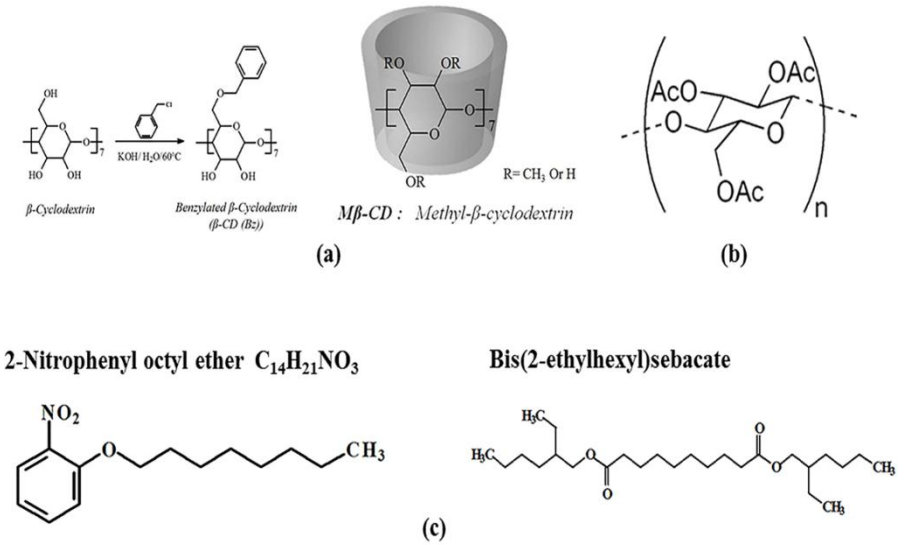

Fig. 1. Molecular structure of β-CD derivatives **(a)**, Cellulose Triacetate CTA **(b)** and the plasticizers **(c).**

Preparation of polymeric membrane: Flat sheet membranes are prepared by dry phase inversion technique (solvent evaporation) as reported by Kumar [28] with slight modifications. In fact, a mixture of 0.2 g of CTA, 0.1g of a plasticizer and the β-CDMe or β-CDBn carrier in various quantities was dissolved in 15 mL of chloroform at room temperature. After vigorous stirring, the obtained solution was homogeneous. The solvent of this mixed solution is slowly evaporated in a 9.0 cm diameter Petri dish, which was covered loosely, overnight. A small quantity of water was deposited on the obtained film to peel it out from the dish and placed in the transport cell. Blank membrane were prepared by the same procedure but without carrier. The obtained thin PIMs were completely clear, homogeneous, and flexible. PIMs exhibited a good mechanical strength, indicating that the CTA serves as a good supporting matrix for the solvent and the carrier. The membrane thickness is determined by measuring different locations of the membrane using a micrometer and calculating the average thickness and confirmed by SEM measurement.

Membrane characterizations: Membranes were characterized using chemical techniques as well as Fourier transform infra-red (FTIR), scanning electron microscopy (SEM) and contact angle.

All the membranes were characterized by FTIR analysis using a Perkin–Elmer Spectrum One FT-IR spectrometer (Thermo Scientific Nicolet IS50ATR) according to the Attenuated Total Reflectance (ATR) technique.

Elastic characterization of CTA blank and PIMs was carried out with samples of 1 cm width and 3 cm length using a force digital gauge (Mark-T, LLOYD LS5 model) with a maximum tension of 100 N and length accuracy of ±0.01 mm connected to a computer. Measurements were performed at a strength rate of 10 mm $sec.^{-1}$.

The morphology of the prepared membranes was investigated by scanning electron microscopy, (SEM) using a FEI QUANTA 200 F microscope at 20 kV. Membrane samples were freezed in liquid nitrogen for producing a clear brittle rupture. All samples were sputter-coated with gold before microscopic analysis.
Contact angle measurements were done with the contact angle measurement instrument GBX Scientifique Instrument (Roman-France). The sessile drop method was used and ultrapure water was the wetting liquid.

Membrane transport experiments: The prepared PIM was inserted between two permeation cell compartments (feed and strip).The effective membrane area contacting the 180 cm^3 aqueous feed and strip phases was 19.6 cm^2. During the transport experiment, both aqueous phases are stirred by a magnetic stirrer and all experiments were carried out in quasi-stationary regime at 25°C. During the process, we measured the concentration of EDA or NH_3 in the feed and in the receiver phase by pH –metric titration.
The kinetics of the transport across membrane was described as a first-order reaction [13a]:

$$Ln(C_t/Ci) = -kt \quad (1)$$

Where C_t is the EDA or NH_3 concentration at a given time in the feed phase, C_i is the initial concentration in the feed phase, k is the rate constant (s^{-1}), and t is the time transport (s). The k values were calculated from the plots of $Ln(C_i/C)$ vs time.

The relationship of $Ln(C_i/C)$ vs time used to plot the data obtained in this work was linear as expected from equation 1. The permeability coefficient (P) was calculated as follows [13a]:

$$P = - (V/A).k \quad (2)$$

Where V is the volume of aqueous feed phase, and A is the area of the effective membrane.
The initial flux (Ji) was determined as [13a]:

$$Ji = Pci \quad (3)$$

In order to express the efficiency of EDA or NH_3 transport from the feed phase, we access to the recovery factor (RF %) by using the following expression:

$$RF (\%) = [(Ci - C_f)/C_i] \times 100 \quad (4)$$

Where C_i is the initial concentration of EDA or NH_3 in the source solution and C_f represents its concentration in the source compartment at a final time ($mol.l^{-1}$).

Water absorption capacity measurement: Water absorption is considered to be important characterization parameters as it indirectly the degree of hydrophilicity or hydrophobicity of the prepared membranes. Water absorption capacity of the membranes was obtained as follows: The pre-weighed membranes were immersed in deionized water for 24 h and weighed after mopping with plotting paper. All gravimetric measurements on water sorption were made with a precision of ±0.1 mg. The percent water absorption capacity was determined:

$$\text{Water absorption (\%)} = \left(\frac{W_{Wet} - W_{Dry}}{W_{Dry}}\right) \times 100$$

Where W_{Wet} is the weight of the membrane soaked in deionised water for 24hours at room temperature and W_{Dry} is the weight of the dry membrane.

RESULTS AND DISCUSSION

Physical and chemical characteristics of cellulose triacetate membranes: In order to evaluate the hydrophilicity of the modified βCDs based membrane, the prepared membranes were tested for their wettability. The contact angle measurements, thickness and the water absorption of (CTA+2-NPOE) membrane, (CTA+2-NPOE+ βCDMe) membrane and (CTA+2-NPOE+ βCDBn) membrane were taken at room temperature for the blank membrane, PIM containing βCDMe carrier and PIM containing βCDBn carrier. The data are presented in Table 1.

The contact angles of the blank and PIM with βCDMe or βCDBn carrier were less than 90°. Indeed, the inclusion of modified βCD in the CTA matrix modifies the membrane behavior passing from a hydrophobic character (θ=79.6°) for CTA+2-NPOE membrane [29] to less hydrophobic (θ = 75.0°) for PIM containing βCDBn and moderately hydrophilic (θ = 58.1°) for PIM containing βCDMe. The hydrophobicity of the membrane based on benzylated βCDBn in comparison with the membrane based on methylated βCDMe.

We investigated membrane thickness and water absorption capacity of the PIMs. As shown in table 1, we observed that inclusion of carriers into (CTA + NPOE) membrane induced a remarkable increase of its thickness (15 to 27 µm for βCDMe membrane and to 94 µm for βCDBn membrane). Water content decreased from 35.48% for CTA+2-NPOE membrane to 27.47% for PIM with βCDMe and to 17.91 for PIM with βCDBn.

Table.1 Chemical and physical characteristics of cellulose triacetate membranes

Membranes	weight of carrier (g)	Thikness (µm)	Water content (%)	Contact angle θ(°)
CTA+2-NPOE	0	15	35.48	79.6
CTA+2-NPOE+ βCDMe	0.13	27	27.47	58
CTA+2-NPOE+ βCDBn	0.13	94	17.91	75

The morphology of the membranes is observed by the SEM images displayed in fig. 2, it appears from the observation of the cross section of three membranes that they have a uniform and dense surface appeared without apparent porosity.

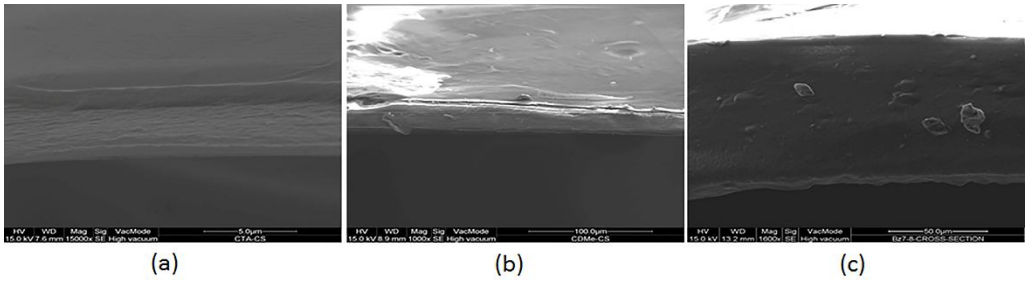

Fig. 2. The SEM images of CTA blank membrane **(a)**, PIM with βCDMe **(b)** and PIM with βCDBn **(c)**.

The FTIR spectra of CTA, β-CDMe and β-CDBn triacetate membrane are shown in fig. 3. It can be observed from FTIR spectra (Fig. 3a), the presence of the bands between 2853 and 2963 cm^{-1} attributed to the stretching vibration of –C–H and $–CH_2–$. The absorption at 1735 cm^{-1} is assigned to the stretching vibration of C=O in CTA.

The IR spectrum of β-CDMe membrane (Fig. 3b) and β-CDBn (Fig. 3c) membrane exhibit large band around 3467 cm^{-1} which is attributed to stretching O-H bond.

Intense bands at 2908 and 1748 cm^{-1} correspond respectively to the stretching vibration of C-H and the carbonyl group. Stretching bands at 3070, 1610, 1519, 674 and 605 cm^{-1} correspond to the benzyl groups. Characteristic bands around 1750, 1043, 1650 and 899 cm^{-1} assigned respectively to the **C-O-C, N=O** and **C-N** band of CTA and plasticizer (2NPOE) were also shown in the two spectra [30].

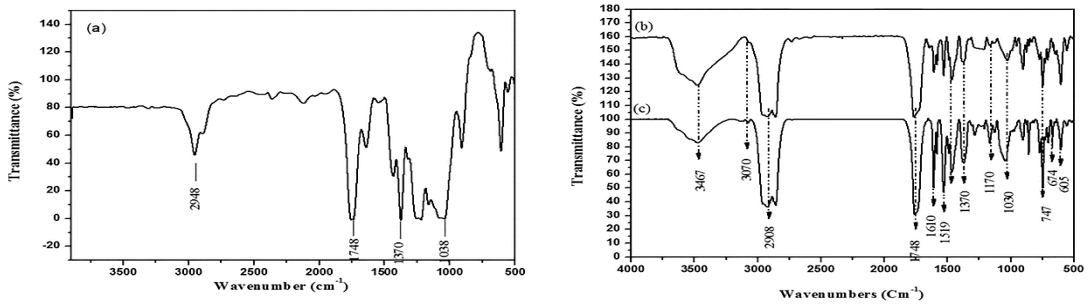

Fig. 3. FTIR spectra of CTA (**a**), βCDMe membrane (**b**) and βCDBn membrane (**c**).

Transport experiment: Based on transport experiment using the PIM without carrier, it has been noted that in absence of carrier, no transport of EDA and NH_3 from the feed phase to the receiver phase was perceived. From these results, it can be proven that the PIM without carrier served as an effective barrier to molecules diffusion. This is in agreement with the results found in the literature [13a, 31].

Influence of the plasticizer type in transport: The nature of the plasticizer used to form the membrane is also a key parameter to consider [31]. The plasticizers play an important role on the membrane mechanical properties and permeability [32, 33], and are often used to increase the flux as well as the membrane softness and flexibility [34]. The action of the plasticizer is attributed to its ability to reduce the intermolecular attraction forces between the chains in the polymer systems [11]. In fact, the role of a plasticizer is to penetrate between polymer molecules and neutralize the polar groups of the polymer with its own polar groups or to increase the distance between the polymer molecules and hence reduce the strength of the intermolecular forces [11]. In this work, two plasticizers with different chemical properties, 2-nitrophenyl octyl ether (2-NPOE) and di- (2-ethylhexyl) sebacate (DEHS), have been evaluated for the elaboration of a membrane useful for the transport of EDA and NH_3. The diffusion experiment was carried out by using 10^{-2}M of EDA or NH_3 in the feed compartment and the deionized water in the strip phase. The transport has been achieved with two carriers (β-CDMe and β-CDB_n) using a same polymer and a same plasticizer (2-NPOE and DEHS).

It can be seen from fig. 4 and fig. 5, the best transport efficiency of EDA was obtained with the 2-NPOE, while the DEHS was less effective for EDA transport because it has a high viscosity (η= 40.4 cP) and low dielectric constant (ε_r = 3.9). As it is known that the most effective plasticizer is one which possesses high polarity (high dielectric constant), this behavior is usually attributed to 2-NPOE due to its quite high polarity (ε_r = 24) [35].

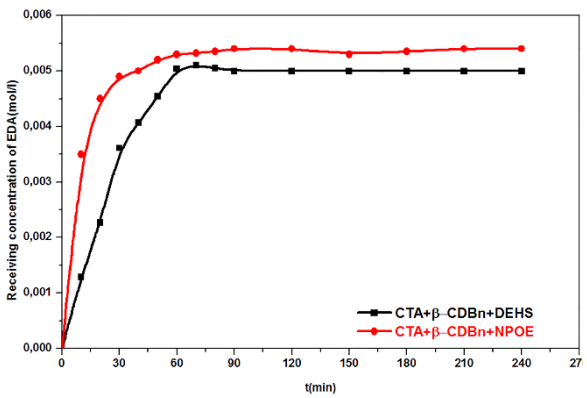

Fig. 4. Effect of the plasticizers nature on the EDA transport accros β-CDB_n membrane.

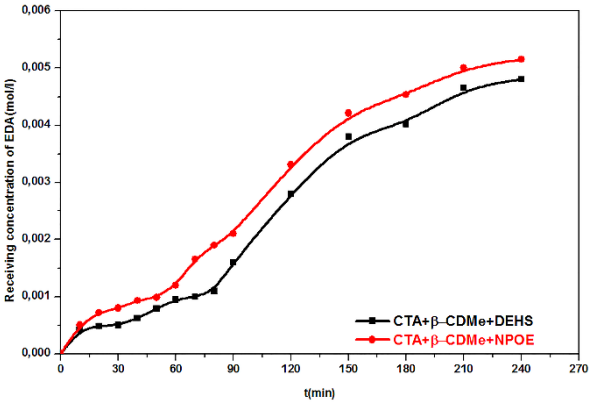

Fig. 5. Effect of the plasticizers nature on the EDA transport accros β-CDMe membrane

Influence of Carrier nature: The main compound, which can influence on the transport, is the nature of the carrier. The transport has been accomplished with two different carriers β-CDMe and β-CDB_n using a CTA as the base polymer and a same plasticizer 2-nitrophenyl octyl ether (2-NPOE).

Each carrier was evaluated in terms of the variation of the EDA and NH_3 concentration in strip phase as a function of time. From the results shown in fig. 6, there has been a rapid increase in receiving concentration of the EDA with β-CDB_n carrier, until t = 90min and then equilibrium is reached. While, with the β-CDMe carrier, the EDA concentration increases until it reaches equilibrium at t = 210 min.

Results illustrated in table 2 show that EDA is effectively removed from the aqueous solution through membrane containing β-CDB_n derivative. According to fig. 6, it is found that the amount of NH_3

transported to the strip phase by β-CDMe membrane is greater than with the β-CDB_n membrane, up to t = 270 min the equilibrium is reached.

While, beyond t > 270 min, we note an inversion in the transport behavior: the receiving concentration of NH_3 diffused across β-CDB_n membrane becomes the most important.

In terms of conclusion, we can consider that the β-CDB_n membrane is the most effective for the transport of both molecules. This result demonstrated that membrane contained β-CDB_n derivatives exhibit higher EDA and NH_3 fluxes. This behavior can be explained by imported molecular recognition properties of β-CDB_n towards EDA and NH_3, which lead to its ability to form inclusion complexes with both molecules.

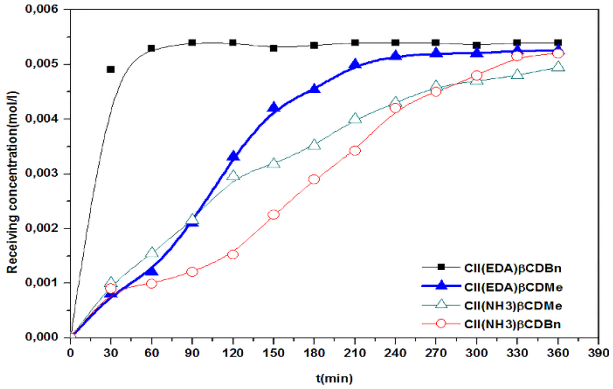

Fig. 6. Evolution of the concentration of EDA and NH_3 in a strip phase versus time using (CTA + β-CDMe + NPOE) and (CTA +β-CDB_n + NPOE) membranes.

Table.2 The initial fluxes and removal factor (RF) of the individual transport of EDA and NH_3 across PIM with βCD derivatives

	Ji(µmol/cm².s)		RF(%)	
	βCDMe	βCDB_n	βCDMe	βCDB_n
EDA	4.32	7.91	48	54
NH_3	2.60	3.459	45	51

Effect of carrier content: Passive transport by using the PIM without carrier has been performed. In fact, we noted that in absence of carrier, no transport of both molecules from the feed phase to the receiver phase was observed. Based on this experiment result, it can be demonstrated that the PIM without carrier served as an effective barrier to molecule permeation. This behavior is in agreement with the results found in the literature [36]. The effect of the percent content of the carrier fixed in the membrane has been considered by using membranes prepared from quantities of 25 % (wt. /w) to 63 % (wt. /w) of each modified β-CD carrier. Table 3 and table 4 represent the effect of the carrier content in the membrane matrix on the transport efficiency. These results show that the flux of transport of the two molecules increases with the quantity of the carrier to reach a maximum percent of 46% (wt. /w). This optimal percent content of modified βCD carrier is supposed to be sufficient to create the liquid pathways inside the membrane required to carry out the transport of the given molecules [37, 38]. Above this value, the flux decreases significantly. It is possibly due to the higher viscosity of the carrier in the organic phase [13]. Therefore, high viscosity in the phase liquid membrane limits the diffusivity of the molecule across the membrane since the carrier is incorporated into a polymeric material gel network [39].

Table.3 The effect of carrier concentration on the transport of EDA through PIM

Carrier	**Modified** βCD (wt./w)**(%)**	$P\times10^4$ ($cm.s^{-1}$)	Ji ($\mu mol.cm^{-2}.s^{-1}$)
βCDMe	25	0.179	0.197
	46	3.927	4.32
	63	2.71	3.26
βCDB_n	25	0.469	0.601
	46	7.19	7.91
	63	3.53	4.24

Table. 4 The effect of carrier concentration on the transport of EDA through PIM

Carrier	Modified βCD w/w(%)	$P\times10^4$ ($cm.s^{-1}$)	Ji ($\mu mol.cm^{-2}.s^{-1}$)
βCDMe	25	0.020	0.023
	46	2.36	2.6
	63	1.58	1.9
βCDBn	25	0.265	0.292
	46	3.13	3.45
	63	2.027	2.23

Effect of the initial concentration in feed phase: The influence of the initial concentration of the EDA and NH_3 were investigated under the optimum conditions. The experiments were performed using a solution of EDA or NH_3, having different concentrations, as the feed solution and the strip solution was deionized water. The concentration of EDA and NH_3 varied in the range 0.001- 0.1 M. Fig. 7 shows the molecular transport is presented in function of different initial concentration of the EDA or NH_3 across a PIM containing a modified β-CD. We observed that the transport of EDA or NH_3 increased with its initial concentration. The flux is enhanced by the increase of initial concentration of each molecule. This can be explained by the accessibility and the ability of the carrier to the formation of inclusion complexes with the both molecules in higher concentration.

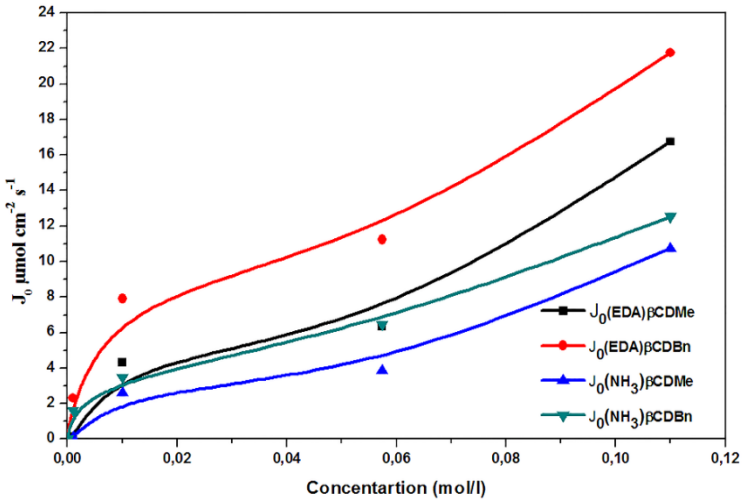

Fig 7. Effect of the initial concentration of EDA or NH_3 in the source phase on the initial flux J.

APPLICATIONS

Study of the case of competitive transport: The competitive transport of EDA and NH_3 across β-CDMe and β-CDB_n is investigated. The selectivity is assuredly a very significant factor. It was performed by determining the selectivity coefficient, S, defined as the ratio between the initial flux of EDA and the NH_3 flux. The obtained results are presented in table 5 and fig. 8.

The diffusion experiment was carried out by using 10^{-2}M of (EDA+NH_3) mixture in the feed compartment and deionized water in the strip phase. The variation of concentration of EDA and NH_3 in the strip phase during 6 h of dialysis as a function of time is displayed in fig. 8.

The efficient transport is achieved by membrane based on β-CDMe derivatives. It is showed from flux values presented in table 5. The initial fluxes of EDA and NH_3 are higher for PIMs with M β-CD carrier than for those with βCDB_n carrier these results can be explained by the strong electrostatic interaction

between the ammonia and EDA and the βCDB_n units, in addition of the encumbered βCDB_n cavity which affect the molecules diffusion. Selectivity factors for the mixture EDA / NH3 by the membrane based on M β-CD is 1.074 while 0.97 by the PIM containing βCDBn are obtained. The low selectivity of both polymer inclusion membranes is attributed to the comparable nature and size of two studied molecules.

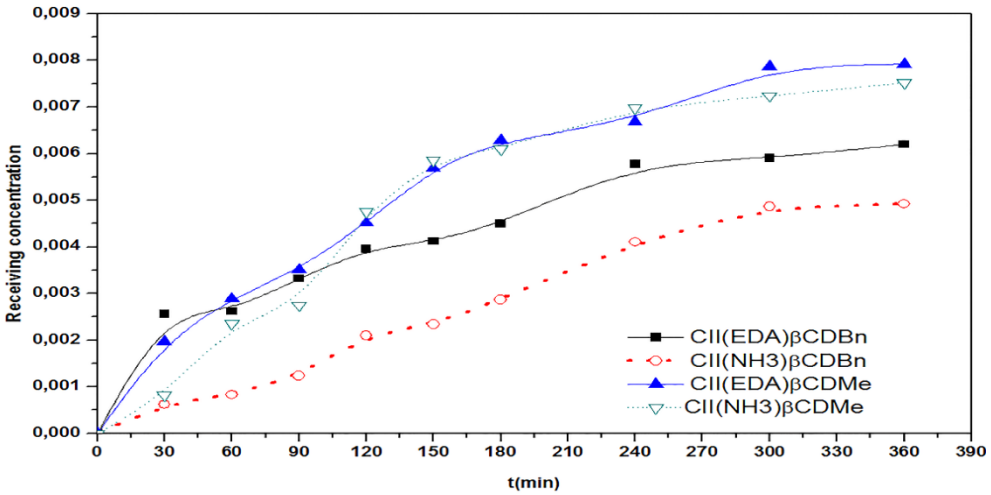

Fig. 8. Evolution of the receiving concentration of EDA and NH_3 versus time using (CTA + β-CDMe + NPOE) and (CTA +β-CDB_n + NPOE) membranes.

Table.5: The initial fluxes and removal factor (RF) and selectivity coefficient of the competitive transport of EDA and NH_3 across PIM with βCD derivative

	Ji (µmol/cm².s)		RF(%)		S	
	βCDMe	βCDB_n	βCDMe	βCDB_n	βCDMe	βCDB_n
EDA	6.96	3.73	61.5	47.5	1.074	0.97
NH_3	6.48	3.83	59	29		

CONCLUSIONS

A cellulose triacetate (CTA) polymer inclusion membranes was elaborated by dry phase inversion technique, using the Methyl-β-cyclodextrin (β-CDMe) and Benzyl-cyclodextrin (β-CDBn), respectively, as a macrocycle carrier and a 2-nitrophenyloctyl ether noted (NPOE) and di(2-ethylhexyl) sebacate (DEHS) as the plasticizer. The composition and morphology properties of the membrane have been investigated. As expected, the results show that the transport efficiency of EDA was improved with the plasticizer 2-NPOE. The (CTA+β-CDBn+2-NPOE) membrane showed higher value of the flux of EDA. Competitive transport of both molecules is performed and results showed that the initial fluxes of EDA and NH3 are higher for PIMs with M β-CD carrier than for those with βCDBn. Selectivity factors are low with both carriers, which is related to the comparable tested molecules properties.

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AUTHORS' ADDRESSES

1. **Fathia Ibn El Haj Amor**
Laboratoire des Interfaces et Matériaux Avancés (LIMA),
Université de Monastir, Faculté des Sciences de Monastir,
Bd. de l'Environnement, 5019 Monastir, Tunisia
2. **Imen Iben Nasser**
Laboratoire des Interfaces et Matériaux Avancés (LIMA),
Université de Monastir, Faculté des Sciences de Monastir,
Bd. de l'Environnement, 5019 Monastir, Tunisia
3. **Zeineb Baatout**
Laboratoire des Interfaces et Matériaux Avancés (LIMA),
Université de Monastir, Faculté des Sciences de Monastir,
Bd. de l'Environnement, 5019 Monastir, Tunisia
4. **Safa Teka**
Laboratoire des Interfaces et Matériaux Avancés (LIMA),
Université de Monastir, Faculté des Sciences de Monastir,
Bd. de l'Environnement, 5019 Monastir, Tunisia
5. **Nejmeddine Jaballah**
Laboratoire des Interfaces et Matériaux Avancés (LIMA),
Université de Monastir, Faculté des Sciences de Monastir,
Bd. de l'Environnement, 5019 Monastir, Tunisia
6. **Mustapha Majdoub**
Laboratoire des Interfaces et Matériaux Avancés (LIMA),
Université de Monastir, Faculté des Sciences de Monastir,
Bd. de l'Environnement, 5019 Monastir, Tunisia
7. **Chedly Ahmed**
Laboratoire des Interfaces et Matériaux Avancés (LIMA),
Université de Monastir, Faculté des Sciences de Monastir,
Bd. de l'Environnement, 5019 Monastir, Tunisia
E-mail: ahmedchedly10@gmail.com
8. **Laura Donato**
Research Institute on Membrane Technology,
ITM-CNR, c/o University of Calabria,
Via P. Bucci, Cubo 17/C,
87030 Rende (CS), Italy