Journal of Inclusion Phenomena and Macrocyclic Chemistry **44:** 433–437, 2002.

Catalytic Behaviour of Carbonate β-CD Entrapped in PEEK-WC Membranes

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(Received: 7 May 2002; in final form: 1 October 2002)

Key words: β-cyclodextrins, membranes, PEEK-WC, catalysis

Abstract

O-octyloxycarbonyl β-cyclodextrins were immobilised in flat sheet PEEK-WC membranes. The membranes were prepared by phase inversion method and characterised. β-cyclodextrin (β-CD) catalytic action in the *p*-nitrophenylacetate (PNPA) hydrolysis to *p*-nitrophenol (PNP) was studied. The β-CD acylic carbonate derivative shows an effective catalytic action when incorporated in PEEK-WC membranes, by showing an enzyme-like behaviour. The membranes were tested at different temperatures and substrate concentrations and the value of activation energy for the reaction was estimated. It is well known that β-CD have a catalytic action, but their immobilisation in a polymeric matrix enhances the reaction rate, in fact the entrapment optimises the interaction with the substrate and increases the chemical stability of the catalyst. In addition, β-CD show more stability when incorporated in the membrane, because of their chemical resistance to alkaline attack.

Introduction

The β-CD non-inverting, somewhat rigid structure may flex or compose, but not collapse, and it can efficiently form molecular inclusion complexes with various organic and inorganic *guest* compounds. Cyclodextrins are water soluble, although enhanced or diminished aqueous solubility can be achieved via chemical or structural modifications. CD are modified chemically in order to alter their solubility behaviour and complexation properties, and to induce groups with certain specific functions. Derivatives that have a greater aqueous solubility than their parental cyclodextrins are desired in many applications. CD can also be chemically modified to produce derivatives that are much less water soluble than their parents, as in this work. A reduced aqueous solubility is necessary, for example, in applications where a low residue of cyclodextrin is required. In this work a *O*-octyoxycarbonyl β-CD derivative was used. The effect of the immobilised CD derivative in polymeric membrane on the rate of the hydrolysis reaction of PNPA to PNP was analysed. In aqueous basic solutions CD cleave phenyl acetates by acyl transfer from the ester to an ionised hydroxyl group of the CD. Catalytic activity of β-CD carbonate is a function of DS and of the strength of the alkaline medium. In homogeneous system the catalytic action of CD derivatives was found to decrease with increasing of the substitution degree[1]. Moreover the β-CD acyclic carbonate derivatives are not stable because of the hydrolysis of carbonate at basic pH, whereas the rate constant for the CD-catalysed reaction is maximal at a pH of 12 to 13 [2].

Membrane preparation and characterization was the first aim of the work, in order to evaluate the possibility to combine catalytic action of β-CD immobilised in polymeric matrix with membrane technology. Membrane technology offer a wide range of applications, but also a great number of advantages with respect to other traditional techniques.

It is well known, however, that the properties of the membranes are widely influenced by membrane morphology and the choice of the polymer. In this work a particular kind of PEEK, named PEEK-WC (poly(oxa-p-phenylene-3,3-phthalido-p-phenylene-oxy-phenylene), was used. The polymer is characterised by the presence of the cumbersome lattonic group that reduces the crystallinity degree thus making it more soluble in some chlorohydrocarbon solvents and also in DMF and DMSO and, as a consequence, it is then possible to obtain PEEK-WC membranes that are now studied for many applications. Various kind of PEEK-WC membranes were prepared and characterised in order to determine best membrane performance and to choice the membrane to charge with β-CD.

A good membrane material must produce a high specific flux, reject targeted species, resist fouling and have high mechanical stability. For every kind of prepared PEEK-WC membranes morphology and permeability properties were examined.

The β-CD acyclic carbonate derivative seems to be an efficient nucleophilic catalyst when incorporated in the PEEK-WC membrane [3]. It posses a high nucleophilicity towards the reagent PNPA with exceptional lability of the intermediate on the reaction pathway leading to the formation of the product by a large rate acceleration. In any case, when the same reaction was carried out in a membrane reactor, even if

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without CD, the reaction rate results higher with respect to the batch reaction.

The PNPA hydrolysis takes place with an inclusion complex in which the phenyl group of the ester stays in the hydrophobic cavity of the CD [2]. The efficiency of the ester cleavage is enhanced in the presence of immobilised membrane β-CD since the PNPA orients its phenyl group into the cavity in geometries that are suitable for the acyl transfer [3].

In previous studies the effect of β-CD derivatives with different DS was investigated and the procedure of membrane preparation was optimised; by using β-CD carbonate with DS equal to 7 and in concentration of 7.5 wt% a conversion degree of 100% was reached [3].

In order to improve the catalysis the β-CD derivative was dispersed in the casting dope. In this way the CD carbonate catalytic activity in the membrane can be reached by the substrate with a better efficiency.

In this study the effect of some parameters on the catalytic activity of the membranes functionalised with β-CD has been examined. The membrane have been characterised and tested at different temperatures and substrate concentrations. The value of activation energy was estimated.

The reaction has been carried out at same temperatures and substrate concentrations, in the same membrane reactor on a membrane made only of PEEK-WC.

By using immobilised membrane β-CD, a significant improvement of reaction rate in comparison with the PEEK-WC membrane was observed.

Experimental

PEEK-WC was supplied from Chanchung Institute of Applied Chemistry, Academia Sinica. The polymer powder was washed with methanol at room temperature and then dried in a vacuum oven before membrane preparation.

β-cyclodextrin was supplied from Roquette Italia (Cassano, Spinola, Italy). Its *O*-octyloxycarbonyl β-CD derivative was synthesised according to the literature and the average degree substitution (DS 7) was determined via quantitative FT-IR analysis [4].

PNPA and PNP were purchased from commercial sources (Fluka Chemicals) and were used without further purification.

The membranes were prepared following the traditional phase inversion process [5] which permits the production of membranes with an asymmetric pore structure. The solvent was N,N-Dimethylformammide (DMF) and non solvent water.

The purified polymer (15 wt%) was dissolved in DMF by magnetically stirring overnight to allow complete solution at room temperature. The solution was cast knife on a glass plate. The knife was supplied from Braive Instruments. The knife high was set at 250 μm and the time of initial evaporation in air, at room temperature, was 10 s, 60 s and 5 min. The cast film was immersed in a coagulation bath containing distilled water for 10 min and then transferred to fresh distilled water for 2 h. To obtain dense membranes, the film was kept in air to allow complete solvent evaporation.

Asymmetric β-CD charged membranes were prepared as above, using 7.5 wt% solution of CD derivative in the polymer solution and the evaporation time was 60 s. β-CD derivative was added after complete dissolution of the polymer and the solution was dissolved by magnetically stirring for a day or more to allow complete solution at room temperature.

β-CD derivative, insoluble in water until 60 °C about, was used instead of β-CD to prevent loss of CD during the membrane formation process. No β-CD trace was found in the coagulation bath.

In the casting solution the ratio PEEK-WC: β-CD derivative was 2:1. It was been supposed that after phase inversion process the ratio is the same and, after drying, all solvent is gone out of the membrane. The utilized membrane had an area of 133 cm^2, so the total β-CD weight was 0.45 g. The molar concentration of β-CD derivative immobilised in membrane in the active area has been determined and it was 0.152 M.

All membranes were stored in water.

The AFM used in this work to investigate membrane morphology was a Nanoscope III, a commercial device from Digital Instruments, VEECO Metrology Group.

A flat cell was used to carry out the hydrolysis reaction. The solution of PNPA in phosphate buffer, pH 8 permeated through the membrane with constant flow rate having a pressure difference as driving force, $\Delta P = 0.01 \pm 0.002$ bar. The reactor calibration has been done at room temperature and with distilled water. Various tests at different temperatures have been carried out by using a thermostatic bath.

A standard solution of PNP 0.02 M in acetonitrile was prepared. In the typical experiment, 1.26×10^{-4}, 9.58×10^{-5}, 7.76×10^{-5}, 5.55×10^{-5}, 4.05×10^{-5} and 2.74×10^{-5} M PMPA solutions in phosphate buffer were prepared. The solution was placed in the membrane reactor and the permeate analysis has been done about every 5 min by spectrophotometry analysis. Initial PNPA and PNP concentrations were determined at 299 nm and 401 nm, respectively, using a 1 cm quartz cell and a Shimadzu UV-160A UV-VIS recording spectrophotometer, at room temperature. The reference compartment contained a phosphate buffer. A calibration curve for PNPA and PNP in the phosphate buffer was made and the curves were approximated with a linear function.

To verify the effective catalysis of β-CD derivative, the same experimental tests have been carried out by using a PEEK-WC membrane prepared in the same conditions, but without β-CD.

Because hydrolysis of esters occurs spontaneously in alkaline solutions, also in the absence of CD an increase of PNP is observed.

The reaction rate has been determined by working at different temperatures (15, 20, 30, 40, and 55 °C).

Results and discussion

It's well known that operative conditions play a fundamental role on the performance of membranes prepared from the same polymers. In this study, the role of evaporation time

on the membrane morphology was investigated. In particular, the cross section of an asymmetric membrane reveals various kind of porosity and pore structure from the top to the bottom of the membrane thickness. When the cast film is kept just in air in order to allow complete solvent evaporation, a thin dense layer is formed on the top side of the membrane. The thickness of this layer influenced the membrane performance, its possible uses and, in particular, also the solvent fluxes through the membranes.

Top layer thickness depends mainly on the evaporation time, being a higher time producing a thicker layer. Polymer concentration also influences membrane morphology. Membranes prepared for different evaporation time show different behaviours in terms of permeability and morphology.

By employing AFM, membrane morphology was studied. All the dense membranes show a regular structure, without any pore over the scanned area, according to the dense structure. Over the surface of asymmetric membranes for which the cast film was immersed in the non solvent bath without any evaporation in air, various pores are present on the surface. In the case of asymmetric membranes prepared by combining controlled evaporation and immersion precipitation, no pores are present, according to the presence of a dense layer.

In Figure 1 it is reported the cross section for the PEEK-WC asymmetric membrane, for which the cast film was kept to evaporate in air for 60 s and then put in the water coagulation bath. In this figure it is possible to see the dense layer at the top of the membrane. No AFM images are reported because of the regularity of superficial morphology among the various membranes, just for the presence of the dense top layer. Scion Image processing programme was used to analyse SEM micrographs and to determine the thickness of the superficial layer. In this way we have determined the thickness of the dense layer for the membranes prepared for the following evaporation time before coagulation immersion: 0, 10 s, 60 s, 5 min. Figure 2 represents dense layer thickness versus evaporation time. It is clear that the thickness is higher with longer air exposition of the cast film before immersion in the coagulation bath. There is no a linear dependence of the thickness with respect to the evaporation time, but it is also clear that higher evaporation time results in higher thickness and lower water fluxes.

According to these measures, also the water fluxes through the membranes are very different.

The concept of phase inversion covers a range of different techniques such as solvent evaporation, precipitation by controlled evaporation, thermal precipitation, precipitation from the vapour phase and immersion precipitation. In this work we employed phase inversion technique to prepare different kind of membranes. In particular, dense membrane were prepared by controlled evaporation, asymmetric membranes were prepared by immersion precipitation and asymmetric skinned membranes were obtained by combining the two previous kind of methods. Different membrane morphologies and performances were so obtained. Water fluxes through the membranes are in accord with the different preparation conditions. The inlet pressure varies with

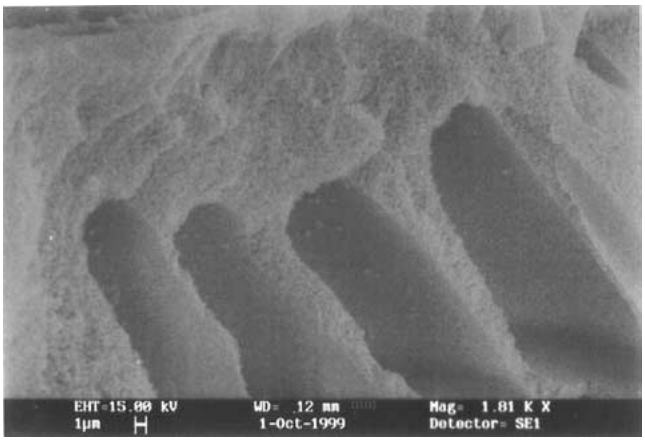

Figure 1. Dense layer thickness versus evaporation time for PEEK-WC asymmetric membranes.

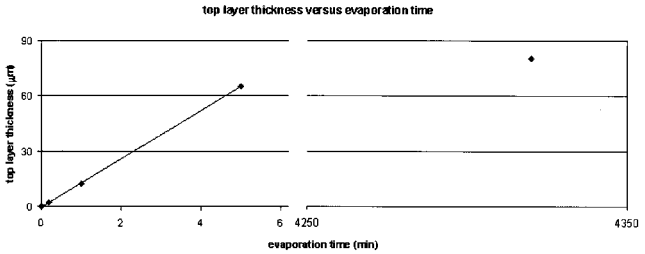

Figure 2. Water flux through dense PEEK-WC membrane.

respect to the evaporation time and, obviously, with the thickness of the dense layer. In particular, it's clear that the performances of the membranes evaporated for 5 min are similar with respect to the dense membrane, according also to the top layer thickness values.

The different structures of phase inversion membranes are related to the polymer and CD concentrations in the casting solution [6]. The actual membrane formation process is usually a diffusion induced phase separation (DIPS) process.

The charged membrane forming system is composed of PEEK-WC, β-CD, DMF as solvent and water as non solvent. All components are only miscible in a concentration range between 15 wt% PEEK-WC/2.5 wt% β-CD and 15 wt% PEEK-WC/7.5 wt% β-CD [3].

The different membrane structure, porosity and permeability properties, mainly depend upon diffusivities and the ratio of solvent and non solvent exchange that are influenced by components concentration.

All membranes show a linear dependence of water flux on the applied pressure gradient, at constant temperature.

Noted above, during the alkaline hydrolysis of PNPA an increase of PNP concentration was observed. In Figure 3 the reaction course in the bulk at different temperatures is shown.

PNPA hydrolysis reaction is an ideal model reaction for its simple mechanism, widely investigated, to obtain information on the catalytic and selectivity properties of CDs [7–9].

Reaction course in the β-CD carbonate membrane reactor and in the same without β-CD derivative at 20 and 55 °C for [PNPA] = 1.26×10^{-4} M are reported in Figure 4.

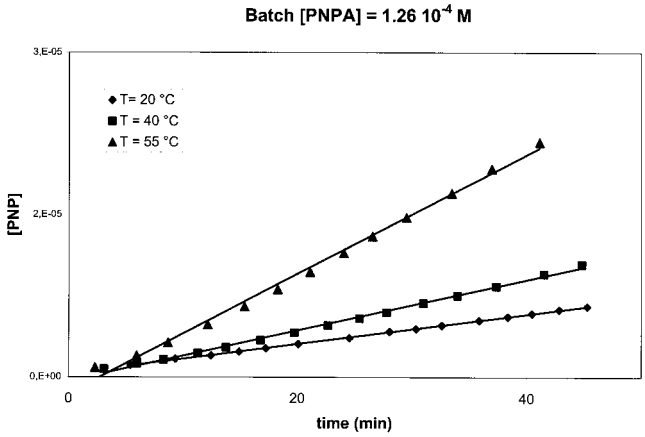

Figure 3. Reaction course in the bulk at different temperatures.

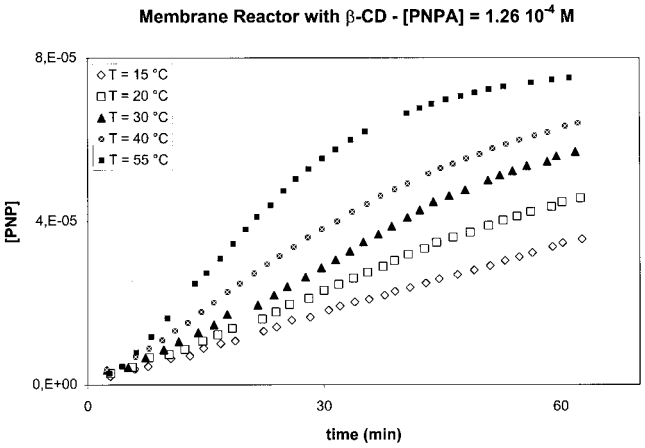

Figure 5. Reaction courses at 15, 20, 30, 40 and 55 °C for initial [PNPA] equal to 1.26×10^{-4} M.

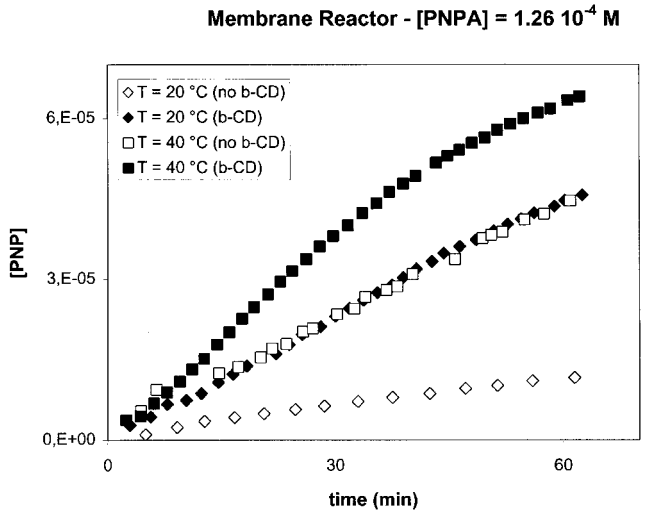

Figure 4. Reaction course in the β-CD carbonate membrane reactor and in the same without β-CD derivative at 20 and 55 °C, for [PNPA] equal to 1.26×10^{-4} M.

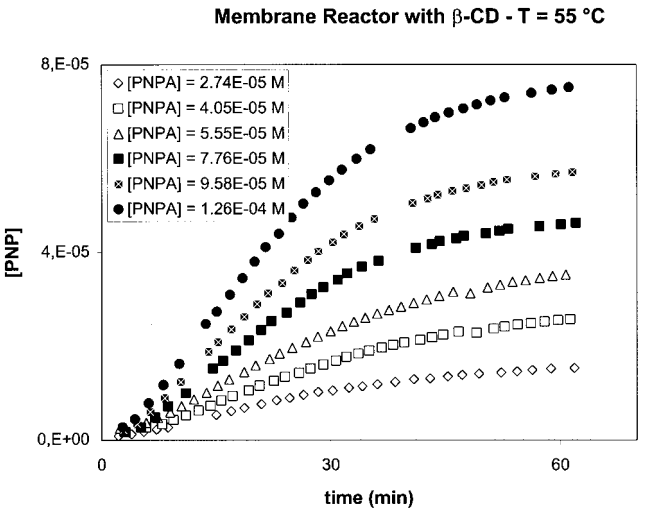

Figure 6. Comparison of reaction rate at 55 °C for initial [PNPA] equal to 2.74×10^{-5}, 4.05×10^{-5}, 5.55×10^{-5}, 7.76×10^{-5}, 9.58×10^{-5} and 1.26×10^{-4} M.

It is clear that the reaction rate was significantly higher when the reaction was carried out in presence of β-CD.

The first step of the reaction mechanism of the CD catalysed hydrolysis of ester is the substrate inclusion into the CD cavity [10]. The second step is the nucleophilic attack of a secondary CD hydroxyl into the carboxyl group of the substrate and CD acylation. Following steps are the dissociation of the inclusion complex and hydrolysis of the acylated CD. CD deprotonated secondary hydroxyl groups are the active species, while the primary ones are not involved.

In Figure 5 are reported the reaction courses at different temperatures for PNPA initial concentrations equal to 1.26×10^{-4} M. A comparison of reaction rate at the same temperature (55 °C) are reported in Figure 6.

The rate of the hydrolysis depends both on the PNPA initial concentration and the temperature at which the reaction is carried out. In particular, higher PNPA concentration and higher temperatures produce a higher reaction rate, by following a pseudo-first order kinetic, as reported in literature [9].

β-CD carbonate derivatives catalysed the hydrolysis reaction acting as synthetic enzymes with lower costs and higher productivity.

Initial rate, V_0, values for the reaction carried out in β-CD carbonate reactor were determined. The Lineweaver–Burk plot for the hydrolysis reaction carried out in the β-CD carbonate membrane reactor is reported in Figure 7.

To estimate the value of activation energy, the Arrhenius equation has been applied (see Figure 8). Even if CD aren't enzymes and don't follow exactly a Michaelis–Menten kinetic, we can use this kind of relation with good approximation.

Conclusions

Symmetric and asymmetric membranes were prepared from PEEK-WC. The influence of preparation technique was analysed and various kind of membranes were obtained.

Top layer thickness depends mainly on the evaporation time, being a higher time producing a thicker layer.

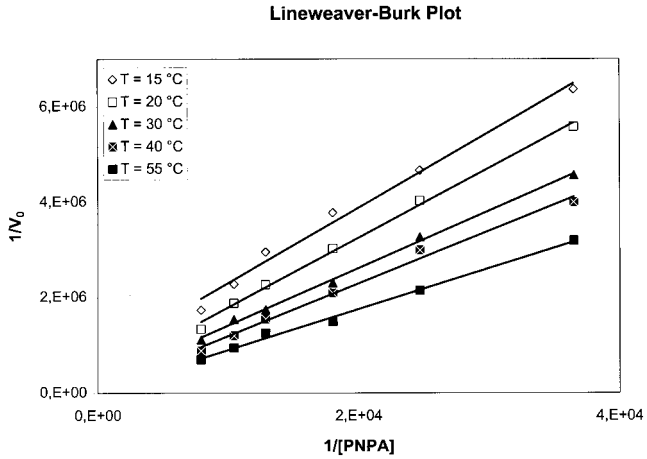

Figure 7. Lineweaver–Burk plot for the hydrolysis reaction carried out in the β-CD carbonate membrane reactor.

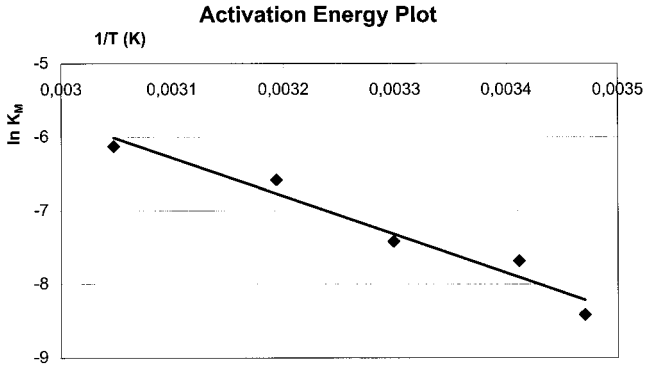

Figure 8. Estimation of the value of activation energy with Arrhenius equation.

In this study we worked in optimal conditions determined previously [3, 10], the effect of temperature has been examined and the value of activation energy has been estimated.

The activation energy for the β-CD catalysed reaction results of 32.6 kJ/mol, significantly lower with respect to the batch hydrolysis with and without β-CD values listed in literature (36.4 and 45.2 kJ/mol, respectively) [11].

In the membrane β-CD show to have more stability because of their chemical resistance to alkaline attack. The entrapment of CD in the polymeric membrane optimises the interaction with the substrate, increases the chemical stability of the catalyst, allows the reuse of the catalytic membrane, in fact the membranes may be easily washed and reused without any lost of activity.

In the membrane the acylic chains form bonds with the PEEK polymer so that the hydrophobic cavity is free and oriented to be more able for carrying out the catalytic action.

In conclusion, the use of a polymeric membrane functionalised with *O*-octyloxycarbonyl β-CD derivative to carry out the hydrolysis reaction of PNPA to PNP in phosphate buffer enhances the reaction rate with an enzyme-like behaviour, but improving productivity and stability and decreasing costs.

This study shows the performance of a novel design of catalytic membrane reactor, in which the specific properties of a non conventional catalyst immobilised in a polymeric membrane can promote and extend new applications of these systems.

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