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Studies on sugars extraction across a supported liquid membrane: Complexation site of glucose and galactose with methyl cholate

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ABSTRACT

A supported liquid membrane (SLM) containing methyl cholate as carrier **1b** has been used for the facilitated transport of monosaccharides from concentrated (0.4–0.025 M) aqueous solutions. The SLM is made of a microporous poly(vinylidene difluoride) film impregnated with a 0.1 M solution of the carrier in cyclohexane. The SLM prepared with cyclohexane is remarkably stable for at least 23 days. The permeabilities of the SLM for various sugars were determinated. On the basis of the flux dependence on the initial concentrations of sugar, the rate-determining step in the transport mechanism is shown to be migration of a carrier–sugar complex within the SLM. The flux of sugar is related to the initial concentration of sugar in the feed phase by a saturation law, which allowed the determination of the apparent diffusion coefficient D^* and the stability constant K of the methyl cholate complexes of sugars formed in the liquid membrane. The variation of K with structure of sugars confirm molecular recognition by the carrier and show that the complexation sites are HO-2,3,6 for glucose and HO-1,2,6 for galactose.

1. Introduction

Sugars are produced each day from water and atmospheric carbon dioxide by photosynthesis. These sugars of various natures are found in the form of mixtures of which degradation to simpler molecules could be used for new synthesis. Indeed, the oil (exhaustible resource) is almost the only organic raw materials for the chemical industry. Therefore, it will be necessary to find new raw materials, either fossil, but renewable. The sugars, abundantly produced by plants, are the most evident raw material. The development of simple and economic methods for separation of the mixtures of sugars would consequently allow obtaining of a renewable source of molecules highly functionalized for the chemical industry. The continuous separation of mixtures, under ambient pressure and temperature is possible by the membrane processes which are particularly economic.

The liquid membranes, introduced more recently, consist of a liquid film (generally an organic solvent) separating two aqueous phases. Transport through a liquid membrane is, in principle, a double liquid–liquid extraction, in which the volume of solvent is very small, and the organic vapour emissions are limited. The liquid membranes allow larger flux than other types of membranes, but their mechanical resistance is bad.

The supported liquid membranes (SLMs) represent an improvement for such applications. They are an elegant solution for the selective extraction of some hydrosoluble species by facilitated transport. The most studied species are the metal ions [1–3] and the acids [4–7] for which several carriers are used, but also the neutral molecules such as various drugs (antibiotic) [8,9], phenols [10,11] and especially sugars [12–14]. SLMs consist of a polymeric support microporous and hydrophobic. The pores are filled with an organic solvent in which the carrier is dissolved. This system offers the advantage of requiring small quantities of carrier and solvent. However, it presents the disadvantage of easy loss of carrier and solvent in the aqueous phases, inducing a limited lifetime of these membranes, which is the essential disadvantage for their practical application [15–17].

The separation of sugars by facilitated transport through a SLM is based on the presence of specific carriers who form complexes with sugars. The first carriers used were the boronic acids which allowed a fast and selective transport of various simple sugars [18–20]. A derivative of calix[4]arene was used later on as specific carrier for the transport of several sugars in aqueous solution in tetrachloromethane [21,22].

We recently suggested another type of macrocyclic carrier which has the advantage of being commercial [23,24]. Since the synthesis of such carriers is difficult, the use of less toxic natural molecule, such as sterols is a good alternative. The biliary acids, especially the cholic acid **1a** and its methyl ester **1b** seem to be particularly appropriate, since their structures present a rigid polycyclic core with three adjacent hydroxyl group (Fig. 1) which

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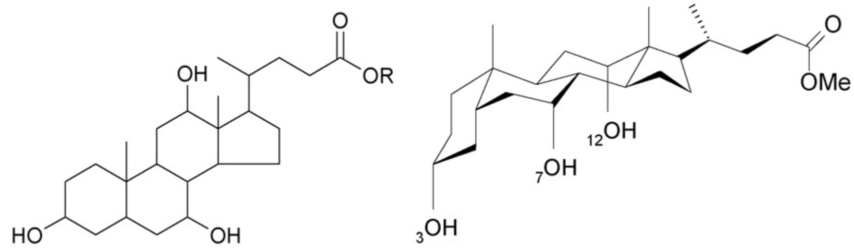

Cholic acid, **1a,** R = H
Methyl cholate, **1b,** R = Me

1b (3 D structure)

Fig. 1. Structure of methyl cholate.

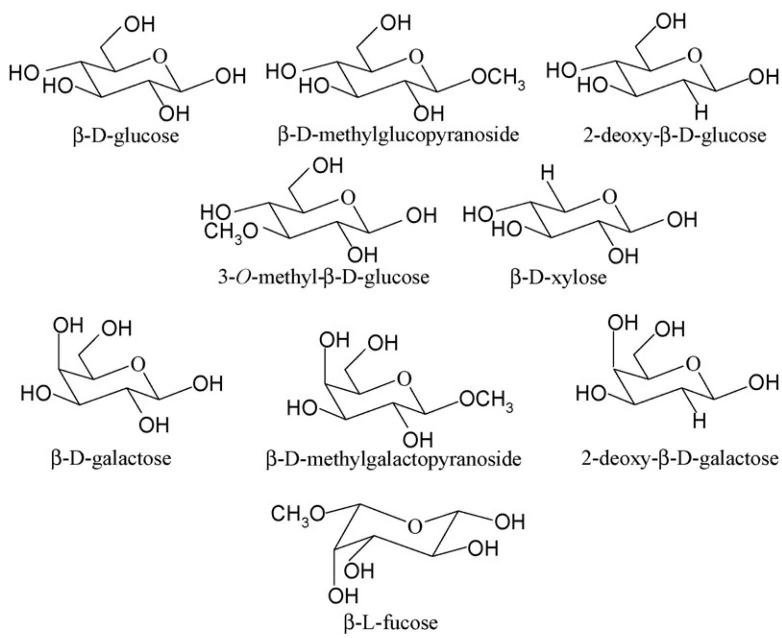

Fig. 2. Structures of sugars used.

can constitute a recognition site for sugars of which the structure presents several adjacent hydroxyl groups.

In this study, we prepared a SLM containing the methyl cholate **1b** (Fig. 1) in cyclohexane, which allows a permeability close to that of benzene and is less toxic than this last [23]. This is of interest for application to industrial process in separation of the mixtures of sugars.

The nature of the complexes involved between sugars and methyl cholate was studied by examining the transport of various sugars (Fig. 2). To specify the characteristics of the sites involved in the complexation with the methyl cholate, we determined the stability constant *K* of the carrier–sugar complexes.

2. Theoretical approach

The transport rate is measured by determining the increase of the sugar concentration c_R in the receiving phase versus time *t*. This rate is related to the flux *J* of sugar by Eq. (1):

$$\frac{dc_R}{dt} = \frac{JS}{V} \tag{1}$$

where *S* is the membrane area and *V* is the volume of the receiving phase.

When the system reaches a quasi-steady-state, the flux *J* is related to Δc, the difference between the concentrations of sugar in the feed phase (c_F) and the receiving phase (c_R), and the membrane thickness *l* by Eq. (2) derived from Fick's first law:

$$J = \frac{P\Delta c}{l} \tag{2}$$

where *P* is the permeability of sugar through the SLM.

Since the flux of sugar is very large, the concentration (c_R) of the receiving phase is not negligible as compared to the concentration (c_F) of the feed phase. Thus, Δc is calculated using Eq. (3) where c_0 is the initial concentration of sugar in the feed phase:

$$c_F = c_0 - c_R \text{ and } \Delta c = c_0 - 2c_R \tag{3}$$

Combining Eqs. (1)–(3) yields differential equation (4):

$$P\,dt = \frac{(lV/S)\,dc_R}{c_0 - 2c_R} \tag{4}$$

Integration of both terms of Eq. (4) yields Eq. (5):

$$P(t - t_L) = \frac{lV}{S}\frac{1}{2}\ln\frac{c_0}{c_0 - 2c_R} \tag{5}$$

which shows that, after an induction period (t_L) that may last up to several hours, the term $-\ln(c_0 - 2c_R)$ is a linear function of *t*. The permeability *P* values for the various sugars were calculated, using