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Selective monosaccharides extraction mediated by methyl cholate in a supported liquid membrane

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ABSTRACT

The separation of aqueous mixtures of monosaccharides has been carried out with a supported liquid membrane (SLM) containing methyl cholate as carrier in cyclohexane. Special attention has been paid to optimizing conditions for effective separation, while retaining large permeabilities. The SLM selectivity slightly increased with increasing substitution of the solvent and decreasing pore size, but at the cost of unacceptable decrease of permeability. The selectivity of the SLM was determined from separation experiments of binary mixtures. The permeabilities are smaller in the mixtures than for the individual components, due to competition between the two monosaccharides of the mixture to form a complex with the limited amount of carrier. This competition depends on the difference of the stability constants between the two carrier–sugar complexes (CS). The SLM allowed some interesting separations ($\alpha > 1.25$). The separation of the monosaccharides depends on three parameters: functional groups, chain length and configuration.

Keywords: Separation; Monosaccharides; Supported liquid membrane; Facilitated transport; Methyl cholate

1. Introduction

The separation of sugars is often a difficult and costly task. Since most sugars are isomers which only differ in the configuration of specific CHOH groups, methods based on differences of chemicals reactivities are generally unsuitable [1]. The separation of sugars is possible by chromatography [1]. However, this process implies expensive installation, low productivity and low yields of the desired product.

Many works have been devoted to the problem of the separation of mixtures of sugars. The solvent extraction that uses an ion-pair of phenylboronate anion and quaternary ammonium cation was proposed to complex the sugars [2]. The liquid membrane process is a technology that combines solvent extraction and stripping processes in a single step [3]. The transport mechanism in a liquid membrane is usually based on facilitated diffusion [4]. Among various liquid membrane configurations, the most attractive for industrial applications is the supported liquid membrane (SLM). In recent years, SLM has received increasing attention as an alternative to liquid–liquid extraction and other membrane separation techniques such as ion exchange, reverse osmosis, ultrafiltration and nanofiltration for the selective removal of ions or neutral molecules from dilute solutions [5].

The methods of separation by facilitated transport through a SLM are based on the principle of the

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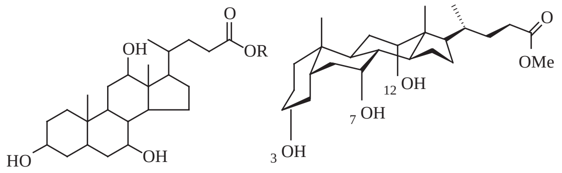

Cholic acid,**1a,** R = H
Methyl cholate, **1b,** R = Me

1b (3D structure)

Fig. 1. Structure of methyl cholate.

molecular recognition. Indeed, the use of a carrier which forms with the substrates complexes differing by their stability constants and their apparent diffusion coefficients allows obtaining the selectivity of transport which ensures the separation of the chemical substances.

Facilitated transport by SLM has been applied to the separation of mixtures of various types of chemicals, in particular organic acids [6], metal ions [5,7–11] and sugars [3,12–14]. For example, lactic and citric acids were extracted and separated with a SLM containing tri-*n*-octylamine in xylene [6]. The presence of lactic acid increased the transport rate of citric acid which diffused more quickly than lactic acid. In the separation of sugars by SLM, few carriers were efficient. The most used carriers are boric acid derivatives. Boronic acids facilitate the transport of sugar in various types of liquid membranes [15–18], and that in certain conditions the liquid membranes show selectivity for fructose over other monosaccharides [19,20]. The use of a liquid membrane containing an arylboronic acid allowed separating several mixtures of sugars [20] in particular fructose mixed with glucose and sucrose [16]. Phenylboronic acid was also used in separation of a fructose–glucose mixture [3,12–14]. In all cases, a distinct difference was observed in transport of the three sugars. Fructose was efficaciously separated from a mixture of fructose, glucose, and sucrose with a large selectivity. Nevertheless, separation by boronic acids is not easy because these carriers form complexes only in alkaline media, in which sugars are quickly degraded. Therefore, the aqueous phases must be buffered, which complicates the final extraction of the separated sugars [22].

A SLM containing a resorcinarene carrier dissolved in CCl_4 was used for the separation of several mixtures of alditols [23] which were transported with large selectivity.

We previously showed that methyl cholate **1b** (Fig. 1) selectively transports the aldoses and their derivatives through SLMs [24,25]. In these studies, however, the SLM was prepared with toxic aromatic solvents [24]. The discovery that a SLM prepared with cyclohexane shows a large permeability [25] opened the way to possible industrial use, prompting us to evaluate the possibility of interesting separations.

In this paper, the separations of binary mixtures of carbohydrates in aqueous solutions with methyl cholate in cyclohexane were explored by the SLM technique. The effects of substitution of cyclohexane and of pore diameter on the selectivity were examined. Selectivity factors based on SLM transport were calculated to discuss the separation characteristics for obtaining optimal operating conditions with a view to development of a selective extraction and separation method for monosaccharides by using SLMs.

2. Theoretical approach

2.1. Measurements of permeabilities and flux

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):

$$\frac{dc_R}{dt} = \frac{J \, . \, S}{V} \tag{1}$$

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 $\triangle c$, 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.

Under our experimental conditions, the concentration of sugar retained in the SLM is negligible. However, the flux of sugar is large and the concentration (c_R) of the receiving phase is not negligible versus the concentration (c_F) of the feed phase. Thus, $\triangle c$ is calculated using Eq. (3) where c_0 is the initial concentration of sugar in the feed phase:

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

Combining Eqs. (1), (2) and (3) yields differential Eq. (4):

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

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

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

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 Eq. (6), from the slopes a of the plots.(6)

$$P = \frac{a \cdot V \cdot l}{2\,S} \tag{6}$$

The intersection of the linear section with the time axis defines the ''true initial time'' t_L at which the sugar concentrations in the aqueous phase are $c_F \approx c_0$ and $c_R \approx 0$. At this instant, the initial value of the flux, J_i, can be calculated by Eq. (7) derived from Eq. (2):

$$J_i = \frac{P \cdot c_0}{l} \tag{7}$$

2.2. *Modelling and parameters of the complex-forming reaction*

The carrier-mediated mechanism for the transport of sugar is based on the rapid formation of a complex between the carrier (C) and the sugar (S) at the interface between the membrane and the feed solution. This complex diffuses in the SLM in the rate-determining step and is eventually dissociated at the membrane-receiving phase interface. Such a mechanism is classically associated with a saturation kinetic law with respect to the sugar concentration. The initial flux of sugar J_i is obtained by Eq. (7).

The experimental rate law shows, for the initial flux J_i of sugar, a linear dependence on $[C]_0$, the concentration of carrier in the membrane. Eq. (8) is a saturation law with c_0, the initial concentration of sugar in the feed phase:

$$J_i = \frac{(D*/l)\,[C]_0\,Kc_0}{1 + Kc_0} \tag{8}$$

Where l is the membrane thickness. D^* is the apparent diffusion coefficient of the complex, and K is the equilibrium constant for the interfacial equilibrium:

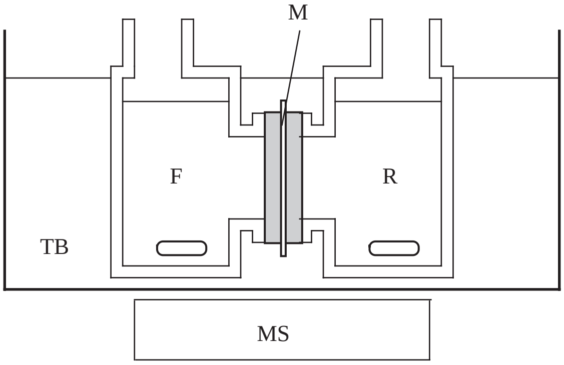

Fig. 2. Scheme of the transport cell. M is the SLM. F is the feed phase. R is the receiving phase. TB is the thermostated bath. MS is the multiple stirrer. Phases F and R are stirred using magnetic bars.

$$\mathrm{C(org)} + \mathrm{S(aq)} \rightleftharpoons \mathrm{CS(org)}$$

Where (org) and (aq) refer to the organic and aqueous phase, respectively.

A linear plot, Eq. (9), can be obtained from Eq. (8) by the Lineweaver–Burk method:

$$\frac{1}{J_i} = \frac{l}{D*[C]_0\,K}\frac{1}{c_0} + \frac{l}{D*[C]_0} \tag{9}$$

Such plots were drawn for various sugars, by performing a series of transport experiments with c_0 varying in the 0.40–0.025 M range. For each sugar, the values of the complexation parameters K and D^* are calculated from the slope and intercept of the plot obtained by linear regression: $K = \frac{\text{intercept}}{\text{slope}}$ and $D* = \frac{l}{[C]_0}$.

3. Experimental

3.1. *Apparatus, membranes and solutions*

The stirred cell and membranes used in the SLM experiments were identical to those employed previously [24,25]. The transport cell (Fig. 2) is made of two compartments of equal volumes (130 mL) separated by the SLM. The cell is immersed in a thermostated bath controlled in the temperature ($T = 25$ °C). The solutions in both compartments are stirred with magnetic bars at a constant rate. Durapore GVHP and HVHP (Millipore) laminar microporous polyvinylidene difluoride (PVDF) films were used as solid support for liquid membranes. The overall film diameter was 9 cm and the effective membrane area was 19.6 cm^2. The determination of thickness was made on a dry and an impregnated film with a Palmer. The porosity was calculated from the known mass, volume and volumic mass of the film ($\rho = 1.75$ g cm^{-3} for PVDF). The GVHP film characteristics are: pore size 0.22 μm, mean mass 465 mg, thickness 98 μm, porosity 57%. For the HVHP film, (pore size 0.45 μm), two batches with different characteristics were used. For batch 1: mean mass 480 mg, thickness 108 μm, porosity 60% and for batch 2: mean mass 380 mg, thickness 96 μm, porosity 64%.

The sugars and other chemicals were supplied by Aldrich as analytical reagent grade. Methyl cholate was purchased from ICN Biomedicals and used as obtained.

3.2. Procedures

The support was first impregnated with a solution of methyl cholate in acetone and evaporated to dryness. The mass of immobilized carrier was determined by weighing the support before and after impregnation. Then, the membrane was impregnated with cyclohexane and inserted in the transport cell. Before use, the SLM was conditioned in pure water. An equimolar solution of two sugars of concentration 0.1, 0.05 or 0.04 M for each one, was introduced into the feed compartment (130 mL). The receiving compartment contained 130 mL of pure water.

The concentrations of the sugars in the receiving phase were analyzed by HPLC apparatus equipped with a 30 cm Phenomenex Rezex column in calcium form, maintained in an oven at 85 °C. The eluent was pure water (deionized by Millipore Milli-Q system), degassed and filtered with a cellulose ester membrane (Millipore, pore diameter 0.45 μm). The flow rate was 0.6 mL/min. The pump was a Shimadzu LC-9A model. Detection was achieved with a Varian RI-4 differential refractometer. Data acquisition was performed with the Varian Star software. Data treatment and accuracy of the permeability values (P) have been discussed elsewhere [24,25]. Typical uncertainties on P are ±5%.

4. Results and discussion

4.1. Choice of experimental conditions

4.1.1. Effect of substitution of cyclohexane on the selectivity of membrane

The influence of three solvents (cyclohexane and two alkyl derivatives) on the facilitated transport of a mixture of sugars was examined. It was reported that the permeability of glucose decreased with the substitution of aromatic solvents [24] in the order: benzene > toluene > ethylbenzene. The same phenomenon was reported for xylose in a series of alicyclic solvents: cyclohexane > methylcyclohexane > ethylcyclohexane [25]. We now examined the influence of the solvent, not only on the permeability of carbohydrates present in mixtures, but also on the separation of such mixtures [26] because the permeabilities of two solutes may vary to different extents. In fact, it may be more interesting to have a very selective membrane rather than a very permeable membrane.

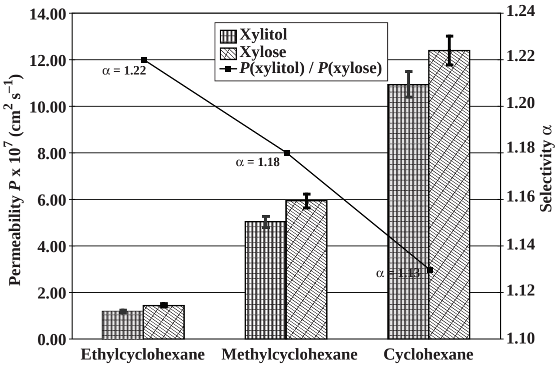

Fig. 3. Effect of substitution of solvent. α is selectivity of SLM ($\alpha = P_{\text{xylitol}}/P_{\text{xylose}}$).

The SLMs used were prepared under identical conditions. The supports containing methyl cholate (weighed mass, $m = 30$ mg) were impregnated with the three solvents. The three SLMs were used for the facilitated transport of a xylitol–xylose mixture (concentration of the two sugars in the feed phase, $c_0 = 0.1$ M). The values of permeability P and of selectivity α (defined as the ratio of permeabilities P(xylitol)/ P(xylose)) obtained for each SLM are represented in Fig. 3.

Fig. 3 shows a clear decrease of the permeability of xylitol and xylose with substitution of the solvent in the order: cyclohexane > methylcyclohexane > ethylcyclohexane, comparable to that reported for xylose alone [25]. However, it must be remarked that while the permeabilities P decrease with substitution of the solvent by alkyl groups of increasing size, the selectivity α increases (1.13 for cyclohexane, 1.18 for methylcyclohexane, 1.22 for ethylcyclohexane). The effect of substitution of the solvent on the sugar permeability was ascribed to changes of the solvent polarity [24,25] because the attachment of alkyl groups to cyclohexane decreases the solvent polarity and hence reduces the stability of the sugar–carrier complex, in which the sugar has a polar character. In contrast, it appears now

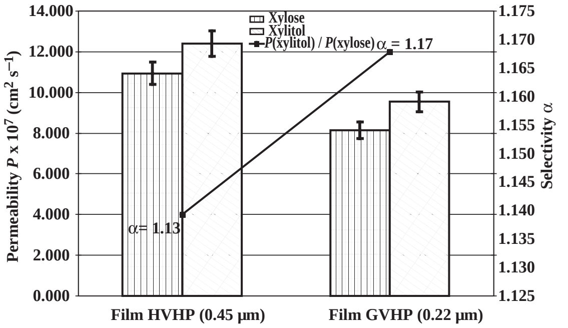

Fig. 4. Effect of the pore diameter. α is selectivity of SLM ($\alpha = P_{\text{xylitol}}/P_{\text{xylose}}$).

that the selectivity based on the *ratio* of the permeabilities of the two complexes of xylitol and xylose, increases when the solvent polarity increases. This finding is consistent with xylitol (with five HO groups) being more polar than xylose (with four HO groups). Thus, the membrane selectivity and its permeability vary in opposite directions.

4.1.2. Effect of pore diameter on the selectivity of membrane

The effect of the pore diameter on the permeability of glucose was previously studied with a SLM prepared with benzene [24]. We studied the influence of this parameter on the selectivity of SLM prepared with cyclohexane.

Two SLMs were prepared using two supports: HVHP film (pores 0.45 μm) and GVHP film (pores 0.22 μm). These SLMs were used for the transport of a xylitol–xylose mixture ($c_0 = 0.1$ M each). The values of permeability P and of selectivity α were determined for each membrane. The results represented in Fig. 4 show that the membrane with 0.45 μm pores is more permeable for the two sugars than the membrane with 0.22 μm pores. This result is in agreement with that obtained previously [24] for the permeability of a single sugar. On the other hand, the selectivity slightly increases when the pore diameter decreases (from 1.13 to 1.17), illustrating again the opposite variation between the selectivity and the permeability. The likely reason for this effect of the support is the porosity difference (57% for GVHP and 60–64% for HVHP). Since the difference in selectivity is small, and the HVHP membrane is the more permeable, all subsequent separation experiments were made with the HVHP membrane.

4.2. Separation of mixtures

The mixtures studied in this work were selected so that they are easy to separate by HPLC. In order to ensure a precise analysis, times of retention of various sugars used were distant from at least 5 min. According to this criterion, we performed the separation of four types of binary mixtures: aldose/alditol, alditol/alditol, aldose/ketose, alditol/methyl glycopyranoside (MGP), in which we combined two sugars of different categories.

4.2.1. Aldose/alditol mixtures

The transport conditions are described in the experimental protocol. The studied aldoses and alditols were: glucose, galactose, xylose, glucitol, galactitol, and xylitol.

The kinetic study led to the values given in Table 1. The application of Eq. (5) allows calculating the values of permeabilities and fluxes of various sugars.

For mixtures of aldose and alditol with the same configuration, the experimental study of transport shows a partial separation (Table 1). Generally, the order of permeabilities in the mixture is the same one as for sugars alone, but these permeabilities are lower. This is probably due to the competition between the two sugars to form a complex with methyl cholate. We also know that the permeability decreases when the concentration of sugar increases and here, the total concentration of the two sugars is 0.2 M whereas each sugar is 0.1 M. The permeability of an alditol is always larger than that of the corresponding aldose. Selectivities α = P(aldose)/P(alditol) observed in the mixtures are larger than the ratios of the permeabilities P(aldose)/P(alditol) for sugars alone. However, the small difference between the values of selectivity for the mixture and sugars alone may be insignificant in certain cases, because of the uncertainty on the permeability values.

Two aldose–alditol mixtures combining two compounds of different sizes were also studied. We crossed the configurations and the sizes by studying the transport of mixture glucose–xylitol and of mixture xylose–glucitol in order to specify the respective influences of each parameter. As previously, the permeabilities of sugars in the mixture (total concentration is 0.2 M) are lower than those of sugars alone in solution 0.1 M. In both cases, we find that the C5 species (xylose or xylitol) has a larger permeability than the C6 species (glucitol or glucose). This shows that the essential factor of the permeability is the size of sugar and not its nature of aldose or alditol. We also observe that the values of selectivity are approximatively equal to 1.30 for the two mixtures, which shows that a separation based on the size of sugars offers favourable perspectives.

Table 1
Transport of equimolar binary mixtures (0.1 M) of aldose/alditols

Sugar	Mode	c_0 (mmol cm^{-3})	10^5a (s^{-1})	10^6P (cm^2 s^{-1})	10^6J_i (mmol cm^2 s^{-1})
Glucose	m	0.10	2.24	0.71	7.41
Glucitol	m	0.10	2.89	0.92	9.57
Glucose	a	0.10	3.37	1.07	11.16
Glucitol	a	0.10	4.16	1.32	13.78
Galactose	m	0.10	2.33	0.82	7.72
Galactitol	m	0.10	2.81	0.99	9.30
Galactose	a	0.10	3.34	1.06	11.06
Xylose	m	0.10	3.12	1.09	10.32
Xylitol	m	0.10	3.52	1.24	11.64
Xylose	a	0.10	4.00	1.43	13.26
Xylitol	a	0.10	4.35	1.52	14.39
Glucose	m	0.10	2.45	0.86	8.11
Xylitol	m	0.10	3.09	1.08	10.21
Glucose	a	0.10	3.37	1.07	11.16
Xylitol	a	0.10	4.35	1.52	14.39
Xylose	m	0.10	3.68	1.29	12.19
Glucitol	m	0.10	2.75	0.96	9.09
Xylose	a	0.10	4.00	1.43	13.26
Glucitol	a	0.10	4.16	1.32	13.78

Mode: m, in the mixture; a, sugar alone; a: slope of the plot $-\ln(c_0 - 2c_R) = f(t)$; J_i: initial flux of sugar; $\alpha = P(\text{glucose})/P(\text{glucitol}) = 1.30$; $\alpha = P(\text{galactose})/P(\text{galactitol}) = 1.21$; $\alpha = P(\text{xylose})/P(\text{xylitol}) = 1.13$; $\alpha = P(\text{glucose})/P(\text{xylitol}) = 1.26$; $\alpha = P(\text{xylose})/P(\text{glucitol}) = 1.34$.

Finally, we observe an inversion of the selectivities. The ratio of the permeabilities P(xylose)/P(glucitol) for sugars alone is lower than the selectivity $\alpha = P(\text{xylose})/P(\text{glucitol})$ observed in the mixture, but for the mixture glucose–xylitol, the ratio of the permeabilities of individual sugars is higher than the selectivity in the mixture.

In conclusion, the major factor of the separation of these mixtures is not the nature of sugar (aldose or alditol) but the size of the molecule: C5 migrate faster than C6.

4.2.2. Alditol/alditol mixture

We performed the competitive transport of an equimolar 0.1 M ribitol–xylitol mixture. These two pentitols have the same size, but different configurations. The permeabilities and initial flux in the mixture are reported in Table 2.

Ribitol and xylitol migrate at slower rates in the mixture than when they are transported only. The selectivity is a little larger for the mixture than for pentitols alone, but remains low. Since the ribitol and the xylitol are isomers and differ only by the configuration from one asymmetrical carbon (C_3; Fig. 5), this parameter seems insufficient to allow a good separation of these two sugars.

4.2.3. Aldose/ketose mixture

We performed the separation of an equimolar mixture (0.1 M) of ribose (aldopentose) and fructose (ketohexose). This model of separation is based on two parameters:

- Difference in molecular mass (150 g mol^{-1} for ribose and 180 g mol^{-1} for fructose).
- Difference in carbonyl function.

Table 2
Transport of an equimolar ribitol/xylitol mixture (0.1 M).

Sugar	Mode	c_0 (mmol cm^{-3})	10^5a (s^{-1})	10^6P (cm^2 s^{-1})	10^6J_i (mmol cm^2 s^{-1})	α
Ribitol	m	0.10	3.36	1.18	11.12	
Xylitol	m	0.10	3.03	1.06	10.03	1.11
Ribitol	a	0.10	4.49	1.58	14.88	
Xylitol	a	0.10	4.35	1.52	14.39	1.03

Mode: m, in the mixture; a, sugar alone; a: slope of the plot $-\ln(c_0 - 2c_R) = f(t)$; J_i: initial flux of sugar; $\alpha = P(\text{ribitol})/P(\text{xylitol})$.

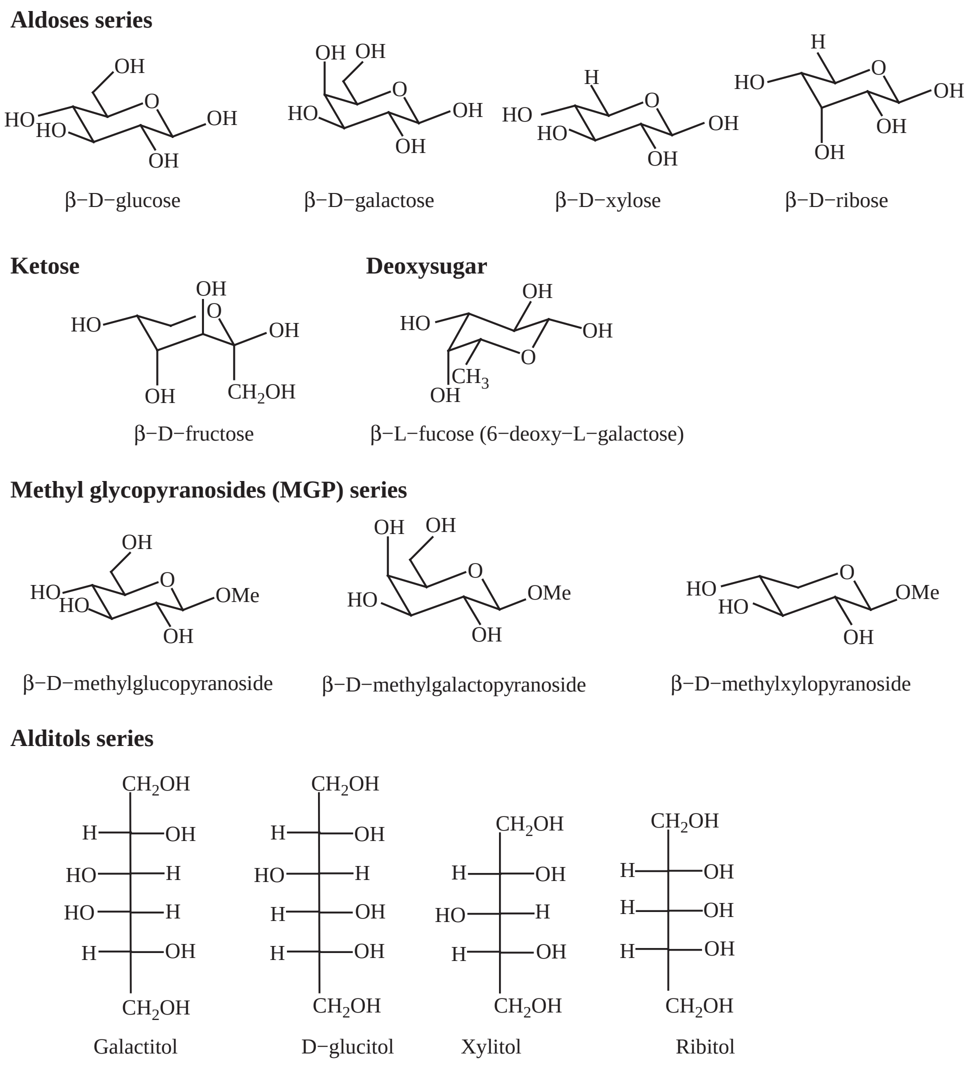

Fig. 5. Structures of carbohydrates used.

Table 3 shows the values of permeabilities, initial flux of sugars alone, and selectivity.

In this mixture, the permeabilities of ribose and fructose have both decreased compared to sugars alone. The ribose molecule is transported faster than fructose by methyl cholate through the SLM because it is smaller. The selectivity in the mixture ($\alpha = 1.33$) is lower than that for sugars individually transported ($\alpha = 1.49$), but remains significant.

4.2.4. Fucose/galactitol mixture

A mixture of two galactose derivatives was studied: fucose (6-deoxygalactose) and galactitol. The choice of

Table 3
Transport of an equimolar ribose/fructose mixture (0.1 M)

Sugar	Mode	c_0 (mmol cm^{-3})	$10^5 a$ (s^{-1})	$10^6 P$ (cm^2 s^{-1})	$10^6 J_i$ (mmol cm^2 s^{-1})	α
Ribose	m	0.10	3.82	1.34	12.64	
Fructose	m	0.10	2.89	1.01	9.57	1.33
Ribose	a	0.10	4.33	1.52	14.34	
Fructose	a	0.10	2.92	1.02	9.66	1.49

Mode: m, in the mixture; a, sugar alone; a: slope of the plot $-\ln(c_0 - 2c_R) = f(t)$; J_i: initial flux of sugar; $\alpha = P(\text{ribose})/P(\text{fructose})$.

Table 4
Transport of an equimolar fucose/galactitol mixture (0.1 M)

Sugar	Mode	c_0 (mmol cm^{-3})	$10^5 a$ (s^{-1})	$10^6 P$ (cm^2 s^{-1})	$10^6 J_i$ (mmol cm^2 s^{-1})
Fucose	m	0.10	2.91	1.02	9.64
Galactitol	m	0.10	3.19	1.12	10.56
Fucose	a	0.10	4.66	1.48	15.43

Mode: m, in the mixture; a, sugar alone; *a*: slope of the plot $-\ln(c_0 - 2c_R) = f(t)$; J_i: initial flux of sugar; $\alpha = P(\text{galactitol})/P(\text{fucose}) = 1.10$.

these compounds is based on the large differences observed between their permeabilities. The initial concentration of each compound in mixture was 0.1 M. Table 4 shows the values of permeabilities, initial fluxes, and selectivity.

We observe that the permeability of fucose is lower in the mixture than when it was individually transported. The transport of galactitol alone was not performed. In the mixture, galactitol migrated more quickly than fucose. The complex of fucose (Fig. 5), which does not have a CH_2OH exocyclic group, essential for the stability of complex formed with methyl cholate, is less stable than that of galactose (*K* large). The stability constant *K* of the complex of galactitol was not determined, but it must be close to that of glucitol and consequently smaller than that of fucose which migrates more slowly. Therefore, the principal factor of separation of this mixture is the carbohydrate configuration.

4.2.5. *Alditol/MGP mixtures*

In this series of experiments, we initially studied the transport of an equimolar mixture (0.05 M) of glucitol and α-D-methyl glucopyranoside (MGlcp) because it presents an example of separation of two glucose derivatives.

Afterwards, we also studied galactitol/α-D-methyl galactopyranoside (MGalp) and xylitol/α-D-methyl xylopyranoside (MXylp) mixtures at initial concentrations of 0.04 M and 0.1 M respectively.

Table 5 shows the values of permeabilities, initial fluxes, apparent diffusion coefficients of sugars alone and selectivities obtained for each mixture.

The results show that the permeabilities in the mixtures are lower than for sugars alone. The selectivity between xylitol and MXylp ($\alpha = 1.09$) in the mixture is lower than that for the substrates alone ($\alpha = 1.20$). In the case of the mixtures of glucitol/methyl glucopyranoside and galactitol/methyl galactopyranoside, the ratio of permeabilities of the substrates alone was not determined. Generally, the alditols migrate more slowly than the MGP, except in the case of the mixture xylitol/methyl xylopyranoside where xylitol is transported better than methyl xylopyranoside. The factor responsible for the separation of these three mixtures is not the difference in configuration, which is the same one between the studied alditols and MGP. However, the alditols are acyclic, whereas the MGP are not only cyclic, but they are blocked in pyranose form.

Table 5
Transport of various alditol/methyl glycopyranoside (MGP) mixtures

Sugar	Mode	c_0 (mmol cm^{-3})	$10^5 a$ (s^{-1})	$10^6 P$ (cm^2 s^{-1})	$10^6 J_i$ (mmol cm^2 s^{-1})
MGlcp	m	0.05	3.40	1.19	5.63
Glucitol	m	0.05	3.04	1.07	5.03
MGlcp	a	0.05	4.24	1.35	7.02
MGalp	m	0.04	3.74	1.31	4.95
Galactitol	m		3.31	1.16	4.38
MXylp	m	0.10	2.72	0.95	8.99
Xylitol	m	0.10	2.96	1.04	9.77
MXylp	a	0.10	3.60	1.26	11.92
Xylitol	a	0.10	4.35	1.52	14.39

Mode: m, in the mixture; a, sugar alone; *a*: slope of the plot $-\ln(c_0 - 2c_R) = f(t)$; J_i: initial flux of sugar; $\alpha = P(\text{methyl glycopyranoside})/P(\text{glucitol}) = 1.11$; $\alpha = P(\text{methyl galactopyranoside})/P(\text{galactitol}) = 1.13$; $\alpha = P(\text{methyl xylopyranoside})/P(\text{xylitol}) = 1.20$.

5. Conclusion

The transport of several binary mixtures of sugars was studied to evaluate the selectivity of SLM. The obtained results showed that: When the cyclohexane solvent is substituted by an alkyl chain of increasing length, the selectivity α slightly increases while the permeability P dramatically decreases.When the pore diameter of the support decreases, the permeability P decreases and the selectivity α increases.

These two observations indicate an opposite variation between the permeability P and the selectivity α.

The study of the transport of the mixtures of sugars shows a decrease of the permeabilities in the mixtures, caused by the competition between the two sugars of the mixture to form a complex with the carrier. This competition depends on the difference of the stability constants between the two formed complexes CS.

The separation of the mixtures depends on three parameters:

- *Functional groups*: Alditols are transported faster in the mixtures than corresponding aldoses, the transport of fucose (that does not possess a HO-6 group) is slower in the mixture than the galactitol which has HO-6 group.
- *Chain length*: Pentoses and pentitols are transported better than hexoses and hexitols.
- *Configuration*: The transport of ribitol is slightly faster than that of xylitol, showing a limited influence of the configuration, as found when comparing xylose and ribose.

List of symbols

a	slope of the plot $-\ln(c_0 - 2c_R) = f(t)$
c_0	initial concentration of sugar in the feed phase (mol dm^{-3} or mmol cm^{-3})
c_R	concentration of sugar in the receiving phase (mol dm^{-3} or mmol cm^{-3})
D^*	apparent diffusion coefficient of the complex CS ($cm^2\ s^{-1}$)
J_i	initial flux of sugar (mmol $cm^{-2}\ s^{-1}$)
K	stability constant of the complex CS
l	the membrane thickness (mm or μm)
α	the selectivity of membrane
P	the permeability of sugar ($cm^2\ s^{-1}$)
S	the membrane area (cm^2)
$[C]_0$	concentration of carrier in the membrane (mol L^{-1})
[CS]	concentration of the complex CS (mol.L^{-1})
T	temperature (K or °C)
t	time (s)
V	volume of the receiving compartment (cm^3)

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