
The permeation of saccharides at the ultra filtration through indigenous polyurethane membranes

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Abstract

The chemical structure at the macroscopic level influences the performances of membranes in different processes and operations. The interactions between the membrane structure and the sugar molecules they are in contact with, determine the capillary flow speed and the retention degree. The kinetic and thermodynamic aspects monitored in the study of aqueous dispersions transformation degree with sugars, emphasizes the influence of temperature on the permeability.

We studied the selective permeation of indigenous polyurethane membranes A, F and Pall import polyamide, compared to the sugars with different molecular mass and volumes. From the calibration curves, we obtained information on the solubility of sugars that diffuse in the membrane, the sieve effect and the absorption of chemical species.

Keywords: polyurethane membranes (PU), ultra and micro filtration (UF,MF), porosity, sieve effect, permselectivity, optic activity, morphological structure

Introduction

The most common membrane materials are cellulose acetate, polyamide and the « thin film composites », prepared by interfacial polymerization on the surface of a porous support. Cellulose acetate (CA) was one of the first membrane materials, and it is still being successfully used especially in water treatment. The rejection of glucose, saccharose, raffinose in solutes of the membranes of CA is 99% [1]. CA membranes are drastically less stable in organic solvents than polyamide.

The recommended pH range is between 3 and 7, they are less resistant to biological attack and the recommended temperature is lower than 50C. The susceptibility to hydrolysis increases with temperature and it is an inverse function of the degree of acetylation. However the possibility of expanding the application in separation which demands membranes with higher performance came only with the advent of the thin film composite (TFC) membranes.

One of the most successful TFC membranes is the FT-30. The polyamide layer is formed on an asymmetric microporous polysulfone support cast on a polyester support web. The rejection of sucrose (MW; 342 g/mol) solutes by FT 30 is 99% [2] Aromatic polyamides have a much higher solvent resistance and may be used in a wider pH range (pH : 4-11).

Micro filtration and ultra filtration, are well established separation processes in the biotechnology and fermentation industry, which can be used as a means of purifying oligosaccharides from high molecular weight enzymes and polysaccharides [3]. However, commercial products often contain low molecular weight sugars that do not contribute to the beneficial properties of the higher molecular weight oligosaccharides.

The sieve effect manifested in the membrane process is considered an electrostatic barrier in the filtration and circulation of permeates through the glomerule system of the capillaries existent in the membrane. For the practice of applications, a membrane having a certain density of electric charge is more interesting. Thus, different industrial fields such as: the food, the medical, the biochemical and textile fields, can apply the sieve capacity of electrically charged membranes.

The current paper studies the behaviour of membranes compared to the sugars with different molecular mass and volume. The characteristics of polyurethane membranes compared to the polyamide import one, are examined through the sugars permeation. We take into consideration the electrostatic interaction between the membrane and the solution. PU membranes have a much higher solvent resistance (benzene, toluene, butanol) and may be used in a wider pH range (pH 3-14). Also, PU membranes exhibit a more stable performance in applications where the feed has a high fouling potential.

Material and method

MATERIALS

We used the PU polyurethane membranes of MABEDAN: A type with the dimension of pores of 3-4 μm and F with the dimension of pores of 0,5 -1 μm and the PALL import polyamide membrane with the pore dimensions of 0,2-0,51 μm .

The experiments have been carried out with distilled water and with solutions of mono and polysaccharides in water, at 25⁰C and 1 atm.: glucose (G), fructose (Fr), galactose (Ga), lactose (La), inuline (I), dextrin (D) and soluble starch (Am).

METHOD

The membranes from polyurethane (PU) type MABEDAN, have been prepared by casting, and the development of membrane structure during the polymer processing has been achieved [4].

The miscibility of the polyurethane system has been characterized by scanning electronic microscopy (SEM). All scanning electron microscopy observations were made with TESLA B.S.300 instrument.

The permselectivity of membranes was tested on an installation of laboratory ultra filtration (vacuum : 60 mm Hg, $S_{\text{mebrane}} = 0,003\text{m}^2$)

The presence of sugars was tested through qualitative analytical determinations. The membrane performance is given by the capacity of retaining $R\% = (1 - C_1/C_2)100$ where C_1 and C_2 represent the permeate concentration, the initial solution concentration respectively.

The dimension of membrane pores was measured on a Bubble Point installation. The angle of rotation of polarized light plan was read on a polarimeter of Carl Zeiss Yena type.

An quality check for membranes has been made by osmotic measurements, with a Zimm-Myerson osmometer. The dynamic method at constant time intervals has been used.

The asymmetry degree was discovered through the developing of supramolecular structure at the PU, A and Pall import membranes, through impregnation with a hydrophobic colorant Sudan red. After drying the samples treated with colorant, we noticed differences in the membrane tissue on the two faces at the PU, A membrane and similarities at the Pall import membrane.

Results and discussions

The structural parameters of the membrane porous space are presented in Table 1. We notice for polyurethane A membrane a smaller degree of hidrophily and a greater value for the permeability constant at the distilled water.

Table 1. The structural and functional parameters of A, F and pall membrane

Membrane	ϕ [μm]	ϵ [%]	δm [μm]	d [g/cm^3]	Hidrophily degree	Const. of water perm.	Optical activity, α	
							G	La
A	2,69	56	870	0,96	0,85	0,22	+1,70	+6,55
F	1	59	1000	0,83	1,07	0,10	+1,55	+6,85
Pall	0,5	56	350	0,74	1,06	0,10	+6,17	+6,95

The water content from the polyurethane membrane pores is smaller than the import membrane. Thus, the great flux of water is explained, especially for the A membrane.

The permeability constant is the product between the solubility constant and the diffusion capacity of the chemical species in the membrane. The higher the chemical species solubility is, the more difficult the diffusion through the membrane becomes.

The solubility of glucose in the membrane structure is more pronounced at the Pall import membrane than at the A polyurethane one.

This may be the result of the different conformations which the monosaccharides adopt in aqueous solution.

Particular conformations of monosaccharides are stabilized by what is thought to be the structure of bulk water. With polysaccharides this facility is lost because the conformation of monomer unites is fixed in the polymer. Long range interaction between water and a polysaccharide depends on the type of macromolecule and its concentration in solution.

The majority of OH groups are in an equatorial configurations and the distance between the groups, in this configuration, or the same side of the ring, e.g. OH groups attached to carbon atoms 1, 3 and 5 of β -D glucose, β -D-galactose is $4,86 \text{ \AA}$ [5,6]. This is compatible with the most probable second nearest neighbour distance in water of $4,9 \text{ \AA}$, which is derived from X-ray data for water assuming a tetrahedral structure, and supports the proposal that hydrogen bonding would be expected between water and the majority of the hexose OH groups.

For example, each of the OH groups of β -Dglucose is in an equatorial configuration and fits very well with the tetrahedral arrangement of water molecules (Fig.1).

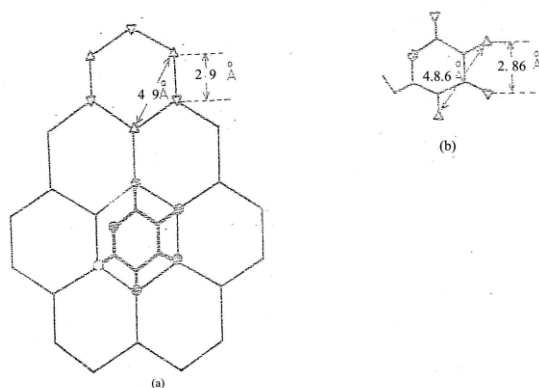


Figure 1. Possible model for hydration of monosaccharides: a) Tridymite water structure at 25°C , b) β -D-Glucose (the orientation of the triangles indicate whether an oxygen atom is above or below the plane of the ring [7]).

It follows that the pyranose forms are stabilized by interaction with water and our NMR measurement provide evidence for the greater hydration of the 6-membered ring conformation and offers a description of the nature of the hydrophilic interaction.

The swelling degree, the flux in the distilled water and the dimensioning of large pores at the A membrane, determine the increase of capillary flow, in the glucose (G), galactose (Ga), fructose (Fr) and lactose (La) (Table 2).

Table 2. The experimental results regarding the capillary speed flow of sugar

Membrane	The experimental parameters	C : 1 g/l						
A		G	Ga	Fr	La	I	D	Am
Pall		0,253	0,125	0,107	0,05	0,015	0,020	0,015
	0,035	0,058	0,057	0,101	0,030	0,068	0,075	
Membrane	The experimental parameters	C ; 10 g/l						
A		G	Ga	Fr	La	I	D	Am
		0,47	0,38	0,12	0,38	0,026	0,0041	0,0025

For the inuline (I), dextrin (D) and starch (Am) larger molecules, greater values are registered for the capillary flow speed than the Pall membrane. This explains the different geometrical form of pores and channels at the two membranes. The sinuosity of A polyurethane membranes is greater than the import one.

The membrane functions are the selective permeability and permeation. The mass transfer depends on the membrane structural architecture and on the nature of solutions in contact with the membrane. The measure and distribution of pores and their nature influence the selectivity and the mass transfer speed. If the solubility of species that diffuse through the membrane is high, the permeation through the membrane is facilitated.

The sieve effect appears according to the molecular mass and the form of species that flow through the membrane. When two species with different speeds diffuse through a membrane, the species with low speed are accumulated on the membrane face they are into direct contact with, on the posterior side of the membrane. These high concentration regions tend to reduce the forces that act on the mass transfer.

From the calibration curves presented in Figures 2 and 3, we noticed differences in the three membranes behavior, compared to the G, Fr, La and Am. At the indigenous membranes, the glucose (G) presents the greatest permeation (especially for A membrane), while the Pall import membrane registers the smallest degree of permeation.

The fructose (Fr) interrupts the sieve effect at the indigenous membranes, and the lactose (La), dextrin (D) and the starch (Am) at the Pall membrane. The starch is more difficult to permeate through the indigenous membranes than through the Pall membrane.

The asymmetrical membrane A, more selective, is constituted of structural plans with different morphologies, unlike the symmetrical Pall membrane. The morphological structure developing at the two membranes, illustrates in fact the asymmetry degree and implicitly the selectivity (Fig. 4).

Figure 2. The diagram flux l/mh according to the molecular mass (log M) of G, Fr, Ga, La, I, D and Am molecules.

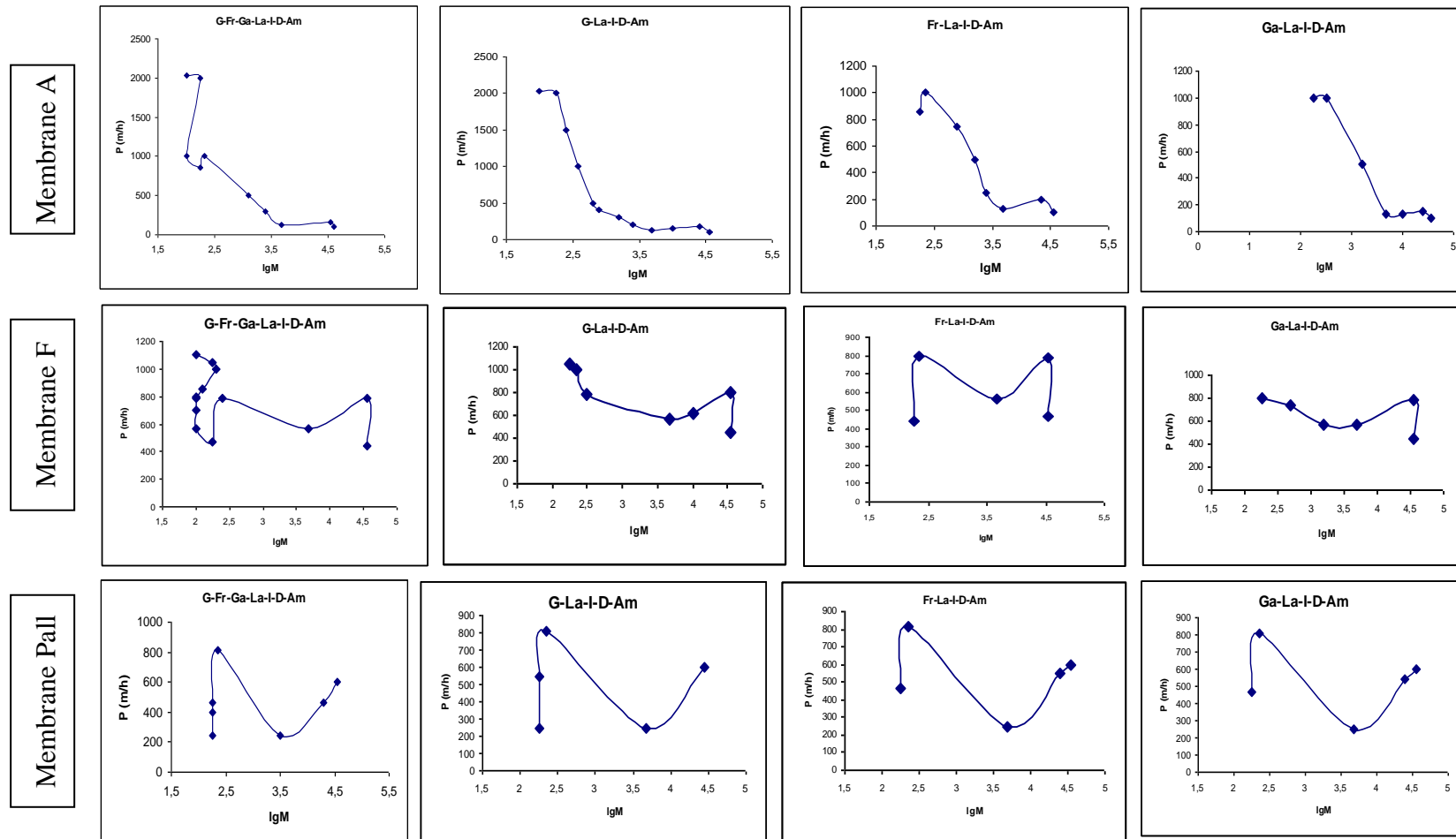
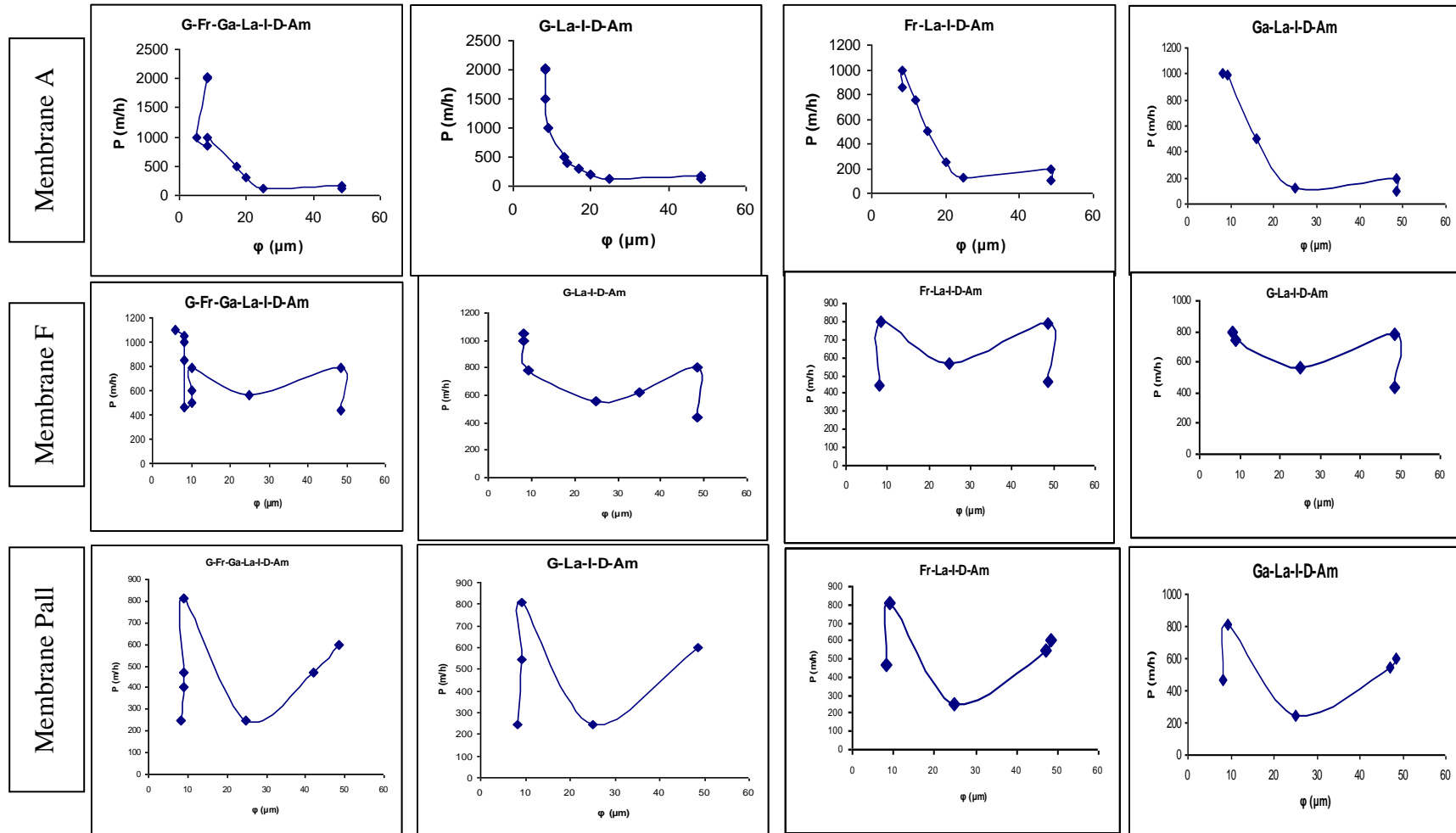


Figure 3. The diagram flux l/mh according to the dimension of G, Fr, La, I, D and Am molecules



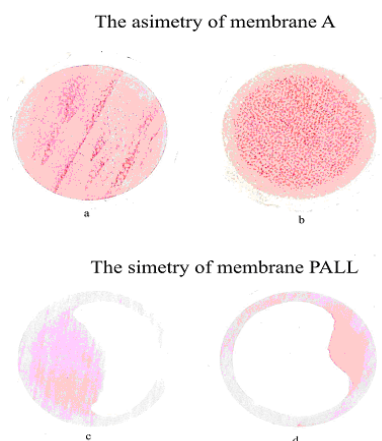


Figure 4. The developing of supramolecular structure at the A and pall membranes; the symmetry of A membrane: anterior face (a,c); posterior face (b,d).

The abundant pigmentation is present on only one face of A membrane while at Pall, the colored images are identical on the two faces. The morphological differences presented by the A, F and pall membranes are illustrated in Figure 5.

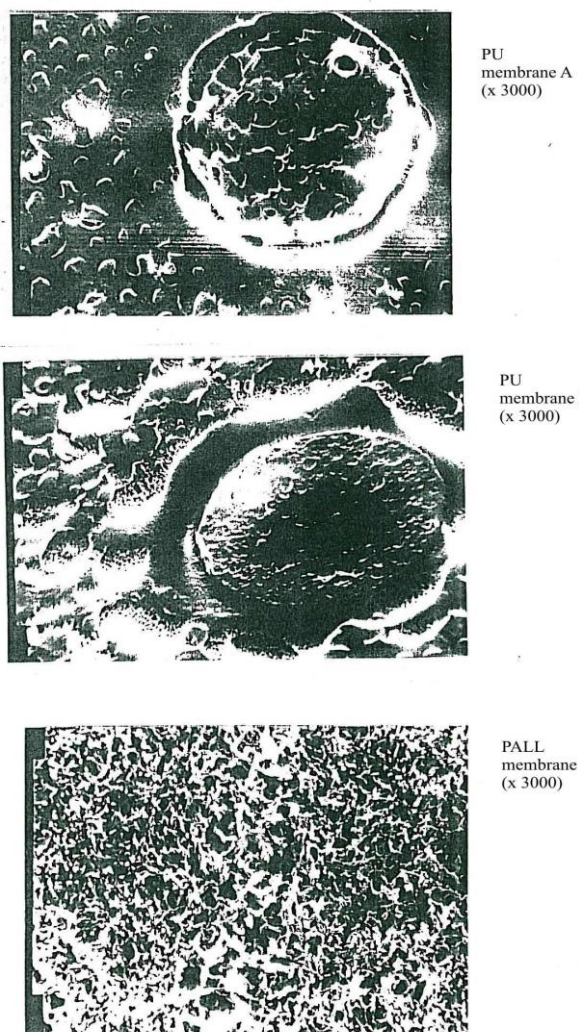


Figure 5. Microscopic balayage images for the A, F, Pall membranes at an increase power factor x 3000.

The morphological details offered by the balayage electronic microscopy images, emphasize the distances between the molecular structures existent in the membrane supramolecular system. The minimal resolution distances between the two points, two micro phases or two molecular structures, can be found on the microscopic electronic balayage photographs. The image is the result of the encounter between the electrons and the atoms from the membrane structure and their reflection in a more or less deviant distribution.

A polyurethane membrane presents globular micro phases greater than the F membrane and with a detail of 200 μm where there are pores with the average dimension of 3-4 μm .

The F polyurethane membrane visualizes photographically through electronic balayage microscopy, globular micro phases with a detail of 25-28 μm in which there appear pores of 1-2 μm , medium diameter.

The selectivity in the separation of glucose (G) from the lactose (La) is manifested in the A and F polyurethane membranes, according to Table 1. The optical activity (α) of Pall membrane permeate indicates the presence of the glucose and lactose : $\alpha(\text{G}) = +6,17$ and $\alpha(\text{La}) = +6,95$ while for the polyurethane membranes, the optical activity registers the absence of glucose in the permeate : ($\alpha(\text{G}) = +1,70$ for the A and $\alpha(\text{G}) = +1,55$ for the F membrane) and the presence of lactose, ($\alpha(\text{La}) = +6,55$ for the A and $\alpha(\text{La}) = 6,85$ for the F membrane) in the permeate.

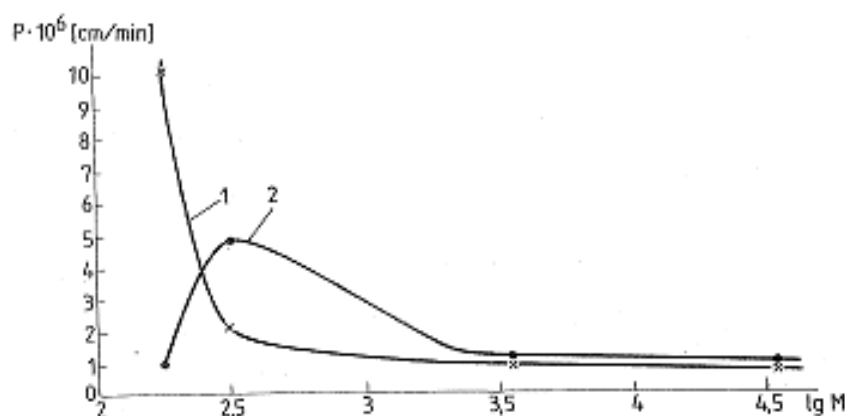


Figure 6. The variation of permeability of solvent (water), function of molecular weight of sugars; $P = f(\lg M)$; 1) the curve of permeability variation (m/min) for the distillate water in presence of sugars registered at the Pall import membrane; 2) the permeability variation curve (m/min) for the distillate water in the presence of sugars registered at the A polyurethane membrane.

The modification of the membranes structure causes changes in the transfer phenomena through it. Osmotic measurements gave information on the transfer of solvent (water), in the presence of saccharides of a certain molecular weight. The permeabilities of polyamide membranes and polyurethane membranes has been studied comparatively, using solutions of saccharides in water. Figure 6 presents the dependence of the membranes permeability to water as a function of the saccharides molecular weight for both type of membrane (import Pall and polyurethane A).

The permeation entropy, water permeability constant, the size of pores and the absorption of water in two hours, greater in the A membranes, expressed the selectivity at the separation of glucose from the lactose. The permeation process is generally spontaneous (ΔG negative) and exothermal (ΔH negative). At the level of monitored membrane process, the ΔS entropies registered by the A membranes are the greatest so that the membrane flux at a temperature degree mainly depends on the porous space permeated and by its hydrophilicity (Table 3).

Table 3. Experimental data regarding the separation of glucose from lactose through the membranes

Membr.	Abs.H ₂ O % in 2 h	ΔH cal/mol			ΔS cal/mol grad			ΔG.10 ³ cal/mol		
		G	La	Am	G	La	Am	G	La	Am
A	241	- 1,1	- 3,1	- 7,9	+10,7	+8,2	+8,7	- 3,2	- 2,5	- 2,6
F	212,9	- 5,3	- 7,5	-	+5,8	+6,6	-	- 1,7	- 2,0	-
Pall	127,1	- 7,3	- 4,6	- 4,0	+10,2	+6,9	+5,8	-3,0	-2,1	- 1,7

$\log P = \log P_0 - E_0/2,303 RT$; Arrhenius relation

$\log K = \Delta S/2,303 R - \Delta H/2,303 RT$; Van` t Hovh relation

$K = C_p/m_m$; permeation equilibrium constant

R : gas constant; T : Kelvin temperature

Dimension of molecules G = 8,23μm., La = 9,16μm; Am = 48,7 μm.

Conclusions

1. The conformational structure of the membranes (PU) and their asymmetry degree, influence the permselectivity of sugars.
2. The impact of indigenous membranes A, F and Pall import and their asymmetry degree suggest information about the membrane porous space: the geometrical form of the pores and channels.
3. The A and F polyurethane membranes present functional selectivity compared to the glucose and the lactose: they practically separate the glucose from the lactose.

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