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## **THE RELEVANCE OF CLASSICAL METHODS TO CHARACTERISE THE HYDROPHOBIC POROUS MEMBRANES USED IN THE PROCESS OF OSMOTIC EVAPORATION**

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1.

**Scientific topic:** II.1.d.

**Abstract:** In osmotic evaporation, the membrane is often considered passive as it provides a support for the vapor-liquid interfaces where evaporation and condensation take place. The mass transfers as well as the non wetting condition depend on the membrane structure, but the conventional characterisation methods do not always provide adequate information.

**Key words:** osmotic evaporation, macroporous hydrophobic membrane, porosimetry, contact angle, scanning electron microscopy.

## **INTRODUCTION**

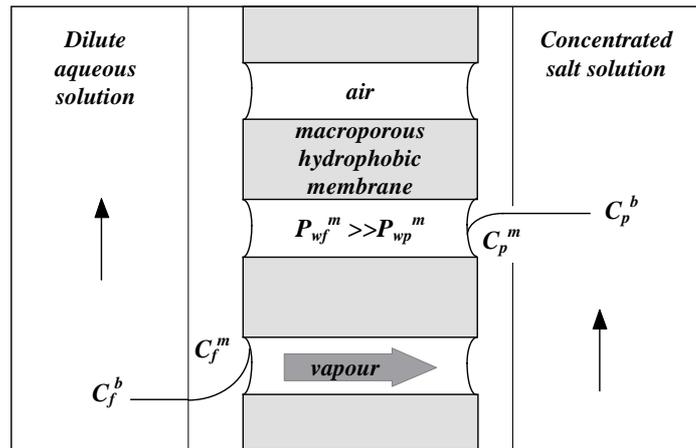
Osmotic evaporation (OE) is a recent membrane technique allowing concentrating fragile aqueous solutions at ambient temperature under atmospheric pressure [1]. Thanks to gentle operating conditions, OE offers main advantages in comparison with the conventional concentration techniques used in the food industry. The low temperature employed can help avoiding the chemical and enzymatic reactions associated with heat treatment. When compared to pressure driven membrane processes, the low operating pressure induces lower equipment costs, lower risks of fouling and lower needs regarding mechanical resistance of the membrane. Since the separation is based on vapour-liquid equilibrium, only volatile compounds can cross the membrane and the non volatile solutes like ions, sugars, macromolecules, cells and colloids are totally retained in the concentrate. These advantages make the process of OE an ideal candidate for fruit juice concentration [2].

This technique is also known as *osmotic distillation*, *isothermal membrane distillation* or *gas membrane extraction*. It is quite similar to membrane distillation (MD), already well known and widely studied, which driving force generally relies on a temperature difference between the processed solutions, instead of a water activity difference. In spite of the proximity of both techniques, OE is suffering a lack of interest from the point of view of industrial applications. Part of the problem might come from the membrane on which we will be focusing in this paper. Even if classical organic membranes are employed, the original utilisation which is made of them in the process would require more specific characterisation than what is conventionally made.

## **THEORETICAL BACKGROUND**

### **1. Principle of the process**

OE consists of evaporating water from an aqueous stream by means of a concentrated salt solution. The liquids are circulated along the 2 faces of a macro porous hydrophobic membrane. Because of its hydrophobicity the polymer cannot be wetted by the liquids; vapour-liquid interfaces are thus formed at each extremity of the pores that may contain air. The vapour pressure difference across the membrane, resulting from the solute concentration difference, causes vapour molecules to be transported from the dilute solution to a hypertonic salt solution (Figure 1). The main variables influencing mass transfer are : water activity of dilute solution and brine, membrane structure and hydrodynamic circulation conditions in the membrane module. The membranes used in OE are made of classical hydrophobic porous polymers designed for microfiltration applications like gas or solvent purification. The pore size ranges between 0.01 and 0.5  $\mu\text{m}$ . Typical polymers with low surface energy like polytetrafluoroethylene (PTFE), polypropylene (PP) or polyvinylidene fluoride (PVDF) have the appropriate hydrophobic properties to comply with non wettability of the porous barrier.



**Figure 1:** General principle of osmotic evaporation; solute concentration ( $C$ ), vapour pressure ( $P_w$ ), feed solution ( $f$ ), permeate ( $p$ ), bulk ( $b$ ), liquid-membrane interface ( $m$ ).

## 2. Mass transfer

The mass transfer can be decomposed into three steps : evaporation at the dilute solution-membrane interface, vapour transport through the pores of the polymer and condensation of the vapour at the membrane-brine interface. Diffusion is the main mechanism involved in the mass transfer during OE : the water needs to be transported from the bulk solution to the porous wall for evaporation, or vice-versa for condensation. The resistance to water transport due to concentration polarisation is usually modelled by the film theory. The water transport in vapour phase can be represented by a diffusion model where the molar flux of water vapour ( $N_w$ ) is related to the vapour pressure difference across the porous membrane by a simple equation (1).

$$N_w = K_m \cdot \Delta P_w \quad (1) \quad K_m \propto \frac{r^b \epsilon}{\chi \delta} \quad (2)$$

where  $K_m$  is the membrane permeability and  $\Delta P_w$  is the transmembrane vapour pressure drop. Taking into account the porous structure,  $K_m$  is expressed as a function (2) of pore radius ( $r$ ), membrane thickness ( $\delta$ ), volume porosity ( $\epsilon$ ) and pore tortuosity ( $\chi$ ). Exponent  $b$  can take a value of 0 or 1, according to the major diffusion mechanism involved in the vapour transport, i.e. molecular or Knudsen diffusion respectively.

As far as OE is concerned, diffusion is the only prevailing mechanism because of the absence of any imposed static pressure drop across the membrane. Knudsen diffusion is usually considered to be present when the pore radii are comparable to the mean molecular free path of the diffusing molecule. On the contrary, if the pore size is large enough, molecular diffusion will be the controlling mechanism. In the first case, the molar flux is proportional the square of the pore radius while it is independent of pore size for the second case.

### 3. The non wetting condition

A crucial prerequisite for the process is to maintain the integrity of the gas phase sustained by the porous polymer. If wetting occurs, the liquid can penetrate into the membrane and a liquid flux is added to the vapour flux, allowing the non volatile solutes to diffuse from one side to another. Such a situation would lead to the production of salty concentrates which is unacceptable to the food industry. The question of how to characterise the wettability of an OE or MD membrane is a very important one, although few fundamental studies can be found in the literature. The wetting condition depends on multiple variables like intrinsic characteristics of the porous material, operating pressure conditions and nature of the solutions processed.

#### 3.a. Hydrophobicity and contact angles

Contact angle measurement is a traditional method to describe the hydrophobicity of a dense material. The contact angle made by a liquid droplet deposited onto the surface of a smooth solid will have a value greater than 90° if there is low affinity between liquid and solid, and lower than 90° in case of affinity. Wetting occurs at 0°, when the liquid spreads onto the surface (Figure 2). The equilibrium at the triple point made by the solid-liquid-vapour interface is represented by Young's equation (3).

$$\gamma_{LV} \cos \theta = \gamma_{SV} - \gamma_{SL} \quad (3)$$

where  $\gamma$  is the interfacial tension for liquid-vapour (LV), solid-vapour (SV) or solid-liquid (SL), and  $\theta$  the contact angle.



**Figure 2:** Contact angle ( $\theta$ ) of a liquid droplet with the surface of a solid and thermodynamic equilibrium condition at the triple point  $C$ .

Relation (3) shows that  $\theta$  can be affected by the presence of organic compounds or surfactant molecules inducing a modification of  $\gamma_{LV}$  and  $\gamma_{SL}$  interfacial tensions. Because surface tensions involving a solid are not directly measurable, Young's equation does not give direct access to the hydrophobicity of the material, which is often characterised by the surface energy  $\gamma_{SV}$ . An equation of state was proposed to relate the various interfacial tensions, and combined with Young's equation to predict the surface energy of a dense polymer from surface tension and contact angle measurements (4) [3].

$$\cos \theta = -1 + 2\sqrt{\gamma_{SV}/\gamma_{LV}} \exp(-\beta(\gamma_{SV} - \gamma_{LV})^2) \quad (4)$$

where  $\beta$  is a parameter independent of the solid and solution used.

The contact angle theory was developed for dense solids with ideal smooth surfaces. However, relation (5) can help to predict the contact angle  $\theta^*$  of a rough and hairy surface, from the contact angle  $\theta$  of the equivalent smooth surface [4].

$$\cos\theta^* = f_1 \cos\theta - f_2 \quad (5)$$

where  $f_1$  and  $f_2$  are the fractions of the surface which are liquid-solid and liquid-air respectively. By assimilating the pores with a surface roughness, this equation has been used to try and predict the contact angles of MD membranes from the polymer characteristics ; but the validity was restricted to surface porosities lower than 50 %.

### *3.b. Wettability under pressure conditions*

Even if OE is run under atmospheric conditions, the circulating liquids exert a pressure on either side of the membrane, that can affect the contact angle and the wetting conditions. The pressure variable can be included in the wettability definition via the liquid entry pressure. It is usually represented by the Laplace equation (6), which gives an expression of the work of the pressure forces, required to wet the surface of a cylindrical pore.

$$\Delta P_{\text{ent}} = \frac{-2 B \gamma_{LV} \cos\theta}{r_{\text{max}}} \quad (6)$$

where  $\Delta P_{\text{ent}}$  is the liquid entry pressure,  $r_{\text{max}}$  is the maximum pore radius and B is a geometry factor being unity for cylindrical shape. This concept was used to assess the wettability of MD membranes under specific pressure conditions with aqueous solutions of varying composition and surface tension [4].

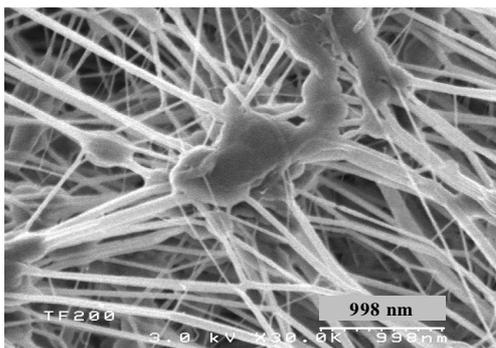
## **MATERIALS & METHODS**

Two commercial flat sheet membranes from Pall-Gelman Company were selected for their good performances in OE. The membranes TF200 and TF450 are made of a thin PTFE layer sealed on a PP supporting net.

The membrane structure was envisaged by means of two classical methods. First, Scanning Electron Microscopy (SEM) was used to observe the morphology of the pores, with a Hitachi S4500 apparatus which resolution is 1.5 to 4 nm at 15 kV and 1 kV respectively. Second, mean pore diameter, pore size distribution and volume porosity were obtained by mercury porosimetry. An apparatus Auto Pore II 9220 was used, allowing to measure diameters from 0.003 to 360  $\mu\text{m}$ . The pore size and its distribution are deducted from the measurement of the volume penetration of mercury under incremental pressure conditions. The principle of the method relies on Laplace equation (6) which supposes pores with cylindrical shape.

Hydrophobicity was analysed by contact angle measurements. Contact angles of pure liquids with the Teflon surface of the membrane are measured in air at ambient temperature with a Kruss equipment. A droplet of liquid with maximum contact radius of 3 mm is placed automatically on the surface of the sample, and the contact angles are calculated by means of a computerised image analyser. 4 to 8 measurements were performed per sample. The surface tension of the pure liquids were measured by the Whilelmy method.

## RESULTS



**Figure 3** : Teflon layer of the TF200 membrane observed by SEM (x 3000)

The pictures obtained from SEM did not show any smooth layer with evenly distributed cylindrical pores, but rather an interlacing of PTFE fibres that did not allow any computerised image analysis to determine pore size and surface porosity (Figure 3). However, the thickness ( $\delta$ ) of the Teflon layer and of the polymer support could be measured (table I).

The volume porosity ( $\epsilon$ ) specified by Pall-Gelman seems to be an average value between Teflon and polymer support that were separated manually for measurement by porosimetry (table I). The diameter ( $d$ ) corresponds to the specific area of the PTFE network in contact with mercury, which is translated into virtual equivalent cylindrical pores. The distribution of the diameters is large and the mean value for all samples is around 0.07 to 0.09  $\mu\text{m}$ , which is significantly different from the manufacturer's specifications of 0.20 to 0.45  $\mu\text{m}$ .

**Table 1** : Comparison of the structural characteristics of two membranes as given by the manufacturer and obtained from experimental measurements.

Membrane characteristics		TF200	TF450	PTFE
$\delta$ ( $\mu\text{m}$ )	MS	165	178	-
	SEM	102 - 165	110 - 178	30 - 70
$\epsilon$ (%)	MS	60	60	-
	MP	67	58	79
$d$ ( $\mu\text{m}$ )	MS	0.20	0.45	-
	MP	$d_{\text{mean}}$ 0.07	0.07	0.09
	Interval	0.01-1.10	0.01-1.10	0.01-1.10

MS : manufacturer specification, SEM : Scanning Electronic Microscopy, MP : mercury porosimetry

The surface tensions of the liquids and the contact angles measured on TF200 and TF450 membranes are reported in table II. The measured values were compared to the contact angles of the dense polymer calculated from equation (4), using a surface energy  $\gamma_{\text{SV}}$  of 19  $\text{mN}\cdot\text{m}^{-1}$  typical of Teflon, and  $\beta = 12.47\cdot 10^{-5} (\text{mN}\cdot\text{m}^{-1})^2$ . Equation (4)

was adjusted to the experimental results to try and extrapolate by a trial and error method, the surface energy obtained for  $\theta = 0$  corresponding to wetting.

The apparent surface energy so obtained, corresponds to critical surface tensions  $\gamma_{SV}^a$  of 1.9 and 3.5 mN.m<sup>-1</sup> respectively for TF200 and TF450 (Figure 4). These values mean that a liquid, which  $\gamma_{LV}$  is higher than the critical value, should not wet the membrane. If it were the case, the contact angles with the three last liquids of table II should not be 0, which is not true. The critical zone where wetting occurs for both membranes is located somewhere between 31.7 and 35.4 mN.m<sup>-1</sup> (Figure 4). The irregular porous surface of the polymer makes equation (4) no relevant relation to predict surface energy or hydrophobicity of OE membranes.

**Table II** : Contact angles of TF200 and TF450 membranes measured with pure liquids of various surface tension  $\gamma_{LV}$ .

Liquid	Surface tension $\gamma_{LV}$ (mN.m <sup>-1</sup> )	Contact angle $\theta$ (°)		
		TF200	TF450	PTFE
Water	72.5	151.1	147.9	106.5
Glycerol	65.0	152.5	147.7	99.8
Formamide	57.5	142.8	131.1	92.5
Diodomethane	50.5	129.8	120.0	85.2
Ethylene glycol	48.0	142.8	133.6	82.4
1-bromonaphtalene	44.0	123.5	114.8	77.5
Dimethylformamide	35.4	125.5	115.3	65.4
Cis-decalin	31.7	0.0	0.0	58.7
Butoxyethanol	27.0	0.0	0.0	48.4
Decane	25.4	0.0	0.0	43.7

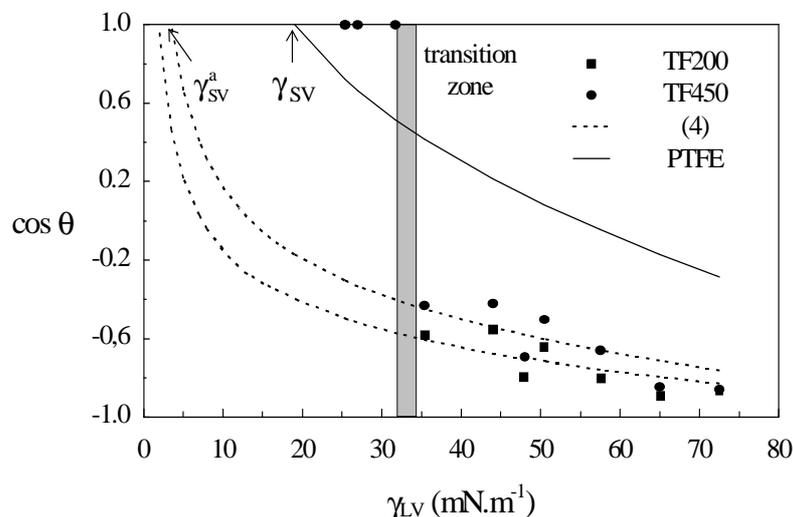
Equation (5) is obtained by applying Young's equation to a porous surface with apparent interfacial tensions  $\gamma_{SV}^a$  and  $\gamma_{SL}^a$ , and by decomposing them into different terms that involve interfacial tensions of the solid and air fractions of the membrane surface. It is possible to establish an improved relation (7), based on a more complex decomposition issued from an analogy with modern theories on liquid binary mixtures.

$$\cos\theta^* = y^2 \cos\theta - (1 - y^2) - 2y(1 - y)\sqrt{Y - \cos\theta} \quad \text{with} \quad Y = \frac{\gamma_{SL}}{\gamma_{LV}} \quad (7)$$

where  $y$  is the surface porosity. Equations (5) and (7) can be adjusted to the experimental results with more or less precision. However, it clearly demonstrates the dependence of the contact angles of a porous surface on the contact angles of the dense constituting polymer. Nevertheless, such relations only apply for high values of  $\theta$  as they implicitly exclude the critical zone where wetting occurs.

## DISCUSSION

The results obtained from SEM observations and porosimetry measurements indicate structural characteristics that are quite different from what is specified by the manufacturer. The thickness as well as the volume porosity are specified for the whole



**Figure 4 :** Contact angles ( $\theta$ ) of TF200, TF450 membranes and dense PTFE as a function of the surface tension of pure liquids ( $\gamma_{LV}$ ) and adjusted by equation (4).

composite material whereas the Teflon layer is probably the only part of the membrane participating to the mass transfer in vapour phase [5]. The specified pore size obviously refers to a filtration utilisation of the membrane where mass transfer is caused by a static pressure drop. Such a definition does not look satisfactory to apply to gas diffusion in OE. Finally, the application to porous PTFE membranes, of the capillary model assuming cylindrical pore shapes leads to the question of how to define a pore radius for such structures. The estimation of the surface energy of porous membranes is quite complex and is not supported by any recent theory. The wetting conditions of such materials can be better defined by a critical surface tension combined with operating pressure conditions, rather than by contact angle measurements. All this clearly underlines the need for a basic physical description of the membrane, that correctly accounts for the function of this element in the considered process, before any sensible characterisation work.

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