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Mechanism of formation of hollow fiber membranes for membrane distillation: 1. Inner coagulation power effect on morphological characteristics

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ABSTRACT

Hollow fiber membrane morphology and inner surface structure were analyzed based on the thermodynamic and kinetics of the phase inversion process. Different nonsolvent mixtures formed by *N,N*-dimethyl acetamide (DMAC) and distilled water were considered. By means of Hansen solubility parameters, lower interaction between the nonsolvent and the mixed solvent (DMAC/trimethyl phosphate, TMP) was observed when greater amount of DMAC was added in the nonsolvent. The spinning solution became thermodynamically more stable and kinetically showed slower coagulation rates, being both related to the resultant membrane formation. In this first study poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP) hollow fiber membranes were prepared by the dry/wet spinning technique employing the above cited nonsolvent mixtures as an internal coagulant. Their effect on the internal structure of the membrane evolved towards a more open-porous inner surface when increasing the solvent content in the bore liquid. Various characterization techniques were used in order to analyze the adequacy of these membranes for desalination by direct contact membrane distillation (DCMD). It was found that all the properties together with the permeability of the hollow fibers improved when the coagulation power of the nonsolvent was reduced.

1. Introduction

Membrane distillation (MD) is a non-isothermal process applied mainly to remove non-volatile solutes such as salts from water. Its driving force is the transmembrane water vapor pressure and the most commonly used MD configuration is direct contact membrane distillation (DCMD) [1]. However, one of the main drawbacks of this process is the unavailability of commercial membranes that meet all the MD requirements [2]. Therefore, the design of MD membranes is nowadays an attractive research topic [3–5], despite the great difficulty associated with understanding the mechanism of membrane formation [6]. Some of the main requirements of an adequate MD membrane are the high hydrophobicity, low thermal conductivity and high porosity [1–3].

Cui et al. [7] reported different hydrophobic fluoropolymers and copolymers that can be employed as suitable materials for MD membranes preparation, such as the well known and commonly used polyvinylidene fluoride (PVDF) [8,9]. Fluoropolymers exhibit excellent properties as materials for a membrane for MD including thermal and chemical resistances [7]. The copolymer poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP) stands out for its excellent hydrophobic character due to the hexafluoropropylene (HFP) group embedment, as confirmed by several researchers [10,11]. Not only does the HFP incorporation improve the hydrophobic character of PVDF due to its fluorine content, but also the crystalline character of vinylidene fluoride (VDF) enhances the mechanical properties of the formed material [7]. Therefore, PVDF-HFP is an advisable copolymer to consider for the preparation of MD membranes as confirmed elsewhere [12–14]. The polymeric matrix selection is also important in terms of thermal conductivity. Nevertheless, there is not much difference between the thermal conductivity coefficients of the majority of the available hydrophobic polymers. That is why the heat transfer by conduction through the membrane must be reduced by enhancing the void volume fraction (i.e. porosity) [2]. High porosity always induces high MD permeability, as it has been confirmed in several studies [1,2,13]. Trying to pursue this objective, it is advised by several membranologists to introduce in the dope solution pore former additives such as polyvinylpyrrolidone (PVP), lithium chloride (LiCl), glycerol, polyethylene glycol (PEG), etc. [12,15].

Besides the aforementioned MD membrane main properties, a proper morphology also plays a key role on membrane performance.

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It would be enhanced if macro-void free structure, skinless and open-porous surfaces conform the membrane morphology [8,9,16]. First, in order to obtain the desired structure, it is necessary to analyze the membrane formation process via the thermodynamic and kinetics of the phase inversion, and to understand the consequence of the variation of each fabrication parameter [6,17–20]. This is even more complicated for hollow fiber membrane preparation, because dry/wet spinning technique involves many fabrication parameters, which directly affect membrane morphology. One of the advantages of using MD hollow fiber membranes is the high packing density that can be easily achieved in tubular membrane modules [1–3].

Several hollow fiber preparation parameters such as spinning dope composition, spinneret dimensions, extrusion pressure, air gap distance, temperatures of the dope and coagulants solutions, coagulants flow rate and composition, take-up speed, etc., can modify the membrane structure [1,21–23]. Although it has been already studied the effect of solvent/water mixture as nonsolvent on the membrane characteristics [24,25], no study is found when the coagulant interacts with a mixed solvent instead of a single solvent for preparing PVDF-HFP hollow fiber membranes. The solvents mixture is formed by two solvents, one is the same main solvent of the nonsolvent aqueous mixtures, and therefore different interaction forces compete between each other simultaneously. The nonsolvent-solvent exchange type during the phase inversion strongly affects hollow fiber membrane morphology and properties as well as membrane performance by MD process. In the first part of this study the solvent-nonsolvent interaction effect on the PVDF-HFP hollow fiber membrane formation mechanism and consequently on its structural cross-section and inner surface morphology have been deeply and exhaustively investigated.

2. Experimental

2.1. Materials

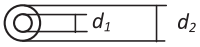
The copolymer poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP; M_w=455,000 g/mol), the solvents *N,N*-dimethyl acetamide (DMAC) and trimethyl phosphate (TMP) and the additive poly(ethylene glycol) (PEG; M_w=6000 g/mol) were used to prepare the spinning solution and were all purchased from Sigma-Aldrich. Isopropyl alcohol (IPA, Sigma-Aldrich) and POREFIL® (Porometer) were employed as wetting liquids for the measurements of the void volume fraction and porometry, respectively. Sodium chloride (NaCl) was employed to prepare the salt aqueous feed solutions for DMCD experiments and it was purchased from Panreac.

2.2. Preparation of hollow fiber membranes

The dry/wet spinning was the fabrication technique employed to prepare all the hollow fiber membranes in this study as it was described elsewhere [26,27]. First, a unique spinning solution was prepared as follows. 5 wt% of the additive (PEG) was first dissolved in 76 wt% of the solvents mixture at 42 °C and 100 rpm using a magnetic stirrer (IKA, RCT basic), and after getting an homogenous mixture, 19 wt% of PVDF-HFP was added to this mixture. Then, the whole solution was introduced in a thermal bath (Stuart SBS40) maintained at 42 °C under an orbital shaker until the whole copolymer was totally dissolved. The solvents mixture used to prepare this spinning solution was 40 wt% DMAC and 60 wt% TMP. This mixture was chosen based on the conclusions drawn in our previous study [17].

Table 1 summarizes the spinning parameters, which were maintained the same except the type of the internal coagulant. After spinning, in order to remove the residual solvents, the fabricated hollow fiber membranes were stored in water bath at room temperature for 48 h. Subsequently, the hollow fiber membranes were dried at room temperature before characterization tests. Several mixtures of DMAC and distilled water were used as internal coagulant, employing the following ratios: 0, 20, 40, 50 and 60 wt% of DMAC. The corresponding fabricated hollow fiber membranes are termed here after 1IND0, 1IND20, 1IND40, 1IND50 and 1IND60, respectively.

Table 1
Spinning parameters of PVDF-HFP hollow fiber membranes.

Parameters	Operating conditions
Spinneret: 	d_1=1.0 mm/d_2=2.4 mm
Extrusion pressure (kPa)	60
Polymeric solution temperature (°C)	42
Internal coagulant	DMAC/distilled water
Internal coagulation temperature (°C)	42
Internal coagulant flow rate (m^3/s)	2.7×10^{-7}
Air gap distance (m)	0.275
Liquid coagulation bath	Tap water
Liquid coagulation bath temperature (°C)	42

2.3. Spinning solution characterization prior to membrane fabrication

2.3.1. Physical properties: surface tension, viscosity and Hansen solubility parameters

The surface tension of the spinning solution was measured at room temperature by the pendant drop shape analysis. An optical contact angle meter (CAM 200) and a stainless steel needle with an outer diameter of 1.832 mm were employed to carry out the measurement, keeping constant the drop volume at 12.4 μl for all the samples.

The viscosity of the spinning solution was determined by a Digital Viscometer (Brookfield, Model DV-I+) using the SC4-31 spindle at 4 rpm and a cylindrical sample container. The temperature of the spinning solution was maintained constant at 42 °C (i.e. the same temperature considered to prepare the hollow fiber membrane) by a thermostat (Techne, Model TU-16D).

Copolymer/solvent/nonsolvent interactions were analyzed via Hansen solubility parameter (*HSP*) distance (R_{HSP}), as it was explained in detail by Hansen [28] and described elsewhere [17]. This parameter informs about the relative affinity between the PVDF-HFP and the solvent, represented by R_{HSP} (P-S); and between nonsolvent (DMAC/water coagulant mixtures) and the mixed solvent, represented by R_{HSP} (NS-S_m). These R_{HSP} values were calculated from the following equations:

$$R_{HSP}(P-S)=\sqrt{4(\delta_{dP}-\delta_{dS})^2+\left(\delta_{pP}-\delta_{pS}\right)^2+(\delta_{hP}-\delta_{hS})^2} \quad (1)$$

$$R_{HSP}(NS-S_m)=\sqrt{4\left(\delta_{d_{NS}}-\delta_{d_{S_m}}\right)^2+\left(\delta_{p_{NS}}-\delta_{p_{S_m}}\right)^2+\left(\delta_{h_{NS}}-\delta_{h_{S_m}}\right)^2} \quad (2)$$

Before R_{HSP} calculation, it is necessary to know the *HSP* components, which includes the polar component (δ_p), the dispersion force component (δ_d), and the hydrogen bonding component (δ_h) [28]. In Table 2, the *HSP* components of all the pure substances are listed [10,28,29], as well as the obtained values of both solvent mixture (S_m) and nonsolvent mixtures (NS), which were calculated from the following Eqs. (3) and (4), respectively [17,30]:

$$\left[\delta_{d_{S_m}}, \delta_{p_{S_m}}, \delta_{h_{S_m}}\right]=[a\delta_{d1}+b\delta_{d2}+c\delta_{d3}, a\delta_{p1}+b\delta_{p2}+c\delta_{p3}, a\delta_{h1}+b\delta_{h2}+c\delta_{h3}]/(a+b+c) \quad (3)$$

where the subscripts 1, 2 and 3 are for each compound present in the solvent mixture (i.e. DMAC, TMP and PEG) and *a, b* and *c* are the volume fraction of the different compounds in the solvent mixture.