Optimization of flat sheet hydrophobic membranes synthesis via supercritical CO$_2$ induced phase inversion for direct contact membrane distillation by using response surface methodology (RSM)

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**Abstract**

Flat-sheet hydrophobic polyvinylidene fluoride (PVDF) membrane was prepared by supercritical fluid induced phase inversion technique. The effects of initial polymer concentration, pressure, and temperature of supercritical fluid on the final membrane structures and surface hydrophobicity were investigated. The morphologies and hydrophobicities of PVDF micro porous membranes were analyzed by means of scanning electron microscopy (SEM) and contact angle (CA) measurement, respectively. The ternary theory phase diagram will evaluate the thermodynamic aspects of the membrane precipitation process for difference ScCO$_2$ pressure and temperature. This phase diagram was constructed by theoretical calculation, based on Flory-Huggins solution theory. Response surface methodology (RSM) was used to optimize the characteristics of membrane structural by setting the parameters of membrane synthesis process (temperature, pressure and polymer concentration) to be used in direct contact membrane distillation (DCMD). Analysis of variance shows significant effects of each variable on the responses. The membrane is optimized under the following conditions: 14.76 wt.% PVDF concentration, 35 °C temperature and pressure of 10 MPa. The fabricated optimum membrane, compared to membrane prepared by conventional wet phase inversion method exhibited a better permeate flux.

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1. Introduction

In recent years, the hydrophobic porous membrane has largely been applied in membrane distillation (MD). MD is a non-isothermal separation process, based on the transmission of volatile compound especially water in vapor phase through a micro porous hydrophobic membrane from the hot side toward the cold side. Direct contact membrane distillation (DCMD) is a type of MD configuration in which the hot solution (feed) and cooled permeate are in direct contact with both sides of the membrane. MD is generally used for desalination, removal of trace, volatile organic compounds from waste water and concentration of ionic, colloidal, or other relatively non-volatile aqueous solutions. Also, MD can be used for liquid low-level radioactive waste treatment [1,2]. In the MD process, pores of the membrane should not be wetted by the aqueous solutions. Thus, the used membrane should be hydrophobic [3].

The morphology of the membranes used in the MD process, has a strong effect on the MD process performance. To obtain a high permeability, the surface layer which controlling the membrane mass transport must be as thin as possible. Moreover, the membrane surface porosity must be large as possible and a high porosity in the cross section. The optimum range for average pore size in surface membrane is 0.01 μm to 1 μm for MD application [4]. In addition, membranes must have good thermal stability and excellent chemical resistance to feed the streams. Polyvinylidene fluoride (PVDF) has received great attention as a membrane material, having excellent properties such as high hydrophobicity, high thermal stability, chemical resistance and mechanical strength in comparison to other commercialized polymeric materials [5].

Phase inversion is a method widely used to prepare micro porous polymer membrane. Phase inversion it pertaining to the process in which a homogenous solution of a polymer and solvent is immersed into the non-solvent bath, inverting a single phase to a two-phase system in total equilibrium with each other. Water is frequently used as non-solvent, a technique called wet phase inversion [6,7]. Recently, an alternative technique has been proposed
that uses supercritical CO$_2$ (ScCO$_2$) as the non-solvent to induce phase inversion [8–24]. In the phase inversion compared to other non-solvents, ScCO$_2$ has liquid-like density and gas-like diffusivity; hence it removes the solvent from the membranes in a short time almost completely without any additional post-treatment. Other advantages of this technique over the wet phase inversion method is that by changing operation parameters such as polymer concentration, ScCO$_2$ pressure and temperature the membrane morphology can be adjusted effectively tailored to our needs. Also, CO$_2$ is not toxic or flammable and it is cheap [11,19,22].

The membrane precipitation is persuaded by mechanisms of liquid–liquid de-mixing and/or crystallization [25]. In fact, for membranes synthesized from semi-crystalline polymers such as PVDF, the structure of the membrane was impressed by a sequence of these phase inversion mechanisms [6].

Depending on operating conditions such as the temperature and pressure of carbon dioxide as well as polymer concentration, the rate of these mechanisms may change in comparison to one another. When liquid–liquid de-mixing dominates the precipitation process, the nascent membrane usually comprises a dense skin and a porous bulk packed with cellular pores or macrovoids. In contrast, when crystallization dominates the precipitation process, a porous membrane packed by embellishments of interlinked crystallites is produced. In intermediate cases, the membranes displayed mixed morphologies, characterized both by crystalline particles and cellular pores [26,27]. In liquid–liquid de-mixing mechanism, the two-phase system consists of a solid phase (polymer-rich phase) that forming the matrix membrane as well as a liquid phase (polymer–poor phase) which forming the pores in the final membrane [28].

The phase diagram is a convenient tool to study the thermodynamic aspects and mechanism of the membrane formation process. The phase diagram of a non-solvent/solvent/polymer system can be constructed by theoretical calculations based on Flory–Huggins theory [29]. The Flory–Huggins theory for polymer solutions was extended to a three-component system and was widely used to describe the ternary phase diagram of the membrane casting system (i.e., polymer/solvent/non-solvent) [30]. The ternary phase diagrams of water/DMF/PVDF and 1-octanol/DMF/PVDF systems have been studied by some researchers. This diagram for semi-crystalline is included in binodal and crystallization curves [31,32].

Flory–Huggins theory involves a series of parameters namely the data of non-solvent/solvent, solvent/polymer and non-solvent/polymer interaction parameters which must be determined to compute the phase diagram. By changing the operating conditions such as the temperature, the ScCO$_2$ pressure and polymer concentration, the membrane morphology was controlled in turn improving the surface hydrophobicity. Response surface methodology (RSM) is a statistical technique used to evaluate the effect of multiple factors on one or more response variables [33]. The hydrophobic property of PVDF membrane can be enhanced with roughness and porous surface. The top surface of the sponge-like porous PVDF membrane showed greatly enhanced hydrophobicity [34].

The present study discusses the effect of operating conditions such as temperature and ScCO$_2$ pressure on the membrane morphology by using phase diagrams and it has been attempted to present the correspondence between theoretical phase diagrams and the morphology of the formatted membranes.

The objective of the research was to appropriate the adjustment of the quantity of ScCO$_2$ temperature and pressure along with the concentration of polymer to optimize the micro porous membrane. The membranes prepared in this study were characterized by their hydrophobicity, surface average pore size and porosity. The Box–Behnken design of the experiments present a mathematical correlation between the temperature and pressure of ScCO$_2$ as well as polymer concentration to obtain maximum porosity and surface hydrophobicity by setting the surface average pore diameter between 0.1 and 1 μm for usage in MD [35]. In order to measure the permeate flux and separation factor of fabricated optimum flat sheet hydrophobic PVDF membrane, it was tested in DCMD.

2. Experimental

2.1. Materials

PVDF (Mw 530000, Aldrich Chemical Company, Inc.) was obtained in pellet form. Dimethylformamide (DMF, Aldrich, HPLC grade) was used as the solvent. Carbon dioxide with the purity of 99.99% was purchased from Farafan Gas Company, Iran.

2.2. Membrane preparation

To prepare the casting solutions, an appropriate amount of PVDF pellets was dissolved in DMF. The components were capped and magnetically stirred at 60 °C until the polymer solution became homogeneous. In order to remove the air bubbles, the polymer solution was to be placed under the vacuum for 12 h at ambient temperature. A thin film was cast onto a glass microscope slide using a doctor blade with a 250 μm gap. Fig. 1 schematically shows the experimental setup for the formation of PVDF membrane by ScCO$_2$ phase inversion. Initially, the casting solution was put inside the vessel with internal volume of 200 ml which got closed quickly. The inlet valve was opened and the vessel was filled with CO$_2$ up to the desired pressure using a high pressure pump (OPET CO Model TB 160-65–2/hv). This pressure inside the vessel was fixed for 45 min by pumping and afterwards the vessel’s outlet valve got opened to dry the phase-separated membrane at the constant pressure and temperature with a CO$_2$ flow rate of 1.5 kg/h for 45 min. Then, the vessel was slowly depressurized for another 45 min.

2.3. Membrane characterization

Structures of the membranes in the surface and cross-section were observed with a scanning electron microscopy (SEM, Seron Technology–AlS2100). The mean pore diameters at the top surfaces of the samples were analyzed by image j software. Contact angles were measured using an OCA40 Micro Tensiometer (Data Physics Corp., Germany) to evaluate membrane hydrophobicity. The volume of the water droplet used in the measurement was 5 μL. The value of contact angle is greater than 90° the material is considered hydrophobic.

The porosity (ε) can be determined by Eq. (1).

$$\varepsilon = 1 - \frac{\rho_m}{\rho_{pol}}$$

where $\rho_m$ and $\rho_{pol}$ are the densities of membrane and polymer material ($\rho_{pol} = 1.78$ g/cm$^3$), respectively. The density of the PEI membrane was obtained by measuring its volume and weight.

2.4. Experimental design and optimization by RSM

Response surface methodology (RSM) which is based on factorial design is a mathematical and statistical technique to design experiments, fitting the models and determining the optimal operating conditions in the target response.

RSM uses an experimental design such as the Box–Behnken design to evaluate the relationship between experimental outputs (or responses) and factors, called $X_1, X_2, X_3$, etc. Adopting Box–Behnken designs can sharply reduce the number of experimental sets without ever decreasing the accuracy of the optimization, in contrast to
traditional factorial design methods [36]. In this research, the influence of these factors, i.e., pressure ($P$), temperature ($T$) and polymer concentration ($C$) was studied. Table 1 demonstrates the minimum and maximum rates of the abovementioned three factors in terms of coded and un-coded symbols.

The relation between the coded and actual values is described as follows:

$$x_i = \frac{X_i - X_0}{\Delta X_i}$$

where $x_i$ and $X_i$ are the coded and actual values of the independent variable, respectively. $X_0$ is the actual value of the independent variable at the center point and $\Delta X_i$ is the step change of $X_i$. The behavior of the system was expressed by the following second-degree polynomial equation:

$$Y = \beta_0 + \sum_{i=1}^{4} \beta_i x_i + \sum_{i=1}^{4} \sum_{j=1, j\neq i}^{4} \beta_{ij} x_i x_j$$

where $Y$ is the predicted response; $\beta_0$ is a constant, $\beta_i$ are model coefficients linked to linear effects, $\beta_{ij}$ are coefficients related to quadratic effects and $\beta_{ij}$ are interaction terms [37].

The Design Expert Software (version 9, Stat-Ease Inc., Minneapolis, USA) was used for model regression, plotted figures and optimization. The analysis of variance (ANOVA) technique was used to check the statistically significant factors and interactions using probability $P$-value. The determination coefficients, $R^2$ and their adjusted value, $R^2_{adj}$ were used to evaluate the adequacy of fit of the regression models [37].

2.5. Direct contact membrane distillation

The experimental apparatus of DCMD used in our study was similar to that described by Shirazi et al. [38]. The fabricated optimum membrane have been tested in DCMD, in which salt aqueous solution (0.1 M) was used as feed solution with distilled water being the permeate side. The operation area of membrane was $4.9 \times 10^{-4}$ m². Concentration of the feed and permeate was determined with a multiparameter meter 900. The salt rejection coefficient, $q$ was determined as follows:

$$q = \frac{C_f - C_p}{C_f}$$

where $C_f$ and $C_p$ denote the sodium chloride concentration of feed solution and permeate, respectively.

3. Theory

3.1. Thermodynamics of a non-solvent/solvent/polymer system

Flory–Huggins theory was used to describe the phase behavior for ternary polymer solutions. The conditions to liquid–liquid equilibrium (i.e., binodal) are:

$$\Delta \mu_{i,a} = \Delta \mu_{i,b} \quad i = 1, 2, 3$$

Subscripts 1, 2 and 3 refer to non-solvent, solvent and polymer; a and b denote polymer-rich and polymer-lean phases, respectively. $\Delta \mu_i$ represents the difference between the chemical potentials of component $i$ in the mixture and in the pure state. $\Delta \mu_i$ derived from the Gibbs free energy ($\Delta G_m$) of the mixing of the membrane casting system [39–41]:

$$\frac{\Delta \mu_i}{RT} = \ln \vartheta_1 + 1 - \vartheta_1 - \frac{V_1}{V_2} \vartheta_2 - \vartheta_1 - \frac{\vartheta_1}{\vartheta_2} \vartheta_3 + \frac{\vartheta_1}{\vartheta_2} \vartheta_3 (\vartheta_2 + \vartheta_3)
- \frac{V_1}{V_2} \vartheta_1 \vartheta_2 \vartheta_3 \vartheta_4 + \frac{V_1}{V_2} \vartheta_1 \vartheta_2 \vartheta_3 \vartheta_4 (\vartheta_1 + \vartheta_2 + \vartheta_3 + \vartheta_4)
- \frac{V_1}{V_2} \vartheta_1 \vartheta_2 \vartheta_3 \vartheta_4 (\vartheta_1 + \vartheta_2 + \vartheta_3 + \vartheta_4)
- \frac{V_1}{V_2} \vartheta_1 \vartheta_2 \vartheta_3 \vartheta_4 (\vartheta_1 + \vartheta_2 + \vartheta_3 + \vartheta_4)
- \frac{V_1}{V_2} \vartheta_1 \vartheta_2 \vartheta_3 \vartheta_4 (\vartheta_1 + \vartheta_2 + \vartheta_3 + \vartheta_4)
- \frac{V_1}{V_2} \vartheta_1 \vartheta_2 \vartheta_3 \vartheta_4 (\vartheta_1 + \vartheta_2 + \vartheta_3 + \vartheta_4)
- \frac{V_1}{V_2} \vartheta_1 \vartheta_2 \vartheta_3 \vartheta_4 (\vartheta_1 + \vartheta_2 + \vartheta_3 + \vartheta_4)
- \frac{V_1}{V_2} \vartheta_1 \vartheta_2 \vartheta_3 \vartheta_4 (\vartheta_1 + \vartheta_2 + \vartheta_3 + \vartheta_4)
- \frac{V_1}{V_2} \vartheta_1 \vartheta_2 \vartheta_3 \vartheta_4 (\vartheta_1 + \vartheta_2 + \vartheta_3 + \vartheta_4)
- \frac{V_1}{V_2} \vartheta_1 \vartheta_2 \vartheta_3 \vartheta_4 (\vartheta_1 + \vartheta_2 + \vartheta_3 + \vartheta_4)
- \frac{V_1}{V_2} \vartheta_1 \vartheta_2 \vartheta_3 \vartheta_4 (\vartheta_1 + \vartheta_2 + \vartheta_3 + \vartheta_4)
- \frac{V_1}{V_2} \vartheta_1 \vartheta_2 \vartheta_3 \vartheta_4 (\vartheta_1 + \vartheta_2 + \vartheta_3 + \vartheta_4)
- \frac{V_1}{V_2} \vartheta_1 \vartheta_2 \vartheta_3 \vartheta_4 (\vartheta_1 + \vartheta_2 + \vartheta_3 + \vartheta_4)
- \frac{V_1}{V_2} \vartheta_1 \vartheta_2 \vartheta_3 \vartheta_4 (\vartheta_1 + \vartheta_2 + \vartheta_3 + \vartheta_4)
- \frac{V_1}{V_2} \vartheta_1 \vartheta_2 \vartheta_3 \vartheta_4 (\vartheta_1 + \vartheta_2 + \vartheta_3 + \vartheta_4)
- \frac{V_1}{V_2} \vartheta_1 \vartheta_2 \vartheta_3 \vartheta_4 (\vartheta_1 + \vartheta_2 + \vartheta_3 + \vartheta_4)
- \frac{V_1}{V_2} \vartheta_1 \vartheta_2 \vartheta_3 \vartheta_4 (\vartheta_1 + \vartheta_2 + \vartheta_3 + \vartheta_4)
- \frac{V_1}{V_2} \vartheta_1 \vartheta_2 \vartheta_3 \vartheta_4 (\vartheta_1 + \vartheta_2 + \vartheta_3 + \vartheta_4)
- \frac{V_1}{V_2} \vartheta_1 \vartheta_2 \vartheta_3 \vartheta_4 (\vartheta_1 + \vartheta_2 + \vartheta_3 + \vartheta_4)
- \frac{V_1}{V_2} \vartheta_1 \vartheta_2 \vartheta_3 \vartheta_4 (\vartheta_1 + \vartheta_2 + \vartheta_3 + \vartheta_4)$

The table provides minimum and maximum levels of three factors considered for Box–Behnken design.

<table>
<thead>
<tr>
<th>Variable</th>
<th>Symbols</th>
<th>Coded and actual levels</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pressure (MPa)</td>
<td>$X_1$</td>
<td>10 15 20</td>
</tr>
<tr>
<td>Temperature (°C)</td>
<td>$X_2$</td>
<td>35 45 55</td>
</tr>
<tr>
<td>Polymer concentration (wt%)</td>
<td>$X_3$</td>
<td>10 15 20</td>
</tr>
</tbody>
</table>
Also, for each phase:

\[ \phi_1^a + \phi_2^a + \phi_3^a = 1 \]  \hspace{1cm} (9)

\[ \phi_1^b + \phi_2^b + \phi_3^b = 1 \]  \hspace{1cm} (10)

where \( V_i \) is the molar volume, \( \phi_i \) is the volume fraction of component \( i \) and the quantities \( u_1 \) and \( u_2 \) are given by \( u_1 = \frac{\rho_1}{\rho_{12}} \) and \( u_2 = \frac{\rho_2}{\rho_{23}} \). Eqs. (5)-(10) were solved to obtain the binodal curve of the \( \text{ScCO}_2/\text{DMF}/\text{PVDF} \), which depict the compositions of the binodal curve.

At the crystallization equilibrium, Chuang et al. [40] derived the modified Flory–Huggins expression for the chemical potential between the liquid phase and the polymer crystal in a ternary system:

\[
\frac{1}{RT} \left[ \Delta H_f \left( 1 - \frac{T}{T_m} \right) + \frac{V_u}{V_s} \ln \phi_3 + \frac{V_u}{V_s} (1 - \phi_3) - \frac{V_u}{V_1} \phi_1 - \frac{V_u}{V_2} \phi_2 \right.
+ \left( \frac{V_u}{V_1} \phi_1 \phi_3 + \frac{V_u}{V_2} \phi_2 \phi_3 \right) \times (\phi_1 + \phi_2) - \frac{V_u}{V_1} \phi_1 \phi_2 \phi_3 
- \frac{V_u}{V_2} \phi_1 \phi_2 \phi_3 dz + \frac{V_u}{V_1} \phi_1 \phi_2 \phi_3 dz \Biggr] \times \phi_3 (\phi_1 + \phi_2) = 0
\]  \hspace{1cm} (11)

where \( V_u, T_m \) is the volume per mole repeating unit, melting temperature of polymer, respectively. The heat of fusion of polymer \( \Delta H_f \) at 25 °C was determined by differential scanning calorimetry (DSC). For the polymer employed in this study, values of \( \Delta H_f \) and \( T_m \) are reported in literature [42].

To obtain the equilibrium binodal curve, three binary interaction parameters \( g_{12} \) (non-solvent/solvent), \( g_{23} \) (solvent/polymer) and \( g_{13} \) (non-solvent/polymer) need to be known. Usually \( g_{12}, g_{23} \) were considered as concentration dependent but \( g_{13} \) concentration-independent [29]. \( g_{12} \) was calculated by using excess Gibbs free energy [41]:

\[ g_{12} = \frac{1}{x_1 x_2} \left[ x_1 \ln \left( \frac{x_1}{\phi_1} \right) + x_2 \ln \left( \frac{x_2}{\phi_2} \right) + \frac{\Delta G^e}{RT} \right] \]  \hspace{1cm} (12)

volume fraction of solvent \( \phi_2 \) and non-solvent \( \phi_1 \) estimated by [43]:

\[ \phi_1 = \frac{x_1 V_1}{x_1 V_1 + x_2 V_2} , \quad \phi_2 = \frac{x_2 V_2}{x_1 V_1 + x_2 V_2} \]  \hspace{1cm} (13)

where \( x_1, x_2 \) mole fraction of non-solvent (1) and solvent (2), respectively.

Excess Gibbs free energy derived by activity coefficients (Eq. (14)). Activity coefficient \( \gamma_i \) ratio of fugacity coefficient of component \( g_i \) in the mixture and fugacity coefficient of pure component \( i \) (\( \psi_i \)). Peng–Robinson (PR) equation of state with Binary interaction parameters \( k_9 = 0.048 \) is maintained for DMF/\( \text{ScCO}_2 \) mixing in high pressure [44]. With equation available at article, the fugacity coefficients are calculated, consequently, the activity coefficient and \( \Delta C^e \) can be predicted as follow [45]:

\[ \frac{\Delta G^e}{RT} = x_1 \ln \gamma_1 + x_2 \ln \gamma_2 \]  \hspace{1cm} (14)

In each volume fraction, the amount of \( g_{12} \) is obtained from Eq. (12).

The polynomial form was used for fitting to data by Tompa [30].

The interaction parameter between polymer and solvent \( g_{23} \) reported in the literature [31]. It is widely accepted in literature that the values of non-solvent/polymer interaction parameter \( g_{13} \) is independent of concentration [29]. This parameter is estimated from Hansen solubility parameters (HSP) [30]:

\[ g_{13} = \frac{V_i}{RT} \left[ (\delta_{11} - \delta_{21})^2 + 0.25(\delta_{11} - \delta_{12})^2 + 0.25(\delta_{11} - \delta_{12})^2 \right] \]  \hspace{1cm} (15)

where \( V_i \) is the molar volume of the non-solvent, \( R \) is the gas constant, \( \delta_i \) and \( \delta_p \) and \( \delta_h \) are called HSP which to quantitatively describe dispersion interactions (\( \delta_d \)) polarity interactions (\( \delta_p \)) and hydrogen bonding interactions (\( \delta_h \)), respectively [46].

Williams et al., presented a relation for determining HSP over the same range of temperatures and pressures that this relation is function of the density [47]. In order to calculate \( \delta \) density at different temperatures and pressures, NIST Database were used. The values of HSP for PVDF and \( \text{ScCO}_2 \) at different temperature and pressure listed in Table 2. According to the above description, interaction parameters at different temperatures and pressures are given in Table 3. After placing the interaction parameter in the binodal and crystallization equations, the equations will be solved. We used Matlab 7.1 to determine the phase diagram of the \( \text{ScCO}_2/\text{PVDF}/\text{DMF} \) system. The details of the theoretical approach drawing the binodal curve are shown by Lai et al. [29]. Also, computational details of crystallization curve are shown by Cheng et al. [48]. The ternary phase diagram in different temperature and pressure is plotted (Fig. 2).

### 4. Results and discussion

#### 4.1. Experimental design with RSM

Table 4 shows the experimental results of the Box–Behnken design tests. Thirteen experiments were performed to investigate the effects of the \( \text{ScCO}_2 \) temperature \( (x_1) \), pressure \( (x_2) \) and polymer concentration \( (x_3) \) along with their interaction on the pore size of the surface \( (\gamma_1) \), porosity \( (\gamma_2) \) and surface hydrophobicity \( (\gamma_3) \). The significance of the fit of the second-order polynomial for the pore size of surface, porosity and surface hydrophobicity were assessed by carrying out an analysis of variance (ANOVA). The results of ANOVA are shown in Tables 5 and 6.

The significance of each coefficient was determined by \( p \)-value. In general, smaller \( p \)-values indicate more significant coefficients. A \( p \)-value lower than 0.05 indicates that the model and the coefficients terms are statistically significant whereas a value higher than 0.1 shows that they are not so [49]. In this work, for all three models, \( p \)-value was lower than 0.05.

The coefficient of determination \( (R^2) \) is defined as the ratio of the explained variation to the total variation and is a measure of the fit degree. A good fit model should yield an \( R^2 \) of at least 0.8 [50]. The coefficient of determination \( (R^2) \) of the model for contact angle, porosity and surface pore size were 0.9511, 0.9935, 0.9689, respectively (Table 6) which indicating that the model adequately represented the real relation among the investigated variables. Moreover, the small difference between \( R^2 \) and \( R^2_{adj} \) suggests a proper adequacy of reduced models to data.

#### 4.2. Ternary phase diagram

Fig. 2 illustrates the ternary phase diagram in different temperatures and pressures. Diagram of ternary system of

<table>
<thead>
<tr>
<th>Component</th>
<th>HSP (MPa)</th>
<th>( \delta_1 )</th>
<th>( \delta_2 )</th>
<th>( \delta_3 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVD*</td>
<td>17.1</td>
<td>12.6</td>
<td>10.6</td>
<td></td>
</tr>
<tr>
<td>DMF*</td>
<td>17.4</td>
<td>13.7</td>
<td>11.3</td>
<td></td>
</tr>
<tr>
<td>( \text{ScCO}_2 ) (35 °C, 10 MPa)</td>
<td>8.6274</td>
<td>4.103</td>
<td>4.5165</td>
<td></td>
</tr>
<tr>
<td>( \text{ScCO}_2 ) (35 °C, 15 MPa)</td>
<td>10.3678</td>
<td>4.416</td>
<td>4.869</td>
<td></td>
</tr>
<tr>
<td>( \text{ScCO}_2 ) (45 °C, 10 MPa)</td>
<td>5.75</td>
<td>3.4902</td>
<td>3.79</td>
<td></td>
</tr>
</tbody>
</table>

* Ref. [43].
<table>
<thead>
<tr>
<th>( \delta_1 )</th>
<th>( \delta_2 )</th>
<th>( \delta_3 )</th>
</tr>
</thead>
</table>

\( \text{Ref. [44].} \)
Table 3
Flory–Huggins binary interaction parameter for different temperature and pressure.

<table>
<thead>
<tr>
<th>Conditions</th>
<th>Flory–Huggins binary interaction parameter</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$g_{12}$</td>
</tr>
<tr>
<td>$T=35 \degree C, P=10$</td>
<td>$0.7627h_1^2 - 1.7973h_2 + 1.7115$</td>
</tr>
<tr>
<td>$T=35 \degree C, P=15$</td>
<td>$1.643h_1^2 - 3.06h_2 + 2.405$</td>
</tr>
<tr>
<td>$T=45 \degree C, P=10$</td>
<td>$0.7158h_1^2 - 1.5337h_2 + 1.5$</td>
</tr>
</tbody>
</table>

Fig. 2. Ternary phase diagram for different temperature ($T$) and pressure ($P$): (a) $T=45 \degree C, P=10$ MPa; (b) $T=35 \degree C, P=10$ MPa; (c) $T=35 \degree C, P=15$ MPa.

Table 4
Three factor Box–Behnken design with experimental and predicted responses.

<table>
<thead>
<tr>
<th>EXP. name</th>
<th>T (°C)</th>
<th>P (MPa)</th>
<th>C (wt%)</th>
<th>Porosity (%)</th>
<th>Average poresize (µm)</th>
<th>Contact angle ($\theta$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>55</td>
<td>15</td>
<td>20</td>
<td>61</td>
<td>0.45</td>
<td>106</td>
</tr>
<tr>
<td>b</td>
<td>45</td>
<td>15</td>
<td>15</td>
<td>65</td>
<td>0.66</td>
<td>109</td>
</tr>
<tr>
<td>c</td>
<td>45</td>
<td>20</td>
<td>20</td>
<td>43</td>
<td>0.59</td>
<td>112</td>
</tr>
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<td>d</td>
<td>55</td>
<td>20</td>
<td>15</td>
<td>70</td>
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<td>117</td>
</tr>
<tr>
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<td>10</td>
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<td>113</td>
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<td>15</td>
<td>75</td>
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<td>105</td>
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<td>g</td>
<td>55</td>
<td>15</td>
<td>10</td>
<td>77</td>
<td>1.1</td>
<td>101</td>
</tr>
<tr>
<td>h</td>
<td>35</td>
<td>15</td>
<td>10</td>
<td>67</td>
<td>1.61</td>
<td>107</td>
</tr>
<tr>
<td>i</td>
<td>35</td>
<td>15</td>
<td>20</td>
<td>42</td>
<td>0.5</td>
<td>118</td>
</tr>
<tr>
<td>j</td>
<td>35</td>
<td>20</td>
<td>15</td>
<td>52</td>
<td>0.52</td>
<td>119</td>
</tr>
<tr>
<td>k</td>
<td>45</td>
<td>10</td>
<td>20</td>
<td>50</td>
<td>0.72</td>
<td>114</td>
</tr>
<tr>
<td>l</td>
<td>35</td>
<td>10</td>
<td>15</td>
<td>71</td>
<td>0.97</td>
<td>125</td>
</tr>
<tr>
<td>m</td>
<td>45</td>
<td>10</td>
<td>10</td>
<td>79</td>
<td>1.4</td>
<td>110</td>
</tr>
</tbody>
</table>

Table 5
Analysis of variance (ANOVA) for quadratic model.

<table>
<thead>
<tr>
<th>Source</th>
<th>Porosity ($\epsilon$)</th>
<th>Pore size ($d_p$)</th>
<th>Contact angle ($\theta$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Regression coefficients</td>
<td>p-Value</td>
<td>Regression coefficients</td>
</tr>
<tr>
<td>Intercept</td>
<td>65.00</td>
<td>0.66</td>
<td>109.00</td>
</tr>
<tr>
<td>$x_1$</td>
<td>-6.81</td>
<td>0.0003</td>
<td>-0.10</td>
</tr>
<tr>
<td>$x_2$</td>
<td>-0.38</td>
<td>0.0004</td>
<td>-0.15</td>
</tr>
<tr>
<td>$x_3$</td>
<td>-10.31</td>
<td>&lt;0.0001</td>
<td>-0.37</td>
</tr>
<tr>
<td>$x_4$</td>
<td>3.50</td>
<td>0.0144</td>
<td>0.10</td>
</tr>
<tr>
<td>$x_5$</td>
<td>-4.63</td>
<td>0.0054</td>
<td>-2.500E-003</td>
</tr>
<tr>
<td>$x_6$</td>
<td>2.25</td>
<td>0.0563</td>
<td>-0.10</td>
</tr>
<tr>
<td>$x_7$</td>
<td>2.94</td>
<td>0.0360</td>
<td>7.500E-003</td>
</tr>
<tr>
<td>$x_8$</td>
<td>-0.94</td>
<td>0.3774</td>
<td>-0.042</td>
</tr>
<tr>
<td>$x_9$</td>
<td>-2.31</td>
<td>0.0707</td>
<td>0.31</td>
</tr>
</tbody>
</table>

Table 6
Reduced models for pore size, porosity and contact angle.

<table>
<thead>
<tr>
<th>Reduced model</th>
<th>Eq.</th>
<th>$p$-Value</th>
<th>$F$-value</th>
<th>$R^2$</th>
<th>$R^2_{adj}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\epsilon = 110.32813 - 0.52625P - 0.24375C + 1.46250C + 0.0007PT - 0.018500C + 0.045000C + 0.0177P^2 - 0.009374C^2 - 0.092C^2$</td>
<td>(16)</td>
<td>0.0005</td>
<td>68.44</td>
<td>0.9935</td>
<td>0.979</td>
</tr>
<tr>
<td>$d_p = 7.46625 - 0.011825P - 0.037375C - 0.53725C + 0.0002PT - 0.000001P - 0.000205C + 3 \times 10^{-6}P^2 - 0.000425P^3 + 0.0124C^2$</td>
<td>(17)</td>
<td>0.0011</td>
<td>46.01</td>
<td>0.9904</td>
<td>0.9689</td>
</tr>
<tr>
<td>$\theta = 213.1562 - 1.0175P - 2.8625C + 0.009PT - 0.0005C - 0.033C + 0.00235P^2 + 0.1625C^2 - 0.105C^3$</td>
<td>(18)</td>
<td>0.0264</td>
<td>8.64</td>
<td>0.9511</td>
<td>0.8409</td>
</tr>
</tbody>
</table>
PVDF/ScCO2/DMF was divided into three regions: one-phase region (above the crystallization line), liquid–liquid phase inversion regions (defined by the binodal phase envelope) and gelation region (between binodal and crystallization curve). In the region between crystallization and binodal curve, crystallization can occur exclusively without being influenced by liquid–liquid de-mixing. In the region within the binodal envelop, both types of phase inversion can occur, implying that as a composition of dope solution during an immersion–precipitation process, it is brought into the binodal envelop and both types of phase inversion compete with one another [26]. Changing the operation conditions such as temperature and pressure, location of the crystallization and binodal curve is varied. When the separation and homogeneous area increase, the liquid–liquid de-mixing mechanism will overcome solid–liquid de-mixing and increases the porosity of membrane [20,51,52]. According to the theory of Flory–Huggins, the size and location of the de-mixing gap depends on their interactions.

The $g_{13}$ determines the surface area of the liquid–liquid de-mixing gap. In addition, $g_{13}$ determines the intersection point between the de-mixing gap and the polymer/non-solvent axis. When $g_{13}$ is high, the area of the de-mixing gap increases and lower parameter interaction between solvent/non-solvent ($g_{12}$) strongly increases the magnitude of de-mixing gaps. Polymers and solvents with high $g_{23}$ increase the extent of the liquid–liquid de-mixing gap [52,53].

4.3. Effects of the temperature on membrane morphology

The effect of temperature on the membrane structure on top of the surface and cross-section in constant ScCO2 pressure and polymer concentration is illustrated in Fig. 5a and i along with Fig. 5d and j. As it can be seen in the first case; $P = 15$ MPa and $C = 20 \text{ wt.}\%$ while in the second case $P = 20$ MPa and $C = 15 \text{ wt.}\%$.

4.3.1. Effects of the temperature on membrane porosity

As shown in Table 5, the results of ANOVA denote that ScCO2 temperature has a major effect on the membrane porosity ($p$-value $< 0.05$). It can also be seen in Fig. 4b and c. So that at a concentration of 15 wt.%, the porosity increases with increasing temperature.

The temperature increase will raise $g_{13}$ and decrease $g_{12}$ (Fig. 3 and Table 3), having two conflicting effects on the phase diagram. The increase of $g_{13}$ will increase the de-mixing gap while reducing $g_{12}$ will decrease them. However, the effect of $g_{13}$ increase will overcome the reduced $g_{12}$, increasing the de-mixing gap (Fig. 2a and b). This is quite similar to the impact of temperature on the phase diagram of the polysulfone membrane [11]. What is more, the crystallization curve moves down, shifting nearer to the binodal curve. Even though, the membrane solution enters the crystallization zone before the binodal, crystallization probably will not happen due to its competition with the liquid–liquid de-mixing process.

With temperature increase, the mechanism of liquid–liquid de-mixing overcomes the solid–liquid de-mixing, creating sponge-like structures composed of cellular pores and consequently, the membrane porosity increases as well. SEM images of the cross-section membranes in constant pressure and concentration show that the porosity in Fig. 5a and d is greater compared to Fig. 5i and j, respectively. The morphology of the prepared membranes showed that in high temperature an instantaneous liquid–liquid de-mixing can be seen that leads to the formation of macro voids inside the resulting structures (see Fig. 5f). Therefore, it results in a typical asymmetric membrane.

4.3.2. Effects of the temperature on average pore size

It can be seen from Table 3 that the ScCO2 temperature has a significant effect on the average pore size ($p$-value $<0.05$). Fig. 4d and j shows the average pore size decreased by temperature increase. According to the left side SEM images mentioned, with an increase of temperature solidification rate of the interfacial polymer becomes speeds-up and a dense skin layer is formed rapidly (see left SEM in Fig. 5f).

4.3.3. Effects of temperature on surface membrane hydrophobicity

The result of ANOVA (Table 3) indicates that ScCO2 temperature is the most important factor, affecting the hydrophobicity of membrane ($p$-value $< 0.05$). According to Fig. 4g and i, the decrease of temperature leads to an increase in the rate of surface hydrophobicity. As the tightness grows and surface roughness decreases, surface hydrophobicity becomes less [54,55]. The profile of water droplet on the top surface shows hydrophobicity of membrane surface in Fig. 5i is larger compared to Fig. 5a. Temperature increase lowers the surface membrane roughness and reduces the hydrophobicity due to the rise in surface hardening.

4.4. Effects of the pressure on membrane morphology

The SEM images in Fig. 5c and k, f and d, m and e, l and j show the top surfaces and cross-sections of the membranes which prepared under different CO2 pressures. Each of the pairwise images demonstrates the effect of pressure change at constant ScCO2 temperature and polymer concentration on the membrane morphology.

4.4.1. Effects of the pressure on membrane porosity

The results of ANOVA in Table 3 indicate that the amount of the $p$-value is less than 0.05, hence the ScCO2 pressure has significant effect on the membrane porosity. According to Fig. 4a and b, pressure increase leads to a decrease in the porosity. The porosity reduction at low temperatures is larger. By increasing the pressure, $g_{13}$ reduces while $g_{12}$ increases. Finally the de-mixing gap in ternary phase diagram is increased and the gelation region is raised (Fig. 2b and c). As a result, the rate of liquid–liquid de-mixing mechanism slows down while the rate of solid–liquid de-mixing mechanism speeds up and the porosity decreases [56,57]. For the polysulfone membrane, the pressure of ScCO2 has the same effect on the phase diagram [11].

4.4.2. Effects of the pressure on surface pore size

Amount of $p$-value for studying the effect of pressure on pore size is equal to 0.0113 that indicating the effect of pressure is not
high. However, Fig. 4e shows that the pore size decreases with pressure increase at low temperatures.

By increasing the pressure at low temperatures (increasing the density of SC\textsubscript{CO}2 due to pressure augmentation at low temperatures is higher), the average diameter of the pores on the surface decreases. It is well known that the density of SC\textsubscript{CO}2 increases as the pressure rises and decreases with the temperature does so. The increase of SC\textsubscript{CO}2 pressure results in an increase of the solubility of the organic solvent in SC\textsubscript{CO}2, owing to SC\textsubscript{CO}2 density increase. This promotes more solvents near the top surface to rapidly diffuse from casting solution into SC\textsubscript{CO}2 and thus the interfacial polymer concentration increases. Therefore, the solidification rate of the interfacial polymer becomes fast and a dense skin layer is formed rapidly which may be the reason behind pore diameter decrease as pressure rises [22]. The mentioned result can be seen in SEM images. For example, the surface average pore size of the membrane in Fig. 5k is larger to Fig. 5c.

4.4.3. Effects of the pressure on surface membrane hydrophobicity

As shown in Table 3, the result of ANOVA demonstrates that SC\textsubscript{CO}2 pressure does not have any significant effect on the membrane hydrophobicity (p-value = 0.3887). It was observed from Fig. 4g that increasing SC\textsubscript{CO}2 pressure caused a very small effect on the hydrophobicity.

According to this figure, at low temperature by decreasing the pressure hydrophobicity increased. Therefore, Fig. 5j and i indicates that the surface roughness occurs at 10 MPa rather than 20 MPa. As a result, the hydrophobicity is major at lower pressure.

4.5. Effects of polymer concentration on membrane morphology

The pairwise images (including Fig. 5a and b, c and e, and h and i) show the effect of polymer concentration on the top surface and cross-section structure of PVDF membranes, measured by SEM. In each of these pairs, the effect of polymer concentration has studied at constant SC\textsubscript{CO}2 pressure and temperature.

4.5.1. Effects of polymer concentration on membrane porosity

From Table 3 it can be observed that the polymer concentration has major effect on the membrane porosity (p-value < 0.0001). In all conditions, increasing the concentration lowers the porosity (see Fig. 4a and c). According to SEM images, by increasing the concentration, the diameter of the pores in the cross-section membrane decreases. At low concentrations, porous morphology indicates liquid–liquid de-mixing as the dominant mechanism of membrane formation. Crystallization-associated morphology (e.g. crystalline particles) was not observed on the walls of the cells, suggesting that liquid–liquid de-mixing has taken place much earlier than crystallization, rapidly fixing the cellular structure before initiating the crystallization in the gel layer that surrounds the formed liquid micelles. In high concentrations, a wall of pore is composed of a relatively loosely-packed agglomerate of particulate crystallites. Evidence of crystallization during the precipitation is also confirmed by Fig. 5c and i. Crystallite particles surrounding the pores, suggest that crystallization occurs rapidly following the liquid–liquid de-mixing and locks the cellular structure. In terms of the three-phase diagram, reducing the polymer concentration makes the membrane solution enter into the binodal rapidly and liquid–liquid de-mixing as the dominant mechanism of membrane formation.
formation. Also, by increasing the concentrations, the fixation of membrane structure will be delayed, leading to a larger pore size (Fig. 5k).

4.5.2. Effects of polymer concentration on average pore size

It can be seen in Table 3 that the amount of $p$-value is very small, indicating significant effect of the polymer concentration on the
average pore size. By increasing concentration, the average pore diameter was significantly reduced (see Fig. 4e and f). According to SEM images, within creasing polymer concentration, the membrane surface is dense. In the phase inversion process by increasing the polymer concentration, solidification happens more, leading to the formation of the skin layer on the top surface [19,23].

4.5.3. Effects of polymer concentration on membrane hydrophobicity

Polymer concentration’s influence on the contact angle is relatively low ($p$-value = 0.0587). According to Fig. 4h and i, contact angle is relatively larger at intermediate concentration. At low concentrations however, the surface pore diameter is large and the hole gets wet with the liquid (Fig. 5e). On the other hand, as the concentration rises, surface roughness and hydrophobicity decrease (Fig. 5c).

4.6. Optimization of PVDF membrane morphology

In order to optimize the hydrophobic membrane, variables including ScCO$_2$ temperature, pressure and polymer concentration must be selected appropriately. Their value should lead to maximum porosity and hydrophobicity of the membrane. Moreover, average diameter of the pore should be between 0.1 and 1 $\mu$m. To increase the porosity, the temperature should be maximum while the pressure and polymer concentration have to be minimum. Temperature increase causes a decrease in surface roughness and reducing the surface hydrophobicity.

Also, at low concentration the average diameter of pores on the surface is grows. These conditions are not suitable for the MD process. By using the optimization section of Design Expert Software, suitable values of these variables are determined. Table 7 shows the experimental conditions for the optimization of the membrane in terms of porosity, pores diameter and hydrophobicity together with the predicted responses. The appropriate variables are $T$ = 35 - $C$, $P$ = 10 MPa and $C$ = 14.7691 wt.% At this point, the amount of porosity, pores diameter and hydrophobicity are 71.29%, 0.99 $\mu$m and 124.883, respectively. Features of optimized membrane are almost similar to the membrane, produced in the EXP.name()! According to Fig. 5f(left), porosity and density of the pores per unit area on the membrane surface is large. This membrane morphology increases the mass transfer flux. The roughness of the surface of this membrane is higher than other images representing the increase in hydrophobicity of the membrane surface.

4.7. DCMD test for the optimum membrane

The rates of permeability and separation percentage for the optimum membrane are measured by DCMD process. Table 8 presents the DCMD performance of the optimum membrane. Khayet et al. optimized the flat membrane by using the conventional wet phase inversion method [58]. Features and performance of these membranes can be seen in Table 4. In order to compare the performance of the two membranes, the same operating conditions of the process are taken into consideration. Using ScCO$_2$ method, the permeate flux for the optimized membrane will be 10.191 L/h.m$^2$ while the value for the wet phase inversion method is 4.41 L/h.m$^2$. The salt rejection coefficient for membrane produced by ScCO$_2$ is scarcely lower. Increasing the membrane hydrophobicity is a more effective way to overcome wetting than decreasing the membrane pore diameter [59]. Thus, the high permeate flux under a high rejection will be obtained.

5. Conclusions

Hydrophobic PVDF membranes were prepared by using the process of ScCO$_2$-assisted phase inversion in different ScCO$_2$ pressures, temperatures and polymer concentrations. The ternary phase diagram was calculated in accordance to the Flory–Huggins theory to study the effects of temperature and pressure on the mechanism of membrane formation. According to the ternary diagrams and SEM images, increasing the temperature and decreasing both the pressure and concentration the liquid–liquid separation mechanism overcomes the solid–liquid separation mechanism which decreasing the porosity. The membrane’s hydrophobicity is greater at lower temperatures, while the average pore size is smaller in high temperature, pressure and polymer concentration. The hydrophobic membrane used in membrane distillation was optimized by suitably adjusting the temperature, pressure and polymer concentration. The suitable conditions obtained are 15 wt.% of PVDF concentration with a temperature and pressure of 35 $C$ and 10 MPa respectively. Under such conditions, salt rejection coefficient is 96.713% and the corresponding DCMD permeate flux is 10.191 L/h.m$^2$.

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