Application of PV in the Separation of Dilute Ethanol, Acetone and Butanol Binary Solution

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Abstract: In this paper, polyethersulfone (PES) ultrafiltration hollow fiber membranes were fabricated employing the dry/wet-spinning method, polydimethylsiloxane (PDMS) composite hollow fiber membranes (PDMS/PES) were prepared by the dip-coating method, their PV performances for the separation of dilute ethanol, acetone and butanol binary biosolvent aqueous were investigated, the effects of process parameters such as temperature, concentration and permeate pressure were discussed. For all of the three systems, with the increases of feed temperature, total fluxes increased significantly and separation factors increased slightly to a maximum at 40℃ or 50℃ then decreased slowly; the permeation rate followed the Arrhenius equation; total permeation fluxes increased and separation factors decreased with the increases of feed concentration; with the increasing of permeate-side pressure from 1 to 40mmHg, total flux decreased and selectivity increased non-linearly.

Keywords: pervaporation; polydimethylsiloxane (PDMS); composite hollow fiber membrane; biosolvent

Introduction

Pervaporation (PV) is an energy-efficient alternative to conditional separation technologies for the removing of volatile organic compounds (VOCs) from water especially biosolvents from their dilute solutions in a fermentation broth[1]. As an efficient tool, it could be used for the separation, concentration and purification of bio-reaction products. The unique features of PV make it very utilizable in fermentation process. For the applications of PV in biotechnological separation fields, there is one area which PV could play an important role in: the continuous removal of biosolvents from fermentation broths[2]. Some biosolvents such as ethanol, butanol and acetone have inhibitory effects on production rate. By integrating a PV unit into a bioreactor, the volatile inhibitory biosolvents could be removed directly. Compared with the traditional separation techniques such as distillation which needs a large a mount of energy, the coupling of PV with fermentation could save some of the intermediate processes which will significantly increase the bioconversion rates and decrease the downstream processing costs[3]. From the point of saving both energy and cost, the applying of PV in biotechnology industry is a better idea.

2. Experiment

2.1 Materials

PES in power form as membrane material was obtained from Jida High Performance Material Co. Ltd. (PR China). Reagent grade N-methyyl-2-pyrrolidone (NMP) was used as solvent, ethanol (reagent grade) used as a non-solvent additive (NSA). PDMS (Silicone Rubber 107, M_w5000), cross linking agent ethyl silicate and curing agent dibutyltin dilaurate were purchased from Shanghai resin Company (PR China). Reagent grade n-Hexane was obtained from Shanghai Ruen Jie chemical reagent Company (PR China). Commercially supplied ethanol, acetone and butanol was used for PV experiments without further purification.

2.2 Dope preparation

PES dope solution was prepared by mixing PES powder with NMP solution; ethanol was used as the non-solvent additive (NSA).

2.3 Spinning of PES hollow fiber support membranes

PES ultrafiltration hollow fiber membranes were spun at 20℃ employing the dry/wet-spinning method described elsewhere [4].

2.4 The preparation of PDMS/PES hollow fiber composite membranes

PDMS/PES hollow fiber composite membranes were prepared by the dip-coating method.

2.5 PV process for the separation of ethanol/water mixtures

Figure.1 is the schematic diagram of PV apparatus used in this case.
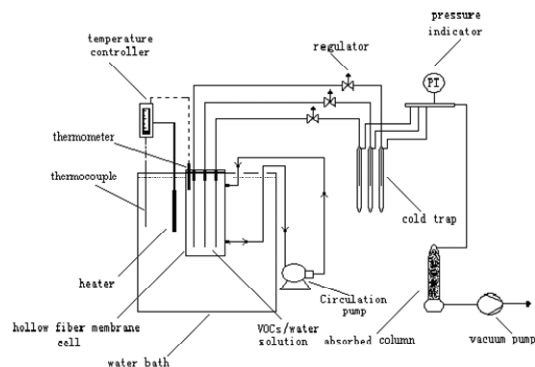
Figure 1. Schematic diagram of PV apparatus.

3. Result and discussion

3.1 Effect of feed temperature on PV performance

In PV temperature is an important process parameter. Temperature affects PV performance by varying vapor-liquid partitioning of the components, changing their diffusion coefficients in liquid as well as in membrane and by altering sorption behavior of the membrane. Temperature affects the diffusivity and sorption behavior of the membrane in two ways[5]: (i) modifying the sorption- diffusion steps inside the membrane and (ii) changing the activity driving force across the membrane. At higher temperature, the frequency and amplitude of polymer molecular motions are greater and the thermal motions of polymer chains in the amorphous region produce larger free volume.

The effects of feed temperature on membrane performance for the PV separation of ethanol, acetone and butanol dilute solutions when permeate-side pressure was 1 mmHg and feed concentrations was 5wt.% were shown in Figure 2. Total flux increased significantly with the increase of feed temperature. As the feed temperature varied from 30 to 60℃, the total flux of ethanol/water mixture increased from 66 to 483 g/(m²·h), acetone/water mixture increased from 112 to 632 g/(m²·h) and butanol/water mixture increased from 107 to 394 g/(m²·h). According to the solution-diffusion mechanism, Arrhenius type function can be used to express the effect of temperature on flux as follows:

$$J_i = J_0 \exp(E_a / RT)$$

Activation energy (E_a) represents the relative change of flux to the change of temperature. When the value of activation energy (E_a) is high, the flux will be more susceptible to the change in temperature. The activation energy values are 55.7, 45.7 and 36.6 KJ/mol for ethanol, acetone and butanol permeation in PDMS hollow fiber membrane calculated from Figure 2. For PV, the separation factor changes with the relative changes of solvent flux and water flux. For the PV separations of ethanol/water, acetone/water and butanol/water solutions,

as the feed temperatures increased, separation factors increased slightly to a maximum value at the temperature of 40℃ or 50℃ then decreased slowly. This phenomenon is due to the varying of the rate of sorption and diffusion which varied with temperature.
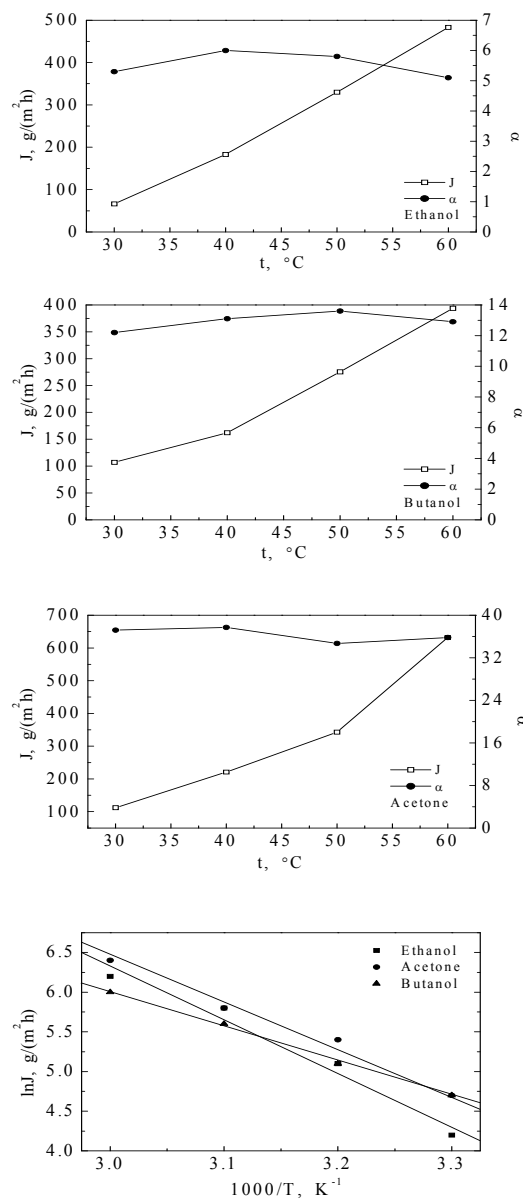

Figure 2. Curve: The effects of feed temperature on total flux and separation factor.

3.2 Effect of feed concentration on PV performances

According to the solution-diffusion model, membrane properties were controlled by the sorption and diffusion behavior of feed components. The fact that the sorption performance at the interface of liquid and membrane varies with the variation of feed composition and the diffusion property in membrane depends on the con-

centration of the components (or the solubility of the components)[6] caused the dependence of permeation characteristics on feed concentration as it showed in Figure 3.
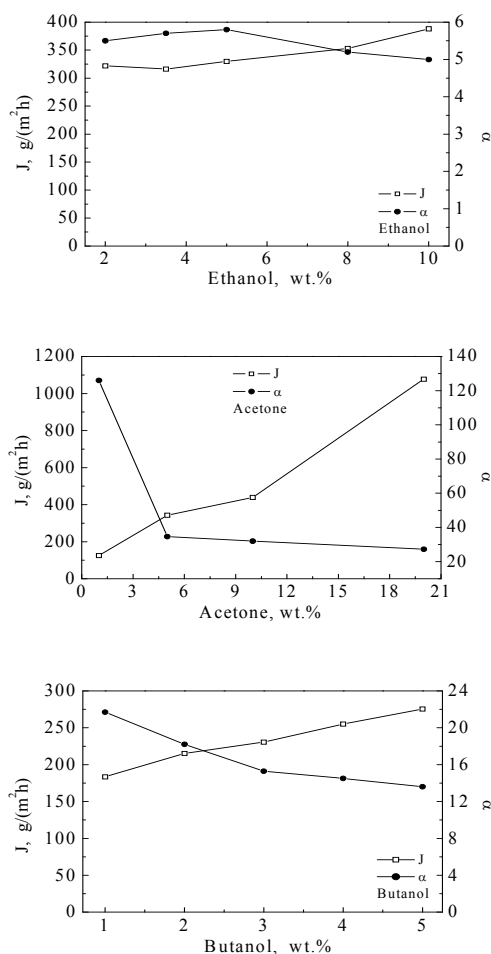

Figure 3. Curve: The effects of feed concentration on total flux and separation factor.

Figure 3 shows the effect of feed concentration on membrane properties for the PV of ethanol, acetone and butanol dilute solution at 50℃ and 1mmHg. It was observed that for all three separations, with the increase of feed concentration, total flux increased and separation factor decreased. When ethanol concentration increased from 2 to 10 wt.%, total flux increased from 322 to 388 g/(m²·h), separation factor decreased from 5.5 to 5.0. When acetone concentration increased from 1 to 20 wt.%, total flux increased from 125 to 1078 g/(m²·h), separation factor decreased from 126 to 27.3. When butanol concentration increased from 1 to 5 wt.%, total flux increased from 184 to 275 g/(m²·h), separation factor decreased from 21.7 to 13.6. This is because that as organic concentration increased, the partial pressure of the solvents in feed-side increased, which caused an increase of

mass transfer driving force of components. If the partial pressure of the organics at the permeate-side of the membrane is negligible and the solute partitioning of the feed and the membrane is ideal, then a linear relationship between flux and concentration will be observed.

3.3 Effect of permeate-side pressure on PV performance

The permeate pressure is directly related to the activity of the components at the down-stream side of the membrane, the permeate pressure strongly influences the PV performance and the maximum driving force could be obtained if a zero permeate side pressure was to be obtained. An increase in the vapor pressure in the down-stream component leads to a decrease of driving force for transport[7]. The change in permeate pressure also affects the selectivity. The selectivity can increases or decreases with increasing permeate pressure, depending on the relative volatility of the permeating components.
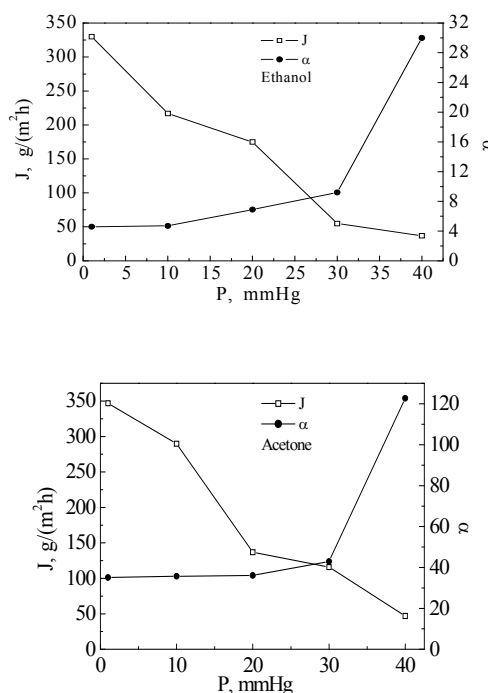

Figure 4. Curve: The effects of permeate-side pressure on total flux and separation factor.

In this paper, the effects of the permeate-side pressure on total flux and selectivity were examined using a 5wt.% ethanol solution and a 5wt.% acetone solution at a temperature of 50℃ and was illustrated in Figure 4. When pressure was increased from 1 to 40mmHg, because of the decreases of driving force, total flux decreased sharply. For the separation of ethanol/water mixture, total flux decreased from 331 to 37g/(m²·h) and for the separation of acetone/water mixture, total flux decreased from 347 to 47g/(m²·h). The relationship be-

tween permeate-side pressure and solution flux can be expressed by the following equation in terms of partial pressure [8,9]:

$$J_i = J_{io} \, (\, C_i' \, \gamma_i' \quad P_{i0} - P_i'' \,)$$

Where J_i (cm^3/(cm^2 ·s)) is the permeation flux of species i, J_{io} (cm^3/(cm^2· s· mmHg)) is the normalized permeation flux of species i through the membrane, C_i' is the mole fraction of species i at the upstream surface of the membrane, P_{i0} (mmHg) is the saturation vapor pressure of pure i at the feed temperature, γ_i' is the activity coefficient of i in the feed and P_i'' (mmHg) is the partial pressure of i on the permeate-side of membrane. As an example, for a 5wt.% ethanol-water solution (ethanol mole fraction 0.02), when feed temperature is 50℃, the activity coefficients of ethanol and water are 4.67 and 1.0 respectively, the saturation vapor pressures of pure ethanol and pure water are 222.0 and 92.9mmHg respectively. The relationship between permeate-side pressure and solute flux then can be expressed as follows:

$$J_{Ethanol} = J_{Ethanolo} \, (\, 20.4 - P_{Ethanol}'' \,)$$
$$J_{Water} = J_{Watero} \, (\, 91.0 - P_{Water}'' \,)$$

4. Conclusions

In this paper, PV performances of PDMS hollow fiber membranes for the separation of dilute ethanol, acetone and butanol aqueous were investigated, the effects of process parameters such as temperature, concentration and permeate pressure were discussed with the following conclusions:

1) s the feed temperature was varied from 30 to 60℃, total flux increased significantly. Permeation rate follows the Arrhenius-type law $J = J_0 \exp (\, E_p / RT \,)$; separation factors increased slightly to a maximum value at the temperature of 40℃ or 50℃ then decreased slowly.

2) otal permeation fluxes increased and separation factors decreased with the increase of feed concentrations.

3) hen permeate-side pressure was increased from 1 to 40mmHg, total flux curves showed non-linear decreases; Selectivity showed non-linear increases.

4) embrane performance for the separation of acetone/water system is better than that of butanol/water and ethanol/water systems when operated under the same conditions.

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