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Efficient Recovery of High-Purity Aniline from Aqueous Solutions Using Pervaporation-Fractional Condensation System

Chuncheng Li, Xinru Zhang, Xiaogang Hao, Minmin Wang, Chuan Ding, Zhongde Wang, and Yinan Wang
Dept. of Chemical Engineering, Taiyuan University of Technology, Taiyuan 030024, China

Guoqing Guan and Abuliti Abudula
North Japan Research Institute for Sustainable Energy (NJRISE), Hirosaki University, 2-1-3, Matsubara,
Aomori 030-0813, Japan

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Selective recovery of valuable minor component with high-purity form from dilute aqueous solution is an interesting issue in the area of organophilic pervaporation. High-purity aniline was recovered with a high production rate from dilute aqueous solution by a pervaporation-fractional condensation (PVFC) coupling system. The effects of downstream pressure and temperature (the first condenser) on the performance of PVFC system were investigated based on experimental measurements and Aspen simulations. Sorption and desorption experiments demonstrated that the sorption selectivity of poly(ether block amide) (PEBA-2533) membrane to aniline was extremely high, indicating excellent pervaporation performance for aniline/water solutions. The perfect integration of high-performance PEBA-2533 membrane with the fractional condensation process yielded high production rate of 1222.5 g/(m^2 h) as well as high recovery efficiency (86.5%) for recovering high-purity aniline in the first condenser when feed concentration and temperature were 1 wt % and 80°C, respectively. © 2015 American Institute of Chemical Engineers *AIChE J*, 61: 4445–4455, 2015
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Introduction

Organophilic pervaporation is an interesting alternative process in distillation or solvent extraction for the separation and concentration of dissolved organics from water.[1,2] It is a continuous process with minimal energy consumption, and no need to regenerate the membrane and add an additional entrainer and thus no secondary contamination.[3,4] Nowadays, it is widely applied for the removal and recovery of trace amounts of organic compounds from aqueous streams such as separation of aromas and biofuels from fermentation broth.[3,5] To date, the performance of existing organophilic membranes still cannot meet the requirements of energy consumption and cost of investment.[6] Most researches are thus concentrated on the development of novel membranes with higher flux and more excellent selectivity. However, the thermodynamic properties of organic compound/water system under vacuum are still not given the attention in the area of organophilic pervaporation, which is in fact the key issue to understand the application potential of pervaporation.[7]

Vacuum pervaporation, in which vacuum is applied in the downstream side of membrane, is the most widely utilized mode of operation.[8] The permeate in this process is generally removed as a low-pressure vapor and then collected by condensation. Because the components of the permeate vapor have different condensation potentials, the permeate vapor can be trapped in cold trap by fractional condensation, which is expected to improve the concentration of target products.[9] For example, for the separation of components (e.g., ethanol or ethyl acetate) with low boiling point from aqueous solutions, when pervaporation is coupled with multistage permeate condensations, the separation performance can be greatly improved.[9–11] In this process, the first stage operated at a higher temperature is mainly used for water condensation while the second stage is mainly for condensing and collecting the target products with low boiling points (low boilers). The target products collected in the second condenser still contain a certain amount of water, though the concentration of target products is significantly improved when compared to the one-stage permeate condensation process with a single condenser. In order to further purify these products (e.g., ethanol) to meet fuel specifications, dehydration by pervaporation with hydrophilic membranes was proposed.[12] In contrast, for the separation of components such as vanillin or phenol with high boiling points (high boilers) from aqueous solutions, the target products are generally trapped in the first condenser with a purity as high as >99%.[13,14] In this case, additional purification steps for the target products such as evaporation, crystallization, or dehydration by hydrophilic pervaporation will be no longer needed. Consequently, investment and operating costs related to additional processing will be saved. Therefore, the aforementioned integrated process for recovering high-boiling point compounds seems to be attractive. Among the organic compounds separated by organophilic

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Additional Supporting Information may be found in the online version of this article.

Correspondence concerning this article should be addressed to X. Hao at xghao@tyut.edu.cn pervaporation, many of them are high-boiling compounds (boiling point >100°C). Apart from being widely studied biofuels (e.g., bio-butanol/bio-ethanol), many high-boiling aroma compounds such as 1-octen-3-ol,[15,16] ethyl hexanoate,[17,18] and vanillin[13,19,20] were also recovered from fermentation broth by organophilic pervaporation. These aromas may be recovered as high-purity forms from aqueous solutions by pervaporation integrated with fractional condensation process. If it could be achieved, the production rate of high-purity target product (e.g., phenol) collected in the first condenser still needs to be improved in order to realize its practicability for industrial applications. Development of high-quality membranes is still the key to tackling this issue; alternatively, when using the existing organophilic membrane materials (e.g., polydimethylsiloxane (PDMS) or poly(ether block amide) (PEBA)), seeking a more appropriate organic compound/water system that simultaneously possesses excellent pervaporation performance and proper thermodynamic properties may be a feasible way because the same membrane could have different separation efficiencies for different organic compound/water systems in a practical process.

Aniline, an aromatic compound, has a high boiling point (184.4°C) and limited solubility in water (3.6 wt % at 25°C). It is widely used in various industries for the manufacture of plastics, rubbers, pesticides, pharmaceuticals, and paints. Conventional methods for the recovery of aniline from wastewater include solvent extraction,[21] adsorption,[22,23] membrane processes.[24–27] Among these processes, pervaporation with different organophilic membranes has been studied for the separation of aniline from aqueous solutions.[27–29] Due to the high solubility selectivity toward aniline, PEBA membrane proved to have excellent pervaporation performance for aniline/water system, and a proposed hybrid process, in which pervaporation is coupled with the liquid-liquid phase separation, is used to further separate the permeate into two phases: the water-rich phase and the aniline-rich phase.[27] Unfortunately, the aniline-rich phase still contains about 5 wt % water, which is difficult to be separated even if a further separation process is combined. However, aniline is a high-boiling organic compound, which may be preferentially condensed compared to water in the downstream condenser. Therefore, in this study, a pervaporation coupled with fractional condensation process was developed for the recovery of aniline from aqueous solutions. To the best of our knowledge, no such a coupling process has ever been investigated for the recovery of aniline from aqueous solutions.

PEBA is a family of copolymers consisting of hard polyamide (PA) and soft polyether (PE) segments in the polymer chains. The hard PA segments provide good mechanical strength, while the soft PE segments offer a better permselectivity.[30,31] PEBA was found to have exceptional selectivity for the separation of aromatic hydrocarbons from water by pervaporation.[32] The good selectivity of PEBA to aromatic compounds permeation derives from the strong affinity between the PE segments and aromatic compounds. Among commercially available PEBA (2533, 3533, 4033, 1657, 1740) with different contents of PA and PE segments, PEBA-2533 membrane was widely investigated for liquid separations such as alcohols-water separation,[33–36] aromatic-aliphatic separation,[37] and aromatic-water separation[38] due to the highest content of PE segment (~80 wt %).[39] On the basis of the aforementioned physical properties, PEBA-2533 was chosen as the membrane material for aniline-water separation in pervaporation-fractional condensation (PVFC) system, which is expected to result in a higher permeation flux. PEBA-2533 membrane was subjected to sorption/desorption studies at first for examining its pervaporation performance. Then the PVFC system was developed to recover aniline from aqueous solution, and its operation feasibility of the proposed coupling process was analyzed and discussed. Thereafter, the effects of operating conditions (feed composition and temperature, temperature of the first condenser, and permeate pressure) and membrane thickness on the production rate of high-purity aniline as well as separation factor were investigated. In addition, the thermodynamic properties of aniline-water mixture under low pressure were also measured in order to understand the separation mechanism.

Experimental and Simulation

Materials

PEBA-2533 was purchased from Arkema Inc., France. *N,N*-dimethyl acetamide and aniline were from Tianjin Damao Chemical Reagent Plant, China and used as analytical reagents. De-ionized water was used in preparing aqueous aniline solutions at various concentrations. All chemicals were used as received without further purification. The membranes with various thickness were prepared using the solvent casting method, which has been described elsewhere.[38] The thickness of each dry membrane was measured by a micrometer over at least five different spots, and the deviation of each membrane was less than ±5 μm.

PVFC system

A schematic of the PVFC system is shown in Figure 1. Briefly, it mainly consists of a feed tank, a recirculation pump, a membrane cell, a condensation subsystem with two parallel two-stage condenser, and a vacuum pump. The testing membrane was mounted in the stainless steel permeation cell, and its effective area for permeation was 16.6 cm^2. The feed solution was circulated over the membrane using a recirculation pump, and its rate was maintained at 120 L/h in all the experiments. The permeate vapor was introduced into two condensers in series. The first one was immersed in a low-temperature brine bath (Shanghai Baidian Instruments Co., China), and the second one was immersed in liquid nitrogen to completely entrap residual permeate vapor escaped from the first condenser. The two parallel two-stage condenser allowed a continuous collection of permeate samples trapped in the first and second condensers. The downstream pressure was controlled with a vacuum regulator located between the condenser and the vacuum pump, and it was measured by a digital vacuum gauge (pressure range 0–10 kPa, Vacuubrand, Germany).

In order to minimize the depletion of aniline from the feed during each experiment, a relatively large volume of feed solution (3 L) was used. After a steady state of permeation was reached, the remaining permeate collected in the second condenser were weighted and then diluted to an appropriate concentration range prior to the composition analysis with an Ultraviolet-visible Spectroscopy (Cary-50, Varian Co.) at a wavelength of 280 nm. The standard deviation in measurement of aniline concentration was ±3%. After closing the Valve 6, the permeate samples (usually high-purity aniline) trapped in the first condenser (pipe coil) were vaporized and collected in the second liquid nitrogen condenser (cold trap) for easy weighting and composition analysis. The moisture content of aniline recovered in the first condenser was measured with a Karl Fisher moisture analyzer (Shanghai Precision Instruments Co., China). The rate of recovery of high-purity

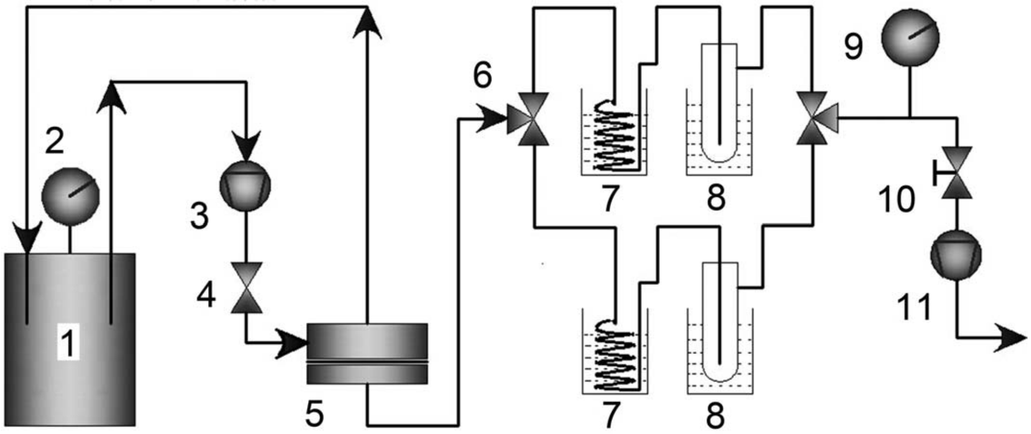

Figure 1. Set-up for PVFC experiments.

(1) Feed tank; (2) thermometer; (3) recirculation pump; (4) valve; (5) membrane cell; (6) three-way valve; (7) red copper pipe coil immersed in brine solutions; (8) cold trap immersed in liquid nitrogen; (9) vacuum gauge; (10) vacuum regulator; (11) vacuum pump.

aniline per unit membrane area (J), the rate of residual aniline collected in the second condenser (J'), were calculated by the following equations

$$J=\frac{Q_a}{A\Delta t} \tag{1}$$

$$J'=\frac{Q_r}{A\Delta t} \tag{2}$$

$$Q_r=QC_r \tag{3}$$

The permeation flux of aniline through the membrane is equal to ($J+J'$). The percentage quantity of high-purity aniline recovered, which is defined as aniline recovery ratio (η), is given by

$$\eta=\frac{Q_a}{Q_a+Q_r}\times 100\% \tag{4}$$

where Q_a is the weight of high-purity aniline collected in the first trap, and Q_r and Q are the weights of residual aniline and the aniline-water mixture collected in the second trap, respectively, over a period of time (Δt). A is the effective membrane area, and C_r is the weight fraction of aniline in permeate samples collected in the second trap. The pervaporation data reported here represent an average of at least three measurements obtained from replicate membrane samples.

Sorption and desorption experiments

Each piece of dry PEBA-2533 membrane (about 2 g) with a thickness of about 100 μm were immersed in different compositions of aniline-water mixtures at 80°C for at least 24 h to reach sorption equilibrium. The membrane sample was then taken out and quickly wiped with absorbent wiper to remove liquid from the membrane surface before measuring the weight of the swollen membrane. Degree of swelling (DS) of membrane sample was determined by the following equation

$$DS=\frac{W_s-W_d}{W_d}\times 100\% \tag{5}$$

where W_s and W_d represent the weight of the swollen and dry membranes, respectively.

The desorption experiment was conducted in one of the parallel two-stage condensers equipped in PVFC apparatus but with Valve 6 closed. The swollen membrane of known weight was put in the first cold trap which was immersed in a hot-water bath of 80°C, and the second cold trap used to collect condensed liquid was immersed in liquid nitrogen. The two cold traps placed in series were connected to vacuum pump. The pressure of the vacuum was maintained at 330 Pa, which was in accordance with the permeate pressure kept in the PVFC experiment. The swollen membrane was removed at different time intervals from the first trap and weighed until no significant weight change was detected. Then, the water content of the condensed liquid collected in the second trap was analyzed by the Karl Fisher moisture analyzer. All the data presented represent an average of three repeated experiments. The sorption selectivity of the membrane was defined as follows

$$\alpha=\frac{Y_a/Y_w}{X_a/X_w} \tag{6}$$

where X and Y represent the weight fractions in the feed and swollen membranes, and subscripts a and w denote the aniline and water components, respectively.

Aspen simulation

The permeate vapor from the downstream side of the membrane successively passed through the first and the second condensers set at different temperatures and was subjected to condensation. After experimental measurement, the condensation process was simulated by Aspen Plus v7.1 software. The flowsheet of condensation process was established in Aspen Plus and shown in Figure 2. The flash tank was functioned as the first condenser (fractional condenser), while the heat exchanger was functioned as the second condenser (complete condenser). At each given permeate pressure, the temperature of the flash tank was adjusted to be a proper temperature range for the preferential condensation of aniline, and then the temperature of the heat exchanger was adjusted to be the highest value at which the residual permeate vapor that escaped from the flash tank was still trapped completely. Then, the purity and production rate of condensed permeate and residual permeate were obtained. Nonrandom two-liquid (NRTL) equation was used to carry out the above calculations and aniline-water phase diagram simulation.

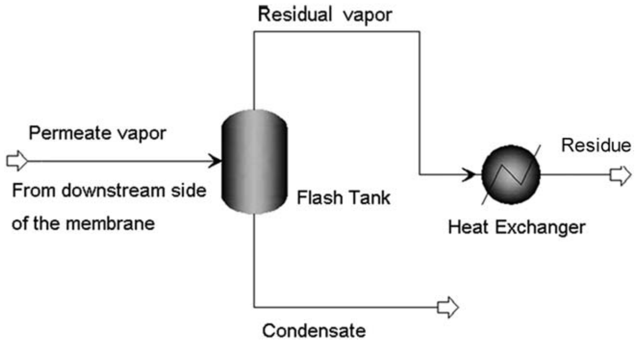

Figure 2. Aspen Plus flowsheet of fractional condensation process.

Results and Discussion

Membrane swelling and preferential sorption

According to the solution-diffusion model, pervaporation is a membrane process that can be described by the combination of sorption and diffusion. In the area of organophilic pervaporation, the molecule sizes of organic compounds are usually larger than that of water molecule, which hinders the preferential transport of the organic molecules through the membrane.[33,40] Therefore, sorption may significantly contribute to the permeability than diffusion. The sorption behaviors of PEBA-2533 membrane in aqueous aniline solutions were thus investigated in terms of the degree of swelling and sorption selectivity. The degrees of swelling of the membranes in aniline/water solutions at different compositions are presented in Figure 3a. It can be seen that the degree of swelling of membrane in pure water was equal to 0, which was due to the negligible sorption of water in PEBA-2533 membrane.[41] The degree of swelling increased significantly from 0 to 56.7 wt % as the feed aniline content increased from 0 to 3 wt %. This result indicated that the membrane had good affinity toward aniline, which may be explained by the solubility parameters of aniline and PEBA-2533 membrane. According to solubility parameter theory, the smaller the difference in their solubility parameters, the greater their mutual solubility is.[8] As can be seen from Table 1, the solubility parameter of PEBA-2533 membrane was 19.51 $(J/cm^3)^{1/2}$, which was close to that of aniline (21.1).[42,43] In addition, aniline is only partially miscible with water. This means that the interaction between aniline and water molecules is relatively weak, which may also favor the sorption of aniline onto the membrane. In order to further investigate the preferential sorption property, the composition of the sorbates in the membrane was measured. The sorption isotherms of aniline and water in the membranes at different aniline concentrations are illustrated in Figure 3b. It can be seen that the sorbed aniline contents were extremely high (96.1–97.2 wt %), and it did not change significantly under a relatively high aniline concentration studied. Therefore, the sorption separation factor, a parameter to describe sorption step, was found to be 6663–796. These results further confirmed the excellent affinity of PEBA-2533 membrane to aniline, which was expected to result in excellent pervaporation performance.

Table 1. The Physical Properties of Aniline and Water

Property	Aniline	Water
Molecular formula	$C_6H_5NH_2$	H_2O
Relative density (water = 1)	1.02	1
Molecular weight (g/mol)	93.1	18
Boiling point (°C)	184	100
Solubility in water (g, 100 ml at 20°C)	3.4	—
Heat of evaporation (kJ/kg)[a]	475.2	2264.7

[a]Calculated using Aspen plus V7.1.

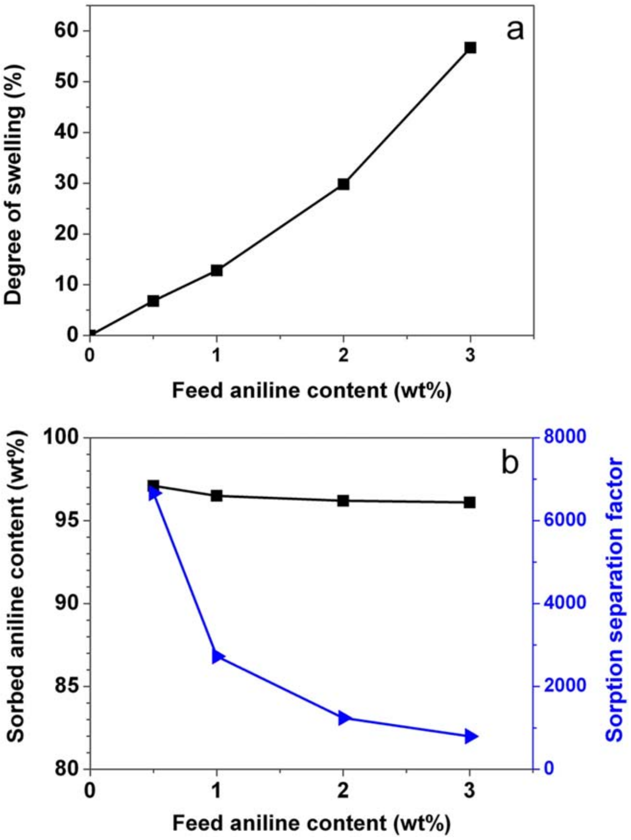

Figure 3. Degree of swelling of membranes in aniline/water mixtures at 80°C (a) and sorption separation factors and sorbed aniline contents in aniline/water mixtures at 80°C (b).

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The operational feasibility of PVFC for aniline/water system

Since aniline is a high-boiling organic compound, its saturated vapor pressure is much lower than that of water at the same temperature. The specific vapor pressures of aniline and water are shown in Figure 4, which were obtained with the aid of the Aspen Plus V7.1 software. As shown in Figure 4, it is evident that vapor pressure of aniline is much lower than that of water at the same temperature. For example, at −20°C, vapor pressure of water is approximately equal to 100 Pa, while vapor pressure of aniline is only 2 Pa. This indicates that equilibrium composition of aniline in binary aniline-water vapor mixture should be at a much lower level. Due to the excellent membrane permselectivity for aniline, the aniline concentration in the permeate could reach up to 70 wt % (see Figure S1b in the Supporting Information), thereby yielding a much higher partial pressure of aniline than its equilibrium partial pressure in the permeate vapor. Therefore, when the

Table 2. Input Parameters for Calculating Energy Requirements by Aspen Plus

Temperature (°C)[a]	Pressure (Pa)[a]	Volume Flow (m^3/hr)[b]	Temperature of Flash Tank (°C)	Temperature of Heat Exchanger (°C)
30	330	187.5	−10	−13
30	480	156.8	−1	−7
30	970	101.5	8	5
30	1800	61.9	17	14

Mass flows of aniline and water were shown in Figure S3 (Supporting Information). The pressures in flash tank and heat exchanger are equal to inlet pressure.
[a] Input parameters of flash tank inlet.
[b] Volume flow-normalized per unit of the permeate.

vaporous aniline-water mixture passes the first condenser, a significant portion of aniline vapor could be preferentially condensed by appropriately regulating its temperature. The partial vapor pressures of aniline and water at the feed side are governed by vapor-liquid equilibrium, whereas the content of aniline in the vaporous aniline-water mixture at the permeate side is significantly enriched by the pervaporation membrane. However, after passing through the first condenser, the composition of the vaporous aniline-water mixture will return back to its equilibrium composition because the thermodynamic equilibrium is established again. As far as the purity of aniline recovered in the first condenser is concerned, the selection of temperature of the first condenser is of great importance. This mainly depends on the vapor partial pressure of water in permeate vapor. For example, the permeate pressure in the present study was maintained at about 330 Pa and the mole fraction of aniline can be estimated using the overall permeate aniline concentration.[14] Therefore, the proper temperature for aniline condensation in the first condenser can be estimated at a given downstream pressure.

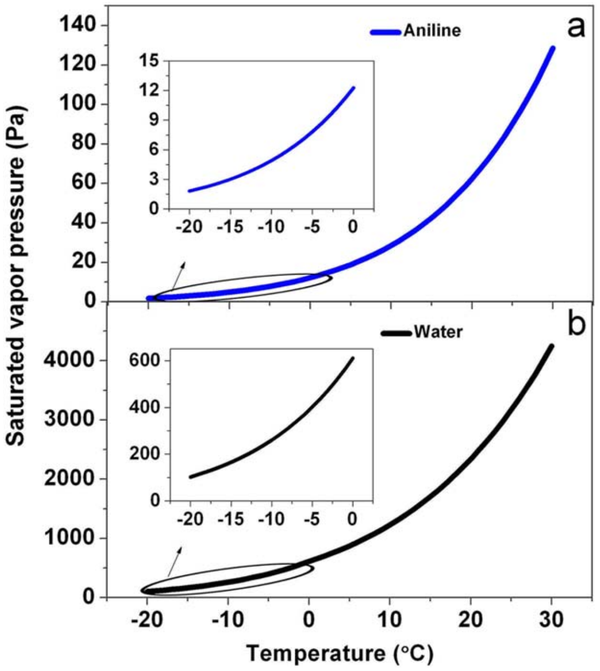

Figure 4. Saturated vapor pressures of water and aniline as a function of temperature.

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Effect of the first condenser temperature on the performance of PVFC at various permeate pressure

Temperature of the first condenser and permeate pressure may have significantly effects on the performance of PVFC system. When the two parameters were investigated, feed concentration and feed temperature were set at the fixed values. At given feed concentration and temperature, the overall permeation rate and permeate composition kept constant. Variation of the first condenser temperature could affect the concentration of residual aniline collected in the second condenser, that is, it could affect the distribution of the aniline permeated through the membrane in each condenser. Variation of the permeate pressure could simultaneously affect the separation performance of pervaporation membrane and thermodynamics of the phase equilibria. By varying the first condenser temperature and permeate pressure, the purity and production rate of aniline recovered in the two condensers can be experimentally measured. In addition, the condensation process was also simulated by Aspen Plus v7.1 software. Various parameters of the flash tank inlet (e.g., total flux, permeate composition, temperature and pressure) were shown in Table 2 and Figure S3 of Supporting Information. The experimental and simulation results of the purity and residual concentration of aniline recovered in each condenser were shown in Figure 5. As can be seen from Figure 5a, the purity of aniline recovered in the first condenser was found to increase sharply and then increase slowly with the increase of the first condenser temperature at various pressures, thus resulting in an inflection point on each curve, and the experimental and simulation results were generally in good agreement. As the permeate pressure increased, the condensation temperature at each inflection point became higher, which was due to the increase of the partial pressure of water in the first condenser. At each given permeate pressure, there is a temperature at which aniline and water vapors were completely trapped in the first condenser. As shown in Figure 5a, the temperatures were −13°C at permeate pressure of 330 Pa, −7°C at 480 Pa, 5°C at 970 Pa, and 14°C at 1800 Pa, respectively. At these four pairs of pressure and temperature, the purity of aniline varied significantly from 69 to 23 wt %, which was due to the significant effect of permeate pressure on the separation performance of pervaporation membrane. This result was also shown in Figure S3 of Supporting Information. As can be seen from Figure 5b, at a given permeate pressure of 330 Pa, the residual aniline concentration increased significantly with the increase in the temperature of the first condenser, and the experimental and simulation values were found to be in good agreement. At −12°C, the measurement result of residual aniline concentration in the second condenser was 4.9 wt %, and the purity of

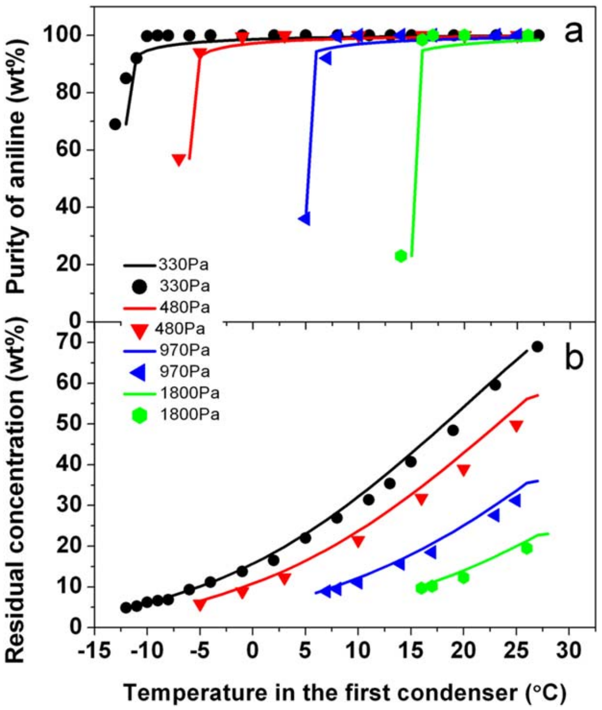

Figure 5. Effect of temperature of the first condenser on the purity of aniline recovered and residual aniline concentration at various permeate pressure (solid line: Aspen simulation, dot: experimental values; feed concentration, 3.6 wt %; feed temperature, 70°C).

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aniline recovered in the first condenser was 85 wt %. This indicates that a small portion of water vapor was also trapped in the first condenser. When the temperature of the first condenser was increased to −10°C, the concentration of residual aniline in the second condenser increased to 6.2 wt %, while the purity of aniline in the first condenser increased drastically to 99.7 wt %. This reveals that almost no water vapor was condensed in the first condenser. This result can be understandable because the partial pressure of water (227 Pa) is lower than its equilibrium pressure (259.9 Pa) at −10°C. It is found that the purity of aniline recovered could reach as high as 99.99 wt % when the temperature of the first condenser exceeded −9°C. However, when the temperature of the first condenser was increased to 27°C, no aniline vapor in the permeate was trapped in the first condenser, and all the permeates were condensed in the second condenser to yield the highest aniline concentration of 69 wt %. Therefore, the temperature in the first condenser should be set in a range of −10 to 27°C in order to condense the aniline vapor in the permeate. However, the proper temperature range for aniline condensation became narrow as the permeate pressure increased, which was mainly caused by two aspects. One is that the phase-change temperature of water in the first condenser became higher due to the increase of partial pressure of water; the other is that the increase of permeate pressure caused the significant decrease of overall permeate concentration (see Figure S3 of Supporting Information), which hindered the increase of partial pressure of aniline. The above-mentioned thermodynamic property of aniline-water vapor mixtures is similar with that of phenol/water mixtures under low pressure.[14]

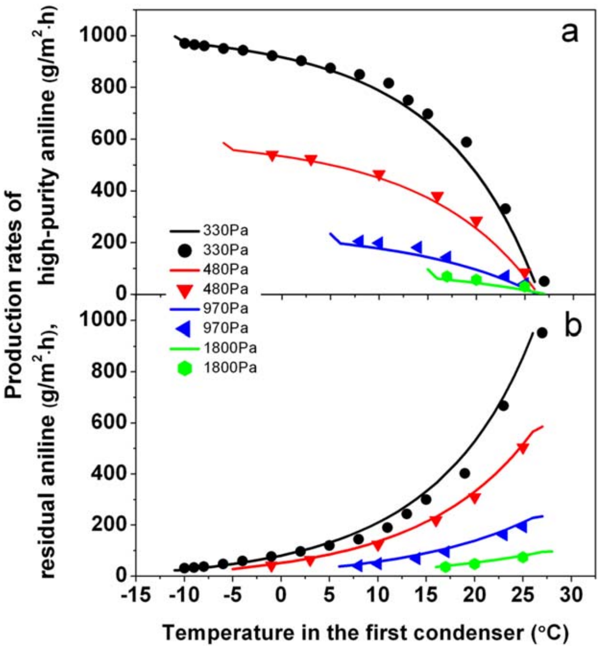

Figure 6. Effect of temperature of the first condenser on the production rate of high-purity aniline and the rate of residual aniline at various permeate pressure (solid line: Aspen simulation, dot: experimental values; feed concentration, 3.6 wt %; feed temperature, 70°C).

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Figure 6 shows the effect of temperature in the first condenser on the production rate of high-purity aniline and the rate of residual aniline at various permeate pressures. It can also be seen that the experimental and simulation results were in good agreement. At a given permeate pressure of 330 Pa, it is evident that with the increase in the temperature in the first condenser, the production rate of high-purity aniline decreased, while the rate of residual aniline increased accordingly due to the constant permeate rate of aniline through the membrane. At a feed concentration of 3.6 wt % and temperature of 70°C, aniline with a high purity of 99.7% can be continuously recovered at a production rate of 965 g/(m^2 h) in the first condenser when its temperature was kept at −10°C. However, the production rate of high-purity aniline decreased significantly as the permeate pressure increased. As far as the production rate is concerned, the permeate pressure should be set at a relatively low value. Figure 7 shows the energy required for evaporation and condensation of per unit of high-purity aniline recovered and the high-purity aniline production rate as a function of permeate pressure. The heat required for condensing the permeate (named as heat duty in Aspen Plus) is the sum of heat duty of flash tank and heat exchanger, and it is approximately the same as the heat required for the evaporation step.[12] As shown in Figure 7, the production rate of high-purity aniline decreased notably with the increase in the permeate pressure, while the energy required for evaporation and condensation of per unit of high-purity aniline recovered increased linearly. This is mainly because the increase of permeate pressure significantly reduced the driving force for aniline permeation, then resulting in the significant decrease of aniline content in the permeate (see Figure S3 in Supporting Information). Taking into account the energy required for evaporation and condensation steps and the production rate of high-purity aniline recovered, the permeate pressure should be set at a relatively low value. However, when the permeate pressure was low enough, energy requirement for vacuum pump will become more significant. The permeate pressure to be maintained and the volume flow rate may be the two major factors for choosing a suitable vacuum pump. The volume flow rate of the vaporous permeate at various permeate pressures, normalized per unit of the permeate, was calculated by Aspen Plus and shown in Table 2. It is evident that the volume flow increased notably with the decrease in the permeate pressure. This variation trend was opposite to that of energy required for the evaporation and condensation steps. However, the final permeate pressure still need to be optimized by engineering costs (e.g., investment costs and operating costs). The above analysis only identified the general trends of permeate pressure effect on energy requirements.

Figure 8 shows pictures of analytical grade aniline and aniline permeate samples obtained by one-stage and two-stage condensers. Analytical grade aniline is colorless, but it is readily oxidized and turns brown when it is exposed to air or sunlight. As shown in Figure 8a,b, analytical grade aniline was found to turn brown when it was exposed to air for one week, while the high-purity aniline recovered in the first condenser operated at −10°C remained colorless. Figure 8c shows the remaining aniline-water mixture collected in the second condenser, which consisted of two phases where the top aqueous phase were colorless and the bottom organic phase were brown, respectively. Figure 8b,c indicate that the colored oxides could penetrate the membrane but be not trapped in the first condenser. The aniline permeate sample shown in Figure 8d was collected by the one-stage condenser, where the bottom organic phase further indicated that the oxides penetrated the membrane. When the aniline recovered in the first condenser was exposed to air, it turned brown again, as shown in Figure 8e.

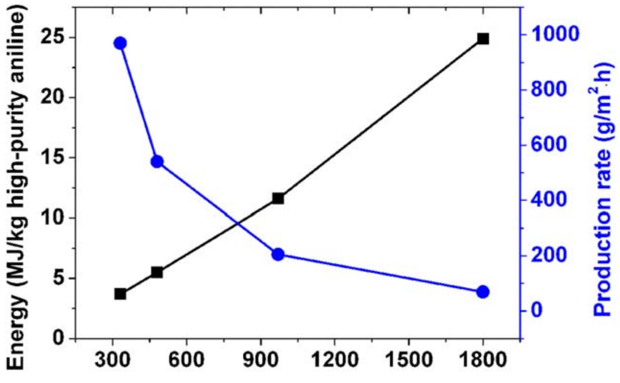

Figure 7. **Energy required for evaporation and condensation of per unit of high-purity aniline recovered and the high-purity aniline production rate as a function of permeate pressure (feed concentration, 3.6 wt %; feed temperature, 70°C).**

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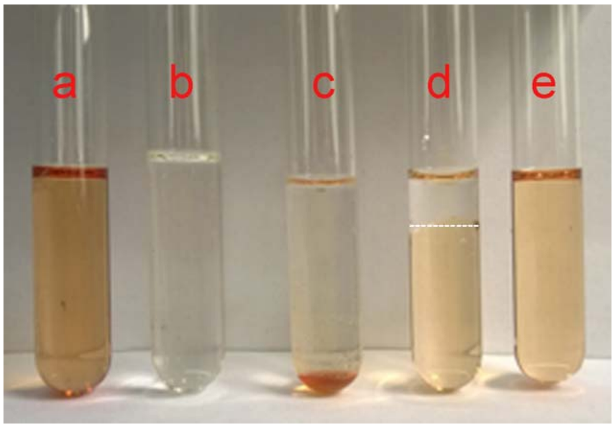

Figure 8. **Photograph of analytical grade aniline (a), pure aniline recovered in the first condenser (b), remaining aniline-water mixture collected in the second condenser (c), aniline-water mixture recovered in a single condenser (d) and pure aniline recovered exposed to air.**

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Effects of aniline concentration in the permeate on the phase-change temperature of aniline and water vapors

Figures 5 and 6 also present the effects of downstream temperature (the first condenser) and pressure on the distribution of aniline in each condenser when the feed concentration and temperature were maintained constant. For example, at a given permeate pressure of 330 Pa, the results shown in Figure 5 indicated that the suitable temperature range for aniline condensation was from −10 to 27°C. However, the permeate composition was mainly affected by the aniline concentration in the feed, which further affected partial pressure of aniline and water in permeate vapor. Therefore, the phase-change temperature of aniline and water vapors at different permeate compositions also need to be investigated. At a given permeate pressure of 330 Pa, the phase-change temperatures of aniline and water were measured at various permeate compositions, respectively. The method for experimentally measuring phase-change temperatures was the same as that used in Figure 5. For aniline vapor, each aniline concentration in the permeate (permeate composition) was determined at first by varying feed concentration from low to high and then the temperature of first condenser was varied from low to high in order to determine the exact temperature at which the concentration of residual aniline in the second condenser was equal to that of the given permeated aniline. For the water vapor, the phase-change temperatures at various permeate compositions were determined by measuring the water content in the aniline recovered in the first condenser. If the water content in the aniline sharply increases at a certain temperature under a given permeate composition, the phase-change temperature of water vapor can be determined. As a matter of fact, these data can be obtained from aniline-water binary phase diagram under a given pressure. However, the phase diagram at a specific pressure was not available from the literature. Aspen Plus V7.1 software was used to calculate the dew point and bubble point temperatures at different permeate compositions, and these data along with the experimental data are shown in Figure 9. As shown in Figure 9, the experimental and simulation values of phase-change temperatures of aniline and water vapors as a function of the permeate composition were found to be in good agreement, and the suitable temperature ranges for aniline condensation became much broader as the aniline concentration in the permeate increased. This indicates that a higher permeate aniline concentration favors the precipitation of

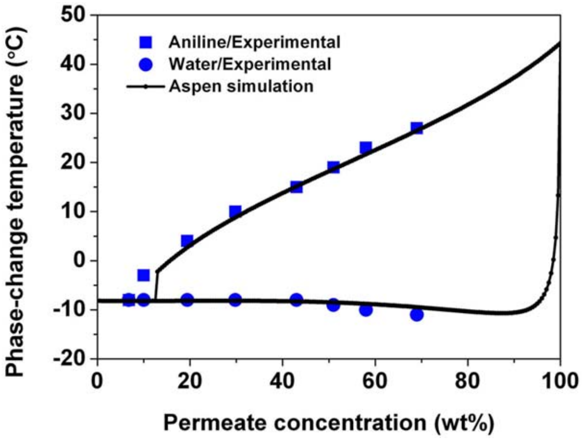

Figure 9. Effect of aniline concentration in the permeate on the phase-change temperature of aniline and water vapors, respectively (permeate pressure used in Aspen simulation: 330 Pa).

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aniline in the first condenser. At the permeated aniline concentration of 6.9 wt %, the phase-change temperature of aniline vapor was equal to that of water vapor. This is the minimum overall aniline concentration in the permeate side for preferential aniline condensation in the first condenser. As the aniline concentration in the permeate increased, the phase-change temperature of aniline vapor increased significantly while the phase-change temperature of water decreased slightly. This is mainly caused by the variation of partial pressure of aniline under a permeate pressure of 330 Pa.

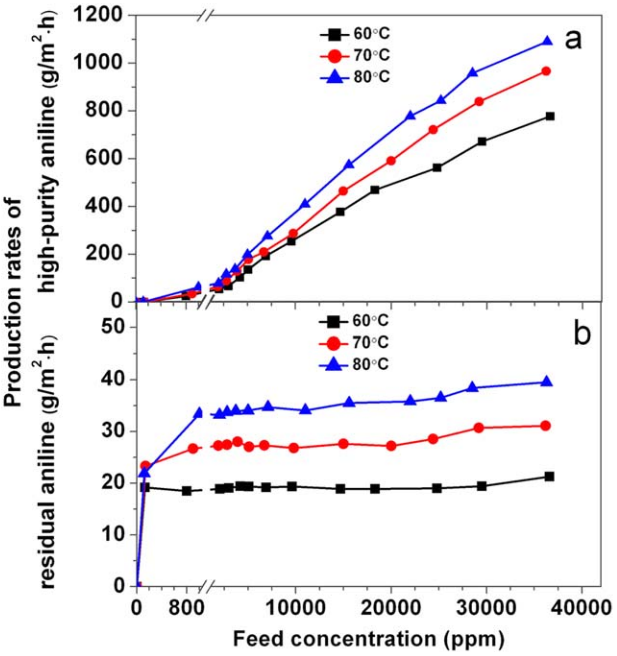

Figure 10. Effects of feed concentration on the production rate of high-purity aniline and the rate of residual aniline collected at various temperatures (temperature of the first condenser: −8°C; permeate pressure: 330 Pa).

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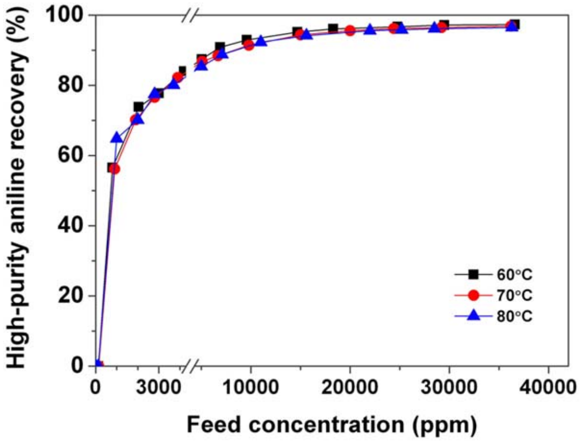

Figure 11. Effect of feed concentration on percentage high-purity aniline produced relative to total quantity of aniline permeated at various temperatures (temperature of the first condenser: −8°C; permeate pressure: 330 Pa).

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Effect of feed concentration and temperature on the performance of PVFC

In order to investigate the influence of feed concentration and temperature on the production rate of high-purity aniline recovered in the first condenser and the rate of residual aniline collected in the second condenser, the temperature in the first condenser was maintained at −8°C at which water vapor

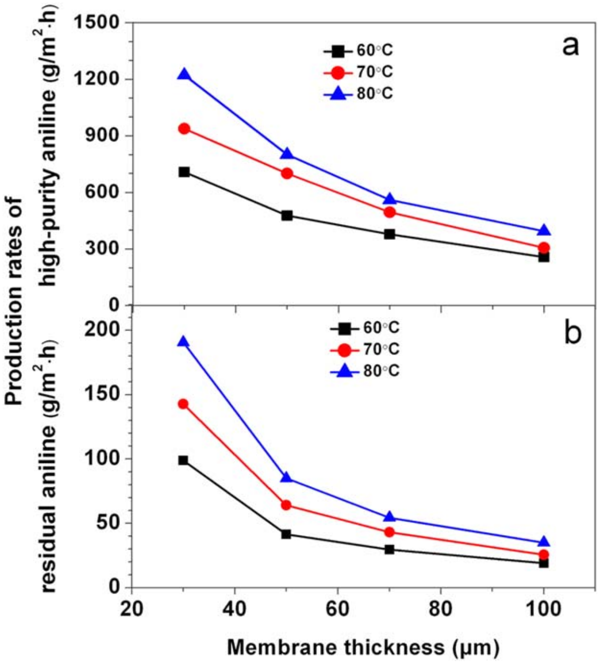

Figure 12. Influence of membrane thickness on the production rate of high-purity aniline and the rate of residual aniline collected at various temperatures (feed concentration, 1 wt %; temperature of the first condenser, −8°C; permeate pressure: 330 Pa).

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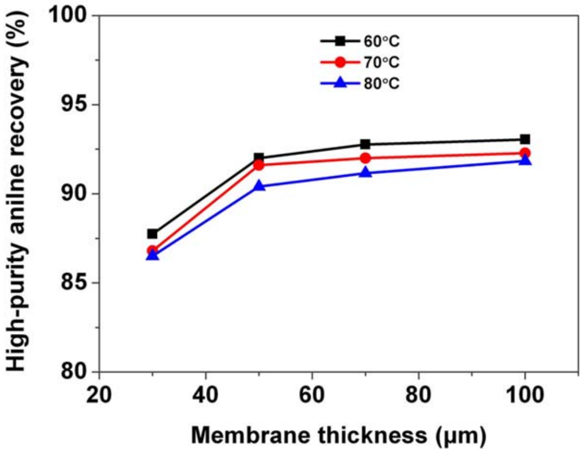

Figure 13. Influence of membrane thickness on high-purity aniline recovery at various temperatures (feed concentration, 1 wt %; temperature of the first condenser, −8°C; permeate pressure: 330 Pa).

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would not be condensed in the first condenser in the concentration range studied. Figure 10 shows the effects of feed concentration on the production rate of high-purity aniline and the rate of residual aniline collected in the second condenser at different temperatures. At a given feed temperature, the rate of high-purity aniline collected was found to increase significantly with the increase in the feed aniline concentration, while the rate of residual aniline collected as an aniline-water mixture was almost constant when the feed aniline concentration was above 800 ppm. When the feed aniline concentration was at a low level (e.g., below 800 ppm), aniline vapor could not be trapped in the first condenser due to the much lower aniline concentration in the permeate (<6.5 wt %). It is also observed that at a given feed concentration, a higher feed temperature resulted in more aniline collected in both condensers. The variation trend of production rate of high-purity aniline and the rate of residual aniline as a function of feed concentration was the same as that of phenol in our previous work.[14] It is possible that the thermodynamic properties of aniline and phenol under low pressure are similar. At a feed temperature of 80°C and a feed concentration of 3.6 wt %, the production rate of high-purity aniline recovered was as high as 1090.2 g/(m^2 h), while the rate of residual aniline collected was only 39.5 g/(m^2 h). These impressive results could be mainly attributed to the perfect integration of high-performance pervaportion membrane with the operation of fractional condensation, where the pervaporation membrane acted as barrier for aniline enrichment while the operation of fractional condensation was used to condense the excessive aniline in the permeate.

Figure 11 shows the effect of aniline concentration in the feed on the percentage high-purity aniline produced relative to the total quantity of aniline permeated at various temperatures. It can be seen that the recovery of high-purity aniline increased significantly with the increase in feed aniline concentration, but the increase rate became slow when the aniline concentration in the feed was sufficiently high. When the feed aniline concentration was about 1000 ppm, the recovery already reached 64.8%. A further increase in the feed aniline concentration to 10,000 ppm yielded a recovery of high-purity aniline of 92.3%. It is found that 97.3% high-purity aniline recovery can be obtained at 60°C with a feed containing 3.6 wt % aniline. These results are easy to be understood because the production rate of high-purity aniline increased significantly with increasing feed concentration, while the rate of residual aniline collected in the second condenser did not change significantly (shown in Figure 10).

Effect of membrane thickness on the performance of PVFC

Due to the high sorption selectivity of PEBA-2533 toward aniline, the pervaporation separation factor was in the range of 200–54 using a membrane with a thickness of 100 μm under the concentration range studied (see Figure S1e in the Supporting Information). It is expected to obtain a high permeation flux with an acceptable separation factor. Therefore, the influence of membrane thickness on the production rate of high-purity aniline and the rate of residual aniline collected at various temperatures were investigated. As shown in Figure 12, the production rate of high-purity aniline and the rate of residual aniline decreased with the increase in membrane thickness. It is evident that the rate of aniline collected in both condensers increased with the increase in feed temperature, and the observed tendency became pronounced when the membrane thickness was 30 μm. The production rate of high-purity aniline varied in the range of 256.8–1222.5 g/(m^2 h) under the membrane thickness range studied while the rate of residual aniline was found to be 19.2–190.7 g/(m^2 h). Especially, at a membrane thickness of 30 μm, the production rate of high-purity aniline was as high as 1222.5 g/(m^2 h) with an acceptable membrane separation factor of 51 in the recovery of aniline from 1 wt % aniline aqueous solution at 80°C (see Figure S2e in Supporting Information).

Figure 13 shows high-purity aniline recovery as a function of membrane thickness at various temperatures. As can be seen from Figure13, high-purity aniline recovery increased with the increase in membrane thickness, but the increase extent became slow when the membrane thickness was above 50 μm. Also, it can be seen that the feed temperature had some influence on the high-purity aniline recovery. In a word, aniline concentration in the permeate side had direct impact on the aniline recovery, and the higher permeate aniline concentration resulted in the higher the aniline recovery. Therefore, the results shown in Figure 13 are easy to be understood because the permeate aniline concentration increased with the increasing of membrane thickness but decreased with the increase of feed temperature (see Figures 1Sb and 2Sb in the Supporting Information). The detailed analysis of the influence of membrane thickness on the pervaporation separation factor has ever been reported by Fouad[44] for the pervaporation of aqueous butanol. From the data shown in Figures 12 and 13, it is clear that in order to obtain a high production rate of high-purity aniline, the recovery had to be compromised. However, in this study, compared to the residual aniline collected in the second condenser, the production rate of high-purity aniline as high as 1222.5 g/(m^2 h) with a recovery of 86.5% should be a satisfactory result for the membrane with a thickness of 30 μm.

Conclusions

Recovery of high-purity aniline with a high production rate was achieved by using a PVFC coupling system. It is identified that this system perfectly integrated the excellent pervaporation performance with the fractional condensation operation. PEBA-2533 membrane displayed excellent sorption selectivity toward aniline and preferential permeance of aniline. The membrane selectivity to aniline was varied from 360 to 33 in the feed aniline concentration range of 5000–36,000 ppm. The temperature of the first condenser and downstream pressure had great effect on the performance of PVFC. The experimental and Aspen simulation results on the purity and production rate of aniline were in good agreement. A relatively low downstream pressure and the first condenser temperature were desired, which were in favor of obtaining a high production rate along with high recovery efficiency. However, the optimum permeate pressure still need to be optimized based on engineering cost evaluation. The phase-change temperature of aniline vapor increased with the increase in aniline concentration in the permeate, while the initial phase-change temperature of water vapor had no change and only decreased a little thereafter, and these experimental results are also in agreement with the simulation results very well. The feed concentration had significant effect on the production rate of high-purity aniline recovered. Production rate of high-purity aniline as high as 1222.5 g/(m^2 h) with a satisfactory pervaporation separation factor of 51 was achieved in the recovery of aniline from 1 wt % aniline aqueous solution at 80°C using the PEBA-2533 membrane with a thickness of 30 μm.

Acknowledgments

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