Separation of Methanol from Methanol/Water Mixtures with Pervaporation Hybrid Membranes

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ABSTRACT: A series of pervaporation (PV) hybrid membranes were prepared via the crosslinking of poly(vinyl alcohol) with formaldehyde solution with N-3-(trimethoxysilyl) propyl ethylenediamine (TMSPEDA) as a hybrid precursor of the sol–gel process. Both the thermal stability and separation performances of the prepared hybrid membranes were investigated. Thermogravimetric analysis showed that the thermal degradation temperature of the hybrid membranes was beyond 250°C. Differential scanning calorimetry indicated that both the glass-transition temperature and the crystallization temperature increased with elevated TMSPEDA contents in the hybrid membranes. PV experiments demonstrated that for membranes A–D, both the permeation flux and separation factor indicated the same trade-off effect. Moreover, it was found that for individual membranes, the permeation flux increased as the feed temperature was increased. Meanwhile, the separation factor revealed an change trend opposite to that of the permeation flux. Furthermore, proper addition of TMSPEDA in the hybrid membrane was found to reduce the permeation activation energy. On the basis of these findings, we deduced that these hybrid membranes have potential applications in the separation of methanol/water mixtures. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 000: 000–000, 2012

INTRODUCTION

Poly(vinyl alcohol) (PVA) is an environmentally friendly biopolymer and is found many applications in various fields.[1–3] For example, PVA has been widely used in the membrane separation field because of its excellent film-forming properties and structural flexibility.[2–4] In particular, PVA-based polymeric membranes can be used to separate volatile liquids by the pervaporation (PV) technique; this indicates promise for applications in alcohol/water mixtures.[3,5] Although organic PVA-based membranes reveal excellent film-forming properties, they also exhibit disadvantages, such as a lower mechanical strength and thermal stability.[4,6] Thus, improving their mechanical strengths and thermal stabilities are a key consideration for expanding their PV applications. Presently, it is well accepted that the addition or grafting of inorganic filler into an organic matrix can effectively improve the separation properties of PVA-based polymeric membranes.[3,7–10] Various related studies via the incorporation of inorganic compositions into PVA-based membranes have thus been developed. For example, Zhang et al.[3] prepared PVA/γ-aminopropyltriethoxysilane (APTEOS) hybrid membranes for the separation of ethanol/water mixtures and found that the trade-off between the permeation flux and water permselectivity could be effectively resolved by the incorporation of inorganic silica. Kulkarni et al.[9] prepared PVA/tetraethoxysilane (TEOS) hybrid membranes to separate water/isopropyl alcohol mixtures and found that a membrane containing a 1.5 : 1 mass ratio of TEOS to PVA gave the highest separation selectivity of 900 at 30°C for 10 wt % water in the feed mixture. On the basis of the inorganic/organic hybrid technique, it was found that the mechanical strength and thermal stability of PVA-based membranes were highly elevated. Meanwhile, the PV separation performances of PVA-based hybrid membranes were also increased. Consequently, PV is a promising and efficient method for the separation of alcohol/water mixtures with hybrid membranes.

Currently, with the development of coal-based methanol to olefins for replacing petroleum-based fuels or natural gas,[11] the demand for coal-based methanol derived from coal gasification has turned into a hot topic in the field of the coal chemical industry. Accordingly, water pollution from volatile methanol has also increased. As a result, a method for methanol removal from wastewater is significantly important and highly in need. Hopefully, this volatile methanol in liquid media can be removed with the PV technique.

Table I. Compositions of the Prepared PV Hybrid Membranes A–D

Membrane	PVA (g)	Formaldehyde (mL)	TMSPEDA (mL)
A	3	3	2
B	3	3	3
C	3	3	4
D	3	3	5

Recently, an attempt was made to prepare PV hybrid membranes.[12] It was found that the thermal stability of these newly developed membranes could be highly increased compared to those of pure organic ones. Our interest in this type of PV hybrid membranes stimulated us to examine them further. Therefore, to get insight into the impact of the inorganic composition on the thermal stability of PVA-based membranes and to remove methanol from methanol/water mixtures, herein, a novel route for synthesizing PVA-based hybrid membranes for PV applications is proposed. A series of PVA-based hybrid membranes were prepared via the crosslinking of PVA with formaldehyde and a subsequent sol–gel process with *N*-3-(trimethoxysilyl)propyl ethylenediamine (TMSPEDA) as a hybrid precursor of the sol–gel process. It was expected that PVA could be used as an organic moiety to improve the affinity for methanol, and TMSPEDA was used as inorganic moiety to increase the thermal stability of the hybrid membranes. Moreover, the PV performances of these hybrid membranes for the separation of methanol/water mixtures were examined. It is hoped that these PV hybrid membranes can be applied in the removal of methanol from wastewater in the coal-based methanol industry.

EXPERIMENTAL

Materials

TMSPEDA (purity $\geq$ 95.0%) was purchased from Jiangsu Chenguang Coincident Dose Co., Ltd. (Danyang City, China) and was used without further purification. PVA (molecular weight = 1750) and methanol (purity $\geq$ 99.5%) were purchased from Shanghai Chemical Reagent Co., Ltd. (Shanghai, China) and were used as received. Other reagents were analytical grade and were used as received.

Hybrid Membrane Preparation

The PV hybrid membranes used in this case were prepared by the reaction of different amounts of TMSPEDA with aqueous PVA solution (3 wt %), which was crosslinked by a formaldehyde solution (the compositions of membranes A–D are listed in Table I). As a typical example, the preparation procedure for membrane A is described briefly as follows.

First, 3 g of PVA was dissolved in 100 mL of deionized water at 90°C to produce an aqueous PVA solution (3 wt %). Second, 2 mL of TMSPEDA was added dropwise to the previously-prepared aqueous PVA solution, and this mixture was stirred vigorously at room temperature for an additional 5 h. Third, 3 mL of formaldehyde solution (40 wt %) was added dropwise to the previously prepared aqueous PVA solution for 2 h to conduct the crosslinking reaction. After the completion of the aforementioned crosslinking

reaction, the mixed PVA solution was aged for 10 h to produce a coating solution for membrane preparation. The coating solution of the PVA-based PV hybrid membranes was thus obtained. Subsequently, the coating solution was cast onto a glass plate and air-dried at room temperature for 2 h. Finally, it was kept at 50°C for 12 h to obtain the desirable PV hybrid membrane.

Thermal Analysis

Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) of the hybrid membrane samples were performed with a Netzsch STA 409 PC/PG thermogravimetric analyzer (Selb, Germany) under a nitrogen flow with a heating rate of 20°C/min from 40 to 400°C.

PV Experiments

PV experiments were conducted with a PV separation setup described in another article.[12] In this study, the feed temperatures were 30, 40, and 50°C, and the methanol contents in the feed were 20, 40, and 60 vol %, respectively. The contents of the feed solution and penetrant were determined with a gas chromatograph equipped with a flame ionization detector (FID) and capillary column (SP-2100A, Beijing Beifen-Ruili Analytical Instrument Co., Ltd., Beijing, China). The membrane PV performances of permeation flux (J_P; g m^{-2} h^{-1}) and the separation factor (α) could be calculated from eqs. (1) and (2):[13]

$$J_P = \frac{w}{At} \quad (1)$$

$$\alpha = \frac{P_m/P_w}{F_m/F_w} \quad (2)$$

where W is the weight of the penetrant collected (g) in permeation time t (min), A is the effective membrane area (m^2), and P and F are the weight fractions in the penetrant and feed solution, respectively. The subscripts of m and w denote methanol and water, respectively.

RESULTS AND DISCUSSION

Hybrid Membrane Preparation

The coating solution for the PVA-based PV hybrid membranes was prepared by the crosslinking of the —OH groups in the PVA molecular chains with the Si—OH groups in the molecular chains of TMSPEDA to produce the O—Si—O linkage via sol–gel process in the presence of formaldehyde; this was similar to the preparation of hybrid proton-exchange membranes reported in an article.[14] The PV hybrid membrane could thus be obtained by the casting of the previously prepared coating solution onto a glass plate and drying in an oven. The possible reaction of PVA-based hybrid membrane formation is illustrated in Scheme 1.

Notice that when PVA was crosslinked with the formaldehyde solution, it got very viscous and hard to be spread to form a membrane. However, it has been reported in some published articles[3,14–16] that when the concentration of an aqueous PVA solution is below 5 wt %, it can be easily spread to produce a membrane. In this case, the concentration of PVA was near 3 wt %, so the preparation of crosslinked PVA membranes could thus be performed.
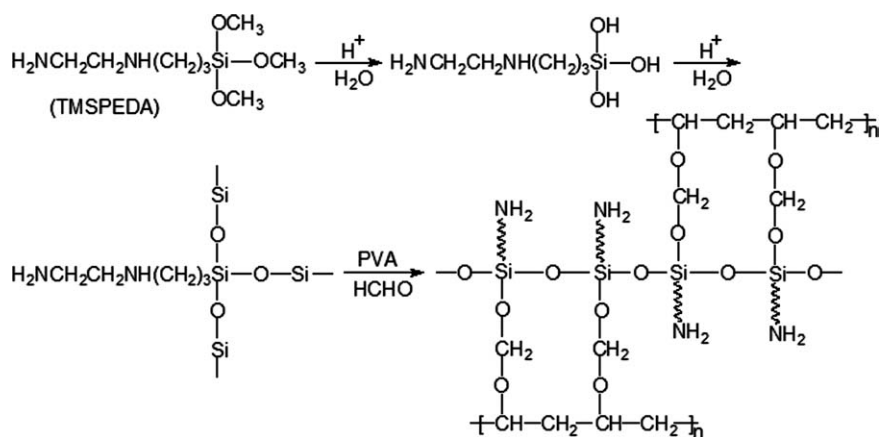
Scheme 1. Possible reaction during PVA-based hybrid membrane formation.

TGA

To examine the thermal stability of the previously-prepared PV hybrid membranes, TGA was conducted, and the corresponding curves are illustrated in Figure 1. For comparison, the thermal analysis data of these membranes obtained from the TGA curves are listed in Table II.

As shown in Figure 1, for membranes A–D, their change trends for weight loss (%) were similar, and two degradation steps were found. Corresponding to these degradation steps, several small exothermic peaks were found in the DSC curves (as indicated in Figure 2). The first weight loss was attributed to the removal of bonded water in these membranes, the decomposition of PVA,[15] and the breakage of functionalized groups in the molecular chains. The second weight loss beyond 250°C was ascribed to the further decomposition of polymer chains and the formation of a hybrid matrix.

Moreover, it can also be seen in Figure 1 that for membranes A–D, the degradation temperature at 5% weight loss (i.e., T_{d5}) decreased with the addition of TMSPEDA; this demonstrated that the functionalized groups in the TMSPEDA chains were easily degraded at low temperature. In contrast, the degradation temperature at 20% weight loss (i.e., T_{d20}) increased with increasing content of TMSPEDA; this suggested that sintering at high temperature benefitted the formation of the hybrid matrix
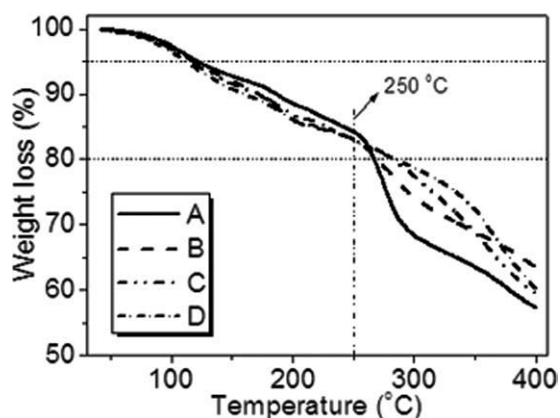
(cf. Table II). In addition, we observed that the weight loss percentage of these membranes increased rapidly when the degradation temperature (T_d) value exceeded T_{d20}. This suggested that the thermal decomposition was accelerated. This finding revealed that the incorporation of an inorganic composition into the hybrid matrix resulted in an increase in the thermal stability of these hybrid membranes.

Furthermore, we found that the residual weights at 400°C (R_{400}; wt %) were 57.3, 63.4, 59.4, and 60.1% for membranes A–D (cf. Table II); this indicated an upward trend from membrane A to membrane D with an increase in the TMSPEDA content, except in membrane B. Such an upward trend was consistent with the theory expectation; that is, an increasing amount of inorganic composition in a substance will produce higher residue in the sintered mixture. As for membrane B, the higher R_{400} value was possibly related to its compact structure in the organic–inorganic hybrid network. The reason could be ascribed to an increase in the inorganic ingredient in membranes A–D; this led to an increase in the weight percentage of residue. This outcome implied that the addition of inorganic composition to the hybrid matrix could be used to adjust the thermal T_d and residue of membranes A–D.

DSC Study

To obtain the glass-transition temperature (T_g) of the PV hybrid membranes A–D, a DSC study was performed, and the corresponding curves are presented in Figure 2.

As shown in Figure 2, for membranes B–D, there existed two exothermic peaks (the values were near 43.8 and 194.6, 43.5 and 190.1, and 49.6 and 195.4°C, respectively). However, for

Figure 1. TGA curves of the PV hybrid membranes A, B, C, and, D.

Table II. Thermal Analysis Data Obtained from the TGA Curves for Hybrid Membranes A–D

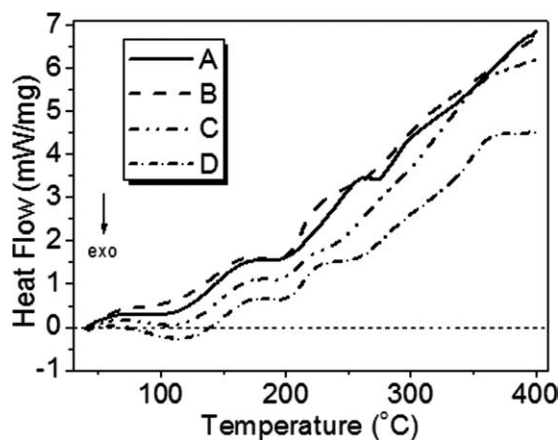| Membrane	T_{d5} (°C)	T_{d20} (°C)	R_{400} (wt %)
A	112.1	267.1	57.3
B	108.9	270.6	63.4
C	107.2	282.3	59.4
D	103.9	283.8	60.1

Figure 2. DSC curves of the PV hybrid membranes A–D.

membrane A, three exothermic peaks near 41.6, 191.8, and 273.5°C were found. Because only these exothermic peaks were found in the DSC curves, the temperature of the first peak could thus be ascribed to the T_g values; that is, the T_g values were 41.6, 43.8, 43.5, and 49.6°C for membranes A, B, C, and D, respectively. This revealed an upward trend as the amount of TMSPEDA in the membranes increased. Such a change trend was similar to the results obtained by Zhang et al.[17] in cagelike octaaminopropyl polyhedral oligomeric silsesquioxane and PVA hybrid materials; they reported that the T_g of octaaminopropyl polyhedral oligomeric silsesquioxane/PVA increased from 53 to 61°C. This outcome suggested that the incorporation of inorganic compositions into the PVA hybrid elevated its T_g.

It was reported[13,18] that in DSC curves, the single or multiple endothermic peaks are the crystal melting, whereas the exothermic peak can be considered the crystallization. Consequently, the temperature of the second peak in DSC curves can be assigned to crystallization. The crystallization temperatures of membranes A–D were located near 191.8, 194.6, 190.1, and 195.4°C, respectively; this also indicated an upward trend with elevated TMSPEDA content in these hybrid membranes, except in membrane C. These findings clearly demonstrated the influence of the TMSPEDA content in the hybrid membranes on the crystallization process of membranes A–D.

Several things might have been responsible for such an upward trend. One was the difference in the crosslinking degree, although the same amount of formaldehyde was used to crosslink —OH groups in the chains of the PVA molecules. Another was the change in the crystallization behavior as the amount of TMSPEDA in these membranes was increased. When the inorganic composition in the hybrid matrix increased, a perfectible hybrid network was created between the organic and inorganic moieties; this resulted in increases in both T_g and the crystallization temperature of these hybrid membranes.

PV Measurements
To gain insight into the PV performances of hybrid membranes A–D, a PV experiment was performed, and the related results are presented in Figures 3 and 4.

Effects of the Methanol Content in the Feed.
Presently, it is accepted that for the PV separation of organic mixtures, understanding of the dependence of the feed concentration on the permeation flux and separation factor is of vital importance.[10] The effects of the methanol content in the feed on the permeation flux and separation factor of membranes A–D are presented Figure 3(a,b).

As shown in Figure 3(a), it was observed that for individual membranes, the permeation flux values all decreased with increasing methanol content in the feed; this indicated a typical trade-off effect, as reported in the dehydration of alcohols.[19] However, for membranes A–D, the permeation fluxes decreased from membranes A to membrane D at different methanol contents in the feed. This outcome demonstrated that the addition of TMSPEDA to hybrid membranes A–D did not favor the elevation of the permeation flux.

Moreover, it can be seen in Figure 3(b) that for individual membranes, the separation factor decreased as the methanol content in the feed increased; this indicated the same trade-off effect reported in the dehydration of alcohols.[19] Through a comparison of the separation factors of membranes A–D, we found that the separation factor increased from membrane A to
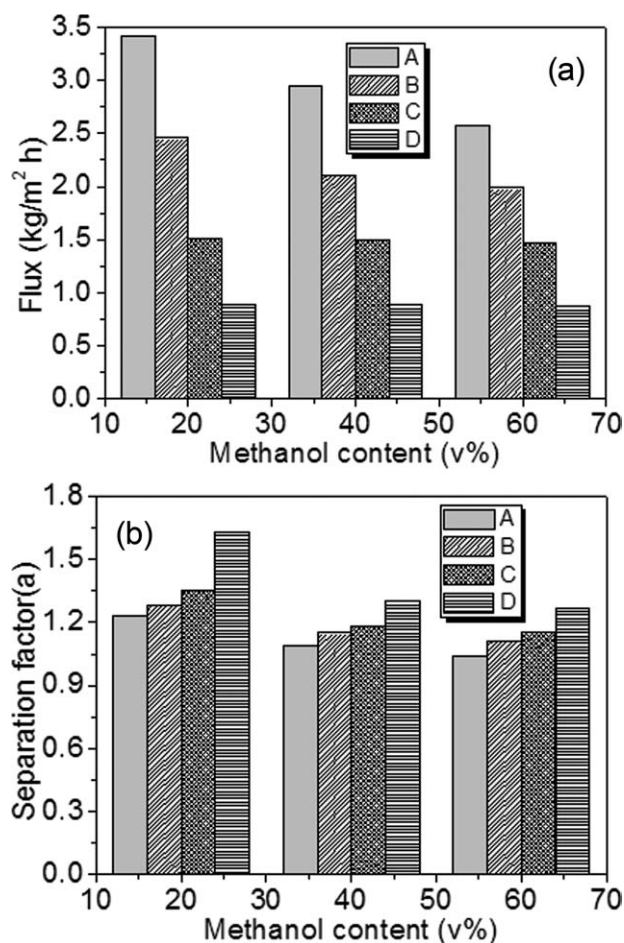

Figure 3. Effects of the methanol content in the feed on (a) the permeation flux and (b) separation factor of membranes A–D at 30°C.
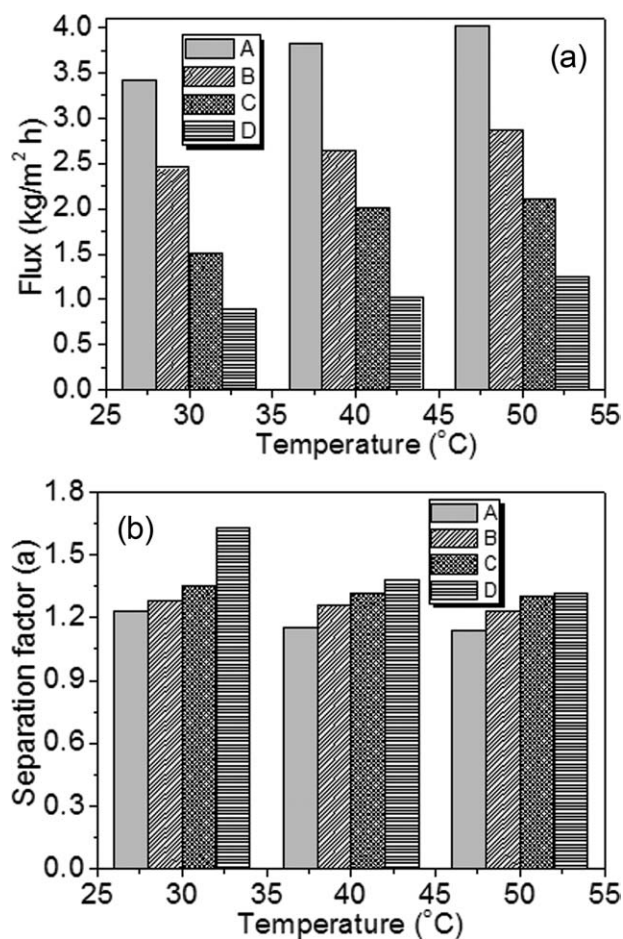
Figure 4. Effects of the feed temperature on the (a) permeation flux and (b) separation factor of membranes A–D with a 20 vol % methanol content in the feed.

membrane D when the methanol content in the feed increased; this demonstrated that the incorporation of TMSPEDA into these hybrid membranes elevated the separation factor of the hybrid membranes as different amounts of methanol in the feed across them.

Two dominating factors were responsible for such change trends. One could be ascribed to the elevated flexibility of the hybrid membrane with the increase in methanol content in the feed. It is well known that methanol is an organic solvent and that it can make polymeric chains become more flexible when its amount in solution is elevated to a relatively high level. The flexibility of the membrane was increased as the methanol content in the feed increased. Accordingly, the permeation of methanol across these membranes was blocked. As a result, the permeation flux of methanol across these hybrid membranes decreased with increasing methanol content in the feed. The other factor was related to an increase in the PVA content in these hybrid membranes. It is well accepted that the higher the organic composition in a polymer membrane is, the more flexibility the polymer chains will have. As shown in Table I, the organic ingredient in these hybrid membranes decreased from membrane A to membrane D, and the flexibility of these mem-

branes decreased with the addition of TMSPEDA, as presented in the DSC curves (cf. Figure 2). Accordingly, their flexibilities decreased with increasing methanol content in the feed; this resulted in a decrease in the permeation flux of methanol across membranes A–D. These effects on the permeation flux of methanol across membranes A–D affected the changes in the related separation factors.

Effects of the Feed Temperature.
To examine the effects of the feed temperature on the permeation flux and separation factor, the dependence of feed temperature on the PV properties of membranes A–D with a 20 vol % methanol content in the feed was determined and is illustrated in Figure 4(a,b).

It can be seen in Figure 4(a) that for individual membranes, the permeation flux increased as the feed temperature was elevated; this demonstrated that the feed temperature could increase the transport of methanol. However, for membranes A–D, we found that the permeation fluxes decreased from membrane A to membrane D at different temperatures. This implied that the addition of TMSPEDA had a negative influence on the permeation flux of methanol. This finding suggested that feed temperature affected the mobility of the polymer chains and the change in free volume, as reported in other articles.[10,20]

Furthermore, as shown in Figure 4(b), for individual membranes, the separation factor decreased when the feed temperature was increased. This revealed an opposite change trend to that of permeation flux and indicated that the feed temperature did not benefit the improvement of the separation factor of these hybrid membranes. However, for membranes A–D, we found that the separation factors were slightly increased at different feed temperatures; this demonstrated that the addition of TMSPEDA improved the separation factors of these hybrid membranes.

The previously discussed change trends can be explained as follows. One reason for the changes was the improvement of membrane flexibility with elevated feed temperature; this resulted in methanol becoming easier transport in membranes A–D at higher temperature. The permeation flux of methanol across these hybrid membranes increased accordingly. Another reason was related to the formation of a hybrid network in the organic and inorganic moieties; this led to the membrane becoming more intimate or denser at high temperatures. As a result, methanol permeation across these membranes turned more difficult, and the methanol permeation flux decreased. In addition, the methanol permeation across these hybrid membranes becoming more rapid at high temperatures was also responsible for a such trend.

Table III. Arrhenius Activation Energy Data

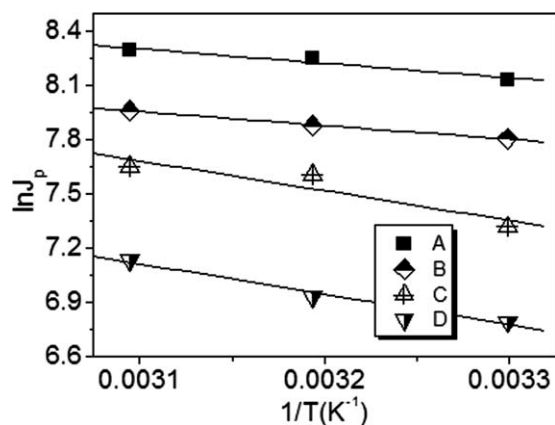| Membrane	E_P (kJ/mol)	J_0 (kg/m^2 h)	R^2
A	6.653	48.268	0.957
B	6.361	30.593	0.997
C	13.658	353.667	0.858
D	13.905	219.509	0.985

Figure 5. Dependence of ln J_P on $1/T$ of membranes A–D with a 20 vol % methanol content in the feed.

It should be emphasized that the permeation activation energy (E_P) also had an effect on the permeation of methanol across membranes A–D (as listed in Table III). The higher E_P blocked the transport of methanol across these hybrid membranes, and the permeation flux was accordingly reduced.

E_P

E_P is a useful tool for understanding the PV separation properties of a hybrid membrane. Some researchers have used the relationship of the permeation flux against the feed temperature to predict the PV separation properties of membranes and have achieved fruitful results.[10,21] As reported, the E_P (J/mol) value can be calculated with the following Arrhenius-type expression:[10]

$$J_P = J_0 \exp\left(-\frac{E_P}{RT}\right) \tag{3a}$$

or

$$\ln J_P = -\frac{E_P}{RT} + \ln J_0 \tag{3b}$$

where J_P is the permeation flux of the component (g m^{-2} h^{-1}), J_0 is the pre-exponential factor, R is the gas constant (8.314 J/mol K), and T is the solution temperature (K).

E_P and J_0, in this case, can be calculated from the slope and intercept of a linear plot according to ln J_P versus $1/T$ (cf. Figure 5). The calculated Arrhenius activation energy data are tabulated in Table III.

As shown in Figure 5, the experimental data showed a good linear relationship [the linear regression coefficient (R^2) values were in the range 0.858–0.997]. This suggested that E_P was dependent on the feed temperature. Moreover, through a comparison of the Arrhenius activation energy data of membranes A–D in Table III, we found that E_P increased with the elevated TMSPEDA content in these membranes, except in membrane B; this suggested that the addition of TMSPEDA into the hybrid membrane affect its E_P

The affinity difference between organic and inorganic compositions for methanol transport might have been responsible for

such a trend. As an organic composition, PVA had a larger affinity for methanol and conduced its permeation across a hybrid membrane. In contrast, the inorganic ingredient TMSPEDA had a weaker affinity for methanol and did not favor its permeation across such a hybrid membrane. Furthermore, it should be noted that membrane B revealed the minimum E_P value among membranes A–D; this indicated that the proper addition of the inorganic ingredient TMSPEDA into the PV hybrid membranes reduced the E_P On the basis of the previous findings, we concluded that these hybrid membranes have potential applications in the separation of methanol from aqueous methanol solutions via the PV technique.

CONCLUSIONS

A novel approach to PVA-based PV hybrid membranes was proposed. TGA and DSC studies confirmed that these hybrid membranes had high thermal stabilities. PV experiments revealed that the incorporation of TMSPEDA into these hybrid membranes improved their separation performances. It was found that for individual membranes, the permeation flux increased with elevated feed temperature. In contrast, the separation factor showed the opposite trend when the feed temperature was increased. These findings are meaningful for the PV separation of aqueous methanol solutions and imply that these hybrid membranes can be potentially used in the coal-based methanol industry for the removal of methanol from wastewater.

Notice that the separation factor of these hybrid membranes was in the range 1.04–1.63. For practical industrial application, further work is thus needed to improve the PV performances so that the separation factor can be elevated to desirable values. It is expected that this problem can be resolved with the preparation of high-flux hybrid membranes.

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