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Short communication

Pervaporation of acetic acid/water mixtures through carbon molecular sieve-filled PDMS membranes

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Abstract

The pervaporation process for acetic/water has been investigated with carbon molecular sieve (CMS)-filled polydimethylsiloxane (PDMS) membranes. The effects of feed temperature, feed acetic acid concentration and CMS content on the performance of the membranes have been studied. It is found that the addition of CMS can improve pervaporation behavior of PDMS membranes to some extent and greatly increases the strength and tenacity of membranes. At a CMS content of 20 wt.%, both permeation flux and separation factor reach maximum values. With an increase of the feed temperature, selectivity decreases and permeation flux increases, but flux of water increases faster than that of acetic acid. With the enhancement of feed concentration, flux and selectivity both get a rise and flux of acetic acid increases faster than that of water.

Keywords: Pervaporation; Acetic acid; CMS; Filled PDMS membrane

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1. Introduction

Membrane pervaporation is becoming one of the most promising candidates for low-cost separation processes, especially for azeotropic mixtures. Its applications can be found in: (1) dehydration of organic/water mixtures; (2) removal or recovery of organic compounds from water; (3) separation of organic mixtures.

Acetic acid is one of the most important chemical stuffs in the chemical industry and belongs to the top 50 chemicals in amount produced [1]. There has been several works done for acetic acid/water system in recent years. Bai et al. [2] attempted to separate acetic acid/water by pervaporation with silicone rubber-coated polyetherimide membranes. They found that the composite membrane could become either water selective or acetic acid selective, depending on the pore size of the support membrane and the condition of the silicone rubber coating. Yoshikawa et al. [3] used cross-linked polybutadiene membranes for preferential pervaporation of acetic acid. The preferential pervaporation of acetic acid was attributed to hydrophobic nature of cross-linked polybutadiene. Deng et al. [4] separated acetic acid/water by pervaporation using polydimethylsiloxane (PDMS) membrane, aromatic polyamide (PA), and laminated PDMS/PA membranes. The results indicated that when the top layer in contact with the feed was PDMS, water selectivity of the bottom PA membrane was intensified. On contrary, when the PA membrane was on the top layer in contact with the feed, the selectivity was weakened. Liu et al. [5] found that silicalite membranes supported on the inner surface of a porous stainless steel cylindrical tube was unable to selectively remove acetic acid from acetic/water mixtures at low acetic acid concentration. Netke et al. [6] studied the separation of acetic acid from water using silicate-filled PDMS membrane. The selectivity of the membrane for acetic acid increased with increasing content of the silicalite and its hydrophobicity in the membrane. The flux of acetic acid was, however, found to behave in an opposite manner. Lu et al. [7] achieved the preferential pervaporation of acetic acid over water with silicalite-filled PDMS membranes. At a feed temperature of 45 °C, silicalite addition enhanced not only the separation factor but also the permeation flux. The pervaporation behavior of the silicalite-filled PDMS membrane seemed to fall in between those of pure PDMS and pure silicalite membranes.

Carbon molecular sieve (CMS) is widely used in adsorption processes because of their high adsorption selectivity toward some organic compounds [8]. In order to influence separation performance of PDMS membrane, addition of

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Nomenclature

c_{fA}	feed acetic acid mole fraction (%)
P_{p}	downstream pressure (Pa)
T	feed temperature (°C)
α	separation factor

CMS into PDMS was carried out in this work to form the filled membrane. It was imaged that doing so would enhance the flux and selectivity of pure PDMS membrane, owing to the preferential sorption of CMS to organics. CMS content in the membrane and several important pervaporation operation parameters, including feed acetic acid concentration, and feed temperature, were investigated.

2. Experimental

2.1. Membrane preparation

Carbon molecular sieve samples were kindly supplied by Southwest chemical institute. The properties of CMS used are given in Table 1. 107 RTV silicone rubber, curing agent (tetraethyl orthosilicate), catalyst (dibutyltin dilaurate), solvent (heptane) were mixed in a certain proportion. CMS was homogeneously dispersed in silicone solution with the help of turbine type impeller. The mixtures were degassed, spread on a perspex sheet and annealed at 80 °C for 24 h. The unfilled PDMS and filled PDMS membranes were about 120 and 160 μm thick, respectively.

2.2. Sorption and permeation studies

Films of known weight were immersed in pure acetic acid and pure water at 30 °C, respectively. After 72 h, they were removed and weighted after the superfluous liquid was wiped. The increase in weight is due to acetic acid or water taken up by the membrane. The permeation experiments have been performed at 300 Pa downstream pressure. After a 2 h steady-state period, the permeate was collected in cold traps (refrigerated by liquid nitrogen). The composition of the feed and the permeate sample was determined by acid–base titration.

2.3. Tensile measurements

For showing the mechanical strength of the above-mentioned membranes, the tensile measurements were performed on a Serials IX Automated Materials Testing System.

Table 1
Properties of CMS used

Particle size (μm)	1.5–2
Specific area (m^2/g)	563
Pore diameter (Å)	6

Table 2
Sorption experiments: the swelling ratio of both membranes in pure water and pure acetic acid; $T = 30$ °C

Swelling medium	Swelling ratio (wt.%)	
	Pure water	Pure acetic acid
Unfilled PDMS	0.1201	0.2734
Filled PDMS (10 wt.% CMS)	0.2218	1.4271

3. Results and discussion

3.1. Sorption

Table 2 shows the swelling ratio of both membranes in pure water and pure acetic acid. It is evident that in Table 2 the inclusion of CMS greatly increases the sorption of acetic acid in the membrane due to its hydrophobicity, whereas the quantity of water absorbed is increased only a little than for the unfilled membrane. The sorption selectivity is thus considerably improved.

3.2. Permeation studies

3.2.1. Effect of incorporation of CMS

Fig. 1 reveals the influence of CMS to flux in a contradictive mode. On one hand, CMS enhances the sorption of acetic acid in the membrane. On the other hand, the distribution of CMS in membrane increases the transport resistance of adsorbed components. Thus, the flux does not take a climbing tendency with the content of CMS in PDMS. Fig. 1 also shows that the inclusion of CMS increases the selectivity of the membranes. This may be explained by preferential adsorption of CMS for acetic acid and the physically cross-linking effects between CMS and polymers. Experimental results also indicate that when CMS weight fraction is approximately 20 wt.%, both total permeate flux and separation factor reach maximal values. When CMS content exceeds 20 wt.%, the particles will bring more defects into the membranes and thus result in lower selectivity.

Duval et al. [9] attempted to separate a toluene/ethanol mixture by pervaporation using active carbon-filled PDMS membranes. However, the filled membrane did not result in

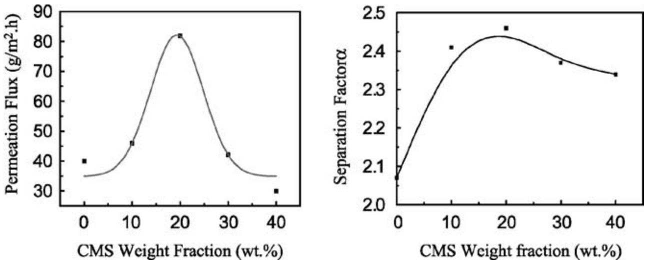

Fig. 1. Separation performance vs. weight fraction of CMS; $c_{\mathrm{fA}} = 5.2$ mol%; $T = 45$ °C.

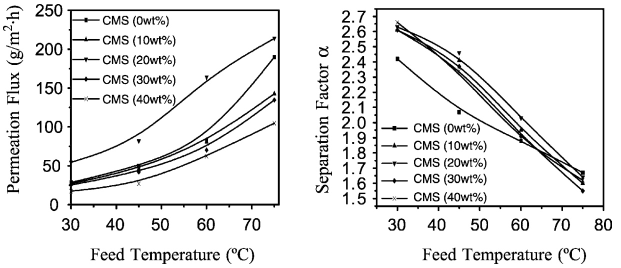

Fig. 2. Separation performance of filled membranes vs. weight fraction of CMS; $c_{\mathrm{fA}} = 5.2\,\mathrm{mol\%}$; $T = 45\,^{\circ}\mathrm{C}$.

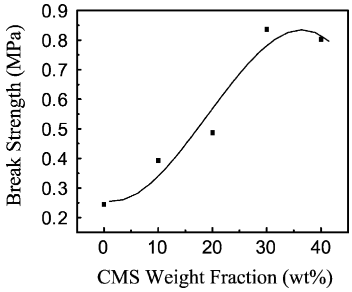

Fig. 4. Break strength vs. CMS content.

an improvement of the selectivity for toluene. Furthermore, the total flux decreased drastically with an increasing amount of active carbons. That was due to the closed pore structure of the carbons. So they suggested using carbon molecular sieve instead of active carbons. These experimental results have supported obviously their suggestion.

3.2.2. *Effect of temperature*

In Fig. 2, total permeate flux increases with increase in temperature. However, it can be seen from Fig. 2 that separation factor has a drop with the rise of temperature. As temperature increases, vapor pressure of water increase much faster than that of acetic acid, which makes flux of water increase faster than that of acetic acid. Meanwhile, going-up swelling of the membrane declines also the selectivity for acetic acid. Lu et al. [7] studied the pervaporation of silicalite-filled PDMS membranes for the mixture of acetic acid and water, and found that the separation factor increased with increasing feed temperature. Our experimental results for the CMS-filled PDMS membranes seem to be opposite to those of Lu et al. [7]. Furthermore, when feed temperature exceeds 70 °C, the inclusion of CMS brings down both selectivity and flux of membranes. This may be explained that when feed temperature is higher, sorption of acetic acid in the filled membrane seems little preferential, which leads to lower selectivity and flux.

3.2.3. *Effect of feed concentration*

From Fig. 3, it can be seen that selectivity of membranes increases with the rise of feed concentration and finally reaches a stable level. When concentration of acetic acid is lower, water molecules hampers the sorption of acetic acid on the surface of membranes. With an increase of the concentration, the barrier is broken, and thus the selectivity has a rise. In Fig. 3, total flux and flux of acetic acid both increase with increase in feed concentration, whereas that of water remains nearly invariable. The increasing feed concentration raises the transport impetus of acetic acid and accordingly, increases the flux of acetic acid. Deng et al. [4] investigated the pervaporation of PDMS for the acetic acid–water solution and revealed that both the flux and selectivity increased with increasing feed acetic acid concentration. Their result is consistent with ours.

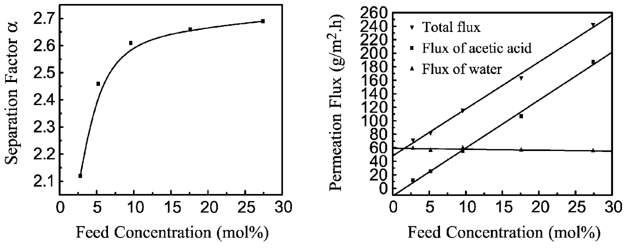

Fig. 3. Separation performance vs. feed concentration; CMS: 20 wt.%; $T = 45\,^{\circ}\mathrm{C}$.

3.3. *Mechanical strength of membranes*

In Fig. 4, proper weight fraction of CMS can obviously increase break strength of filled membranes. CMS added into the membranes closes together with polymer chains, which plays a role of physical cross-linking and makes mechanical strength to increase. When the addition is overmuch, densification is spoiled and mechanical strength appears to decline.

4. Conclusions

The preferential pervaporation of acetic acid over water by using CMS-filled PDMS membranes is studied. The addition of CMS improves the pervaporation behavior of pure PDMS to some extent, and increases greatly the strength and tenacity of membranes. At a CMS content of 20 wt.%, both permeation flux and separation factor reach maximum values. As the feed temperature is increased, selectivity decreases and permeate flux increases, because flux of water increases faster than that of acetic acid with temperature. With the increasing in feed concentration, flux and selectivity simultaneously rises because flux of acetic acid increases faster than that of water with the concentration.

Acknowledgements

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