Asian Journal of Chemistry; Vol. 24, No. 4 (2012), 1793-1797

ASIAN JOURNAL OF CHEMISTRY

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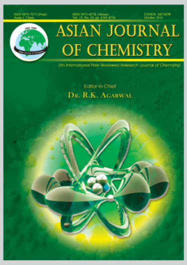

Pervaporative Removal of Propylene Glycol Monomethyl Ether from Water Using Polydimethyl siloxane Membranes Filled with SiO_2

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(*Received*: 2 May 2011; *Accepted*: 28 November 2011) AJC-10764

Polydimethyl siloxane (PDMS) membranes filled with nano-silicon dioxide (nano-silica) were prepared for pervaporative removal of propylene glycol monomethyl ether (PGME) from water. The structure of the filled and unfilled membranes was observed by scanning electron microscopy (SEM). The fourier transform infrared spectroscopy analysis (FTIR) revealed that only a little SiO_2 reacted with PDMS, while most of SiO_2 and PDMS were mixed physically. The experiment results of pervaporative removal showed that the methyl block RTV 103 (103-PDMS) membrane presented better separation performance than the methyl RTV 107 (107-PDMS) membrane. With increasing content of SiO_2, separation factor increased firstly and then decreased for both 103 (103-PDMS) membranes and 107 (103-PDMS) membranes, whereas permeation flux increased continuously. When the addition of SiO_2 was 1.2 wt % (based on PDMS component), the two kinds of membranes possessed the best separation performance.

Key Words: Polydimethyl siloxane, Propylene glycol monomethyl ether, Nano-silicon dioxide, Pervaporation.

INTRODUCTION

Pervaporation is a promising membrane-based technique for the separation of liquid chemical mixtures, especially in azeotropic or close-boiling solutions. The advantage of this process lies in high separation degree, simple operation, environmental protection and lower energy consumption. Organosilicon is a kind of polymer with inorganic and organic composite structure, which has a good prospect for using as membrane[1,2]. Polydimethyl siloxane (PDMS) membrane is a well-known hydrophobic membrane for removing organics from aqueous mixtures[3]. In recent years, PDMS membranes have been widely modified with nano-silicon dioxide (nano-silica), because the silica could greatly improve the permeation flux and enhance the thermal stability of membranes[4-7].

Nowadays, most studies of PDMS membrane mainly focuses on the system of alcohol/water[8-10]. But the research on the pervaporation which segregates propylene glycol monomethyl ether (PGME) from water can hardly be found both home and abroad.

It is well-known that PGME is a kind of solvent with low toxicity and has been widely used in fields of the coating, painting and dyeing and agriculture *etc.*[11]. Compared with water, PGME has a more complex structure and bigger size. Then, PGME has a azeotropic point with water due to its boiling point is 121 ºC. Accordingly, it is difficult to obtain the qualified product of PGME by traditional rectification method. In this paper, PDMS membranes filled with nano-silica were prepared for separating PGME from water by means of homemade pervaporation unit. The structure of the filled membranes was observed by scanning electron microscopy (SEM). The fourier transform infrared spectroscopy analysis (FTIR) revealed that only a little SiO_2 reacted with PDMS, while most of SiO_2 and PDMS were mixed physically. The permeation flux (J) and separation factor (α) were calculated and the separation performance of unfilled and SiO_2 filled PDMS membranes was discussed.

EXPERIMENTAL

Two kinds of silicone rubber, methyl block RTV 103 (103-PDMS) and methyl RTV 107 (107-PDMS), were purchased from Beijing Xintaoda Chemical Plant, China. The viscosity of the two kinds of silicone rubber was 2090 and 1000 mPa s, respectively. Propylene glycol monomethyl ether (PGME), ethyl silicate (TEOS), triethoxymethylsilane (MTES), N-heptane and dibutyltin dilaurate were obtained from Tianjin No. 1 Chemical Reagent Company, China. Nano-silica (TS-610) was obtained from Taida Chemical Institute, USA.

The pervaporation membranes were prepared by 103-PDMS, 107-PDMS, cross-linking agent, catalyst and nano-SiO_2. The feed solutions of PGME/water with different concentrations were separated by a homemade apparatus, then the permeation flux and separation factor were calculated by means of analyzing the component of penetrating fluid.

General procedure: Unfilled and SiO_2 filled PDMS membranes (103-PDMS membranes and 107-PDMS membranes) were prepared. The compositions of preparing the composite membranes were given in Table-1. 107-PDMS and 103-PDMS were respectively dissolved in *n*-haptane, according to various PDMS concentrations of 8, 9 and 12 wt %. After thoroughly mixing, cross-linking agent (TEOS for 107-PDMS and MTES for 103-PDMS), catalyst (dibutyltin dilaurate, 1 wt %) and nano-SiO_2 were added to the mixture solutions to prepare a liquid for shaving. The liquid was subsequently exposed in room temperature to get rid of lather for 0.5 h and then poured onto a glass plate with non-woven fabrics for shaving membranes. The obtained membranes were vulcanized for 24 h at room temperature before high-temperature vulcanization in an oven at 130 ºC for 3 h. Finally, the impurity, micro-molecule and solvent left were erased by immersing in the absolute alcohol for 0.5 h and washing with the deionized water for 10 min. Then the membranes were soaked for 2 h using pure water. The effective area and osmotic pressure on a side of the membrane were 0.0127 m^2 and 100 Pa, respectively.

TABLE-1
COMPOSITIONS OF THE COMPOSITE MEMBRANES

Number	Membrane materials	Weight ratio
107-1	107-PDMS: TEOS:SiO_2	5:1.5:0.01
107-2	107-PDMS: TEOS:SiO_2	5:1.5:0.006
107-3	107-PDMS: TEOS:SiO_2	5:1.5:0.002
107-4	107-PDMS: TEOS:SiO_2	5:1.5:0
103-1	103-PDMS: MTES:SiO_2	5:1.5:0.01
103-2	103-PDMS: MTES:SiO_2	5:1.5:0.006
103-3	103-PDMS: MTES: SiO_2	5:1.5:0.002
103-4	103-PDMS: MTES: SiO_2	5:1.5:0

The feed solutions (concentration changed from 0.5 to 10 wt %) was prepared by mixing pure PGME and distilled water.

A pervaporation experiment was conducted using a homemade apparatus, as shown in Fig. 1. It was composed of three parts, which were upstream at atmospheric pressure, downstream at a vacuum pressure of 460 Pa and the pervaporation cell. The feed tank was maintained at constant temperature by controlling the water bath. The downstream component consisted of a vacuum pump, a vacuum regulator to control the permeation side pressure and a cold trap, which was kept at 3 ºC using a cryostat.

The propylene glycol monomethyl ether concentrations in the permeation sides were obtained by Abbe refractometer to determine the total flux (*J*) and separation factor (α)[12], which were defined as follows:

$$J = \frac{M}{A \times t}$$

$$\alpha = \frac{Y_b / Y_w}{X_b / X_w}$$

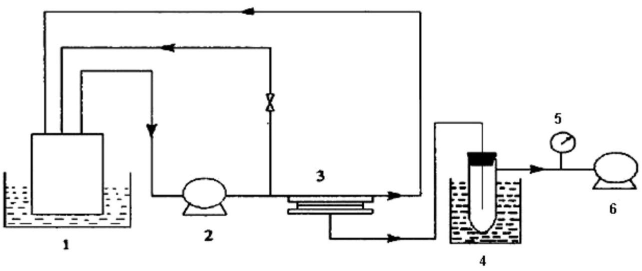


Fig. 1. Schematic diagram of the apparatus used for pervaporation. (legend: 1-feed; 2-feed pump; 3-pervaporation pond; 4-cold trap; 5-vacuum regulator; 6-vacuum pump)

where M (g) is the total mass of penetrating fluid collected in t hours and A (m^2) denotes the effective area of the membrane; X_w and X_b represent the water and PGME concentrations (wt %) in the feed solution respectively, Y_w and Y_b represent the water and PGME concentrations (wt %) in the penetrating fluid.

Detection method: The cross-sectional morphologies of the PDMS membranes were characterized by SEM (QUANTA-200). FTIR (TENSOR37) was applied to detect the presence of nano-SiO_2 in the filled PDMS membranes. The refractive index (*n*) of penetrating fluid was obtained by Abbe refractometer (WAY870587) and then the corresponding concentration was known according to Fig. 2.

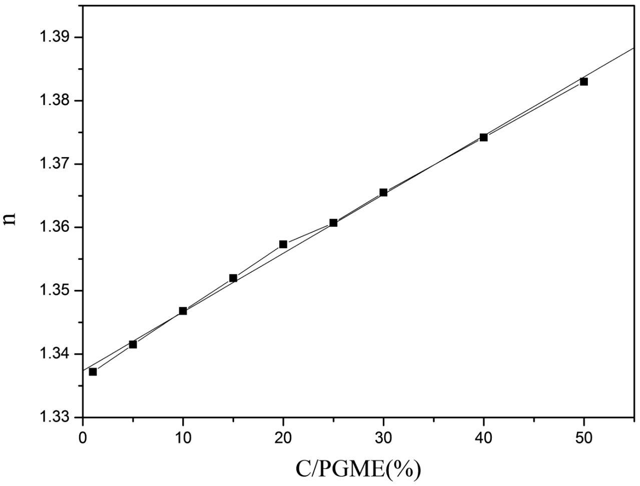
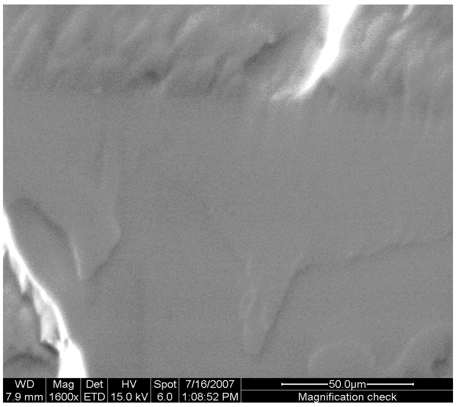


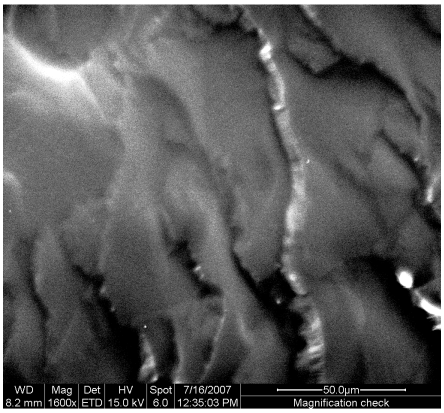
Fig. 2. Relationship of refractive index (n) and the concentration of PGME

RESULTS AND DISCUSSION

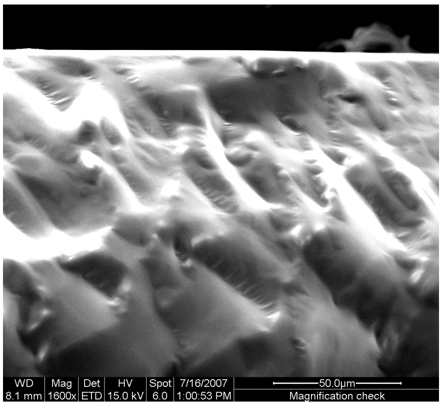
Morphology: The cross-sectional images of the 103-PDMS membranes by SEM were shown in Fig. 3. It could be observed that the cross sections of the four membranes had great differences in regard to structure and morphology. In Fig. 3(a), a relative smooth surface was observed, indicating a completely dense structure. In Fig. 3(b), the structure of cross section was still intensive when the silica content was 0.04 wt % in 103-3 membrane. It was clear in Fig. 3(c) that the silica particles (0.12 wt %) presented well dispersion in the membranes because the interfacial region between the particles and membranes was ambiguous, which indicated a good miscibility. According to Fig. 3(d), when the filler amount was up to 0.2 wt %, the structure and performance of the membrane



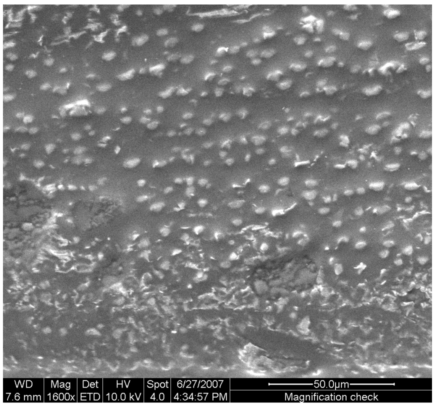
(a) cross section of 103-4



(b) cross section of 103-3



(c) cross section of 103-2



(d) cross section of 103-1

Fig. 3. SEM images of 103-PDMS membranes

deteriorated owing to the accumulative morphology among the mountains of silica. The tendency of morphology alteration in the 107-PDMS membranes was similar to 103-PDMS membranes.

FT-IR spectroscopy: The infrared spectrograms of the 103-PDMS membranes and SiO_2 were showed in Figs. 4 and 5, respectively. Compared with Fig. 4, it was observed that when SiO_2 was filled into the membrane the absorptive peak caused by Si-OH (3436.94 cm^{-1}) in Fig. 5 was disappeared. This showed that a chemical linkage between SiO_2 and PDMS was yielded. Meanwhile, for the unfilled and SiO_2 filled 103-PDMS membrane in Fig. 4 both the number and location of the peak were not changed. This depicted that only a little SiO_2 reacted with PDMS, while most of SiO_2 and PDMS were mixed physically.

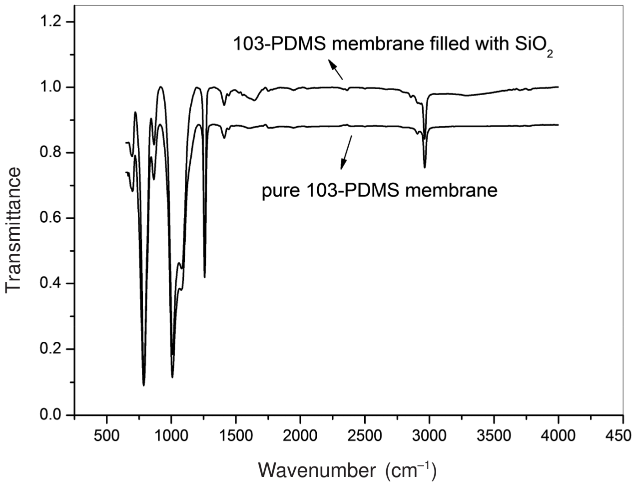


Fig. 4. IR spectrum of 103-PDMS membrane filled with SiO_2 and pure PDMS membrane

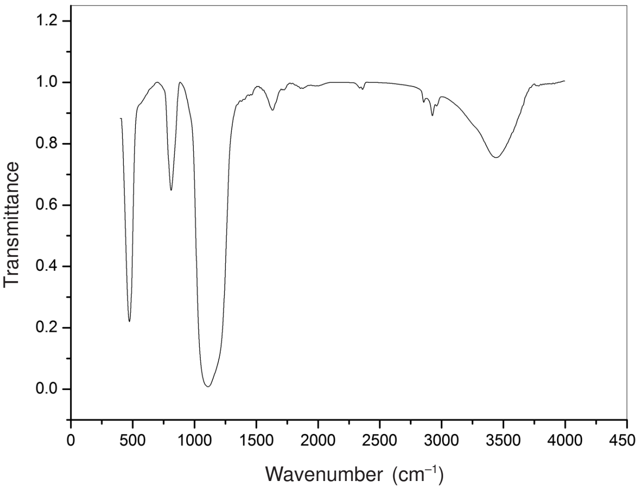


Fig. 5. IR spectrum of SiO_2

Comparative analysis of pure 103-PDMS and 107-PDMS membranes: Fig. 6 showed the effect of PGME concentration on the separation factor and permeation flux of 107-4 and 103-4 PDMS membranes. It can be seen that, for both 103-PDMS and 107-PDMS membranes, the separation factor

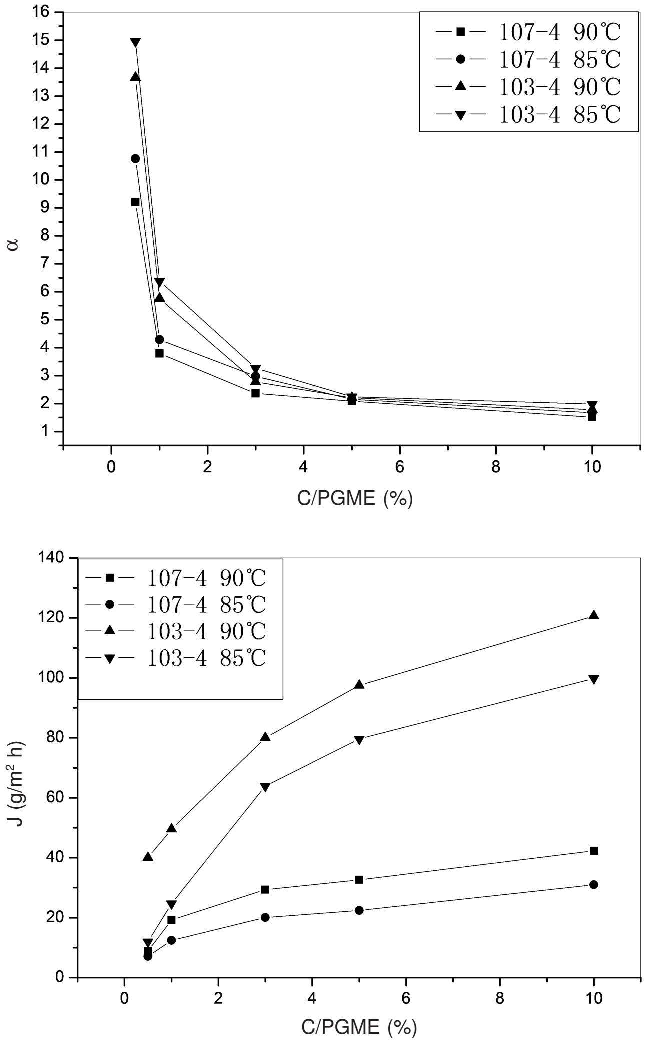


Fig. 6. Effect of PGME concentration on the separation factor and permeation flux of 107-4 and 103-4 PDMS membranes

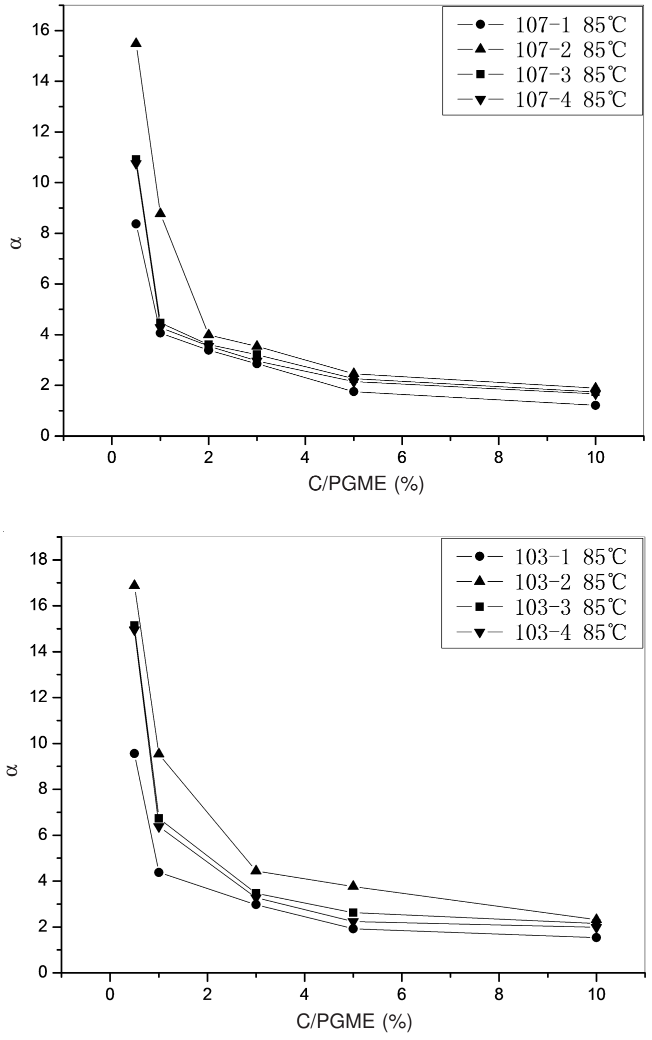


Fig. 7. Effect of PGME concentration on the separation factor of 107-PDMS and 103-PDMS membranes

decreased with increasing PGME concentration while the flux increased. However, the change rate of separation factor and flux of 103-PDMS membrane was higher than that of 107-PDMS membrane, which indicated that pure 103-PDMS membrane worked more efficiently than 107-PDMS membrane. The reason can be attributed to a polymer with three directions in 103-PDMS membrane, which yielded from the curing reaction between the hydroxyl of 103-PDMS and the ethoxy group of MTES. Thus, the strength of this crosslinked elastomer was stronger than 107-PDMS and the free volume had little change. Further, 103-PDMS membrane had more hydrophobic groups (-CH_3) which efficiently stopped the water molecules from passing through. In addition, with an increase in feed temperature, selectivity decreased and permeation flux increased. That was because the movement of chain segments in the membranes intensified and the free volume expanded. Therefore, the kinetic energy of the permeated materials improved, leading to the increase of swelling degree and diffusion rate of molecules in the membrane.

Influence of SiO_2 on the properties of membranes: It was obvious from Fig. 7 that, the separation factor would firstly increase and then decrease with increasing SiO_2 content, both in 103-PDMS and 107-PDMS membranes. That is, when the mass fraction of nano-SiO_2 was 1.2 wt % (based on PDMS component), the 103-2 and 107-2 membranes possessed the best separation performance. For example, when the concentration of feed liquid was 0.5 wt %, the 107-2 membrane had a separation factor of 15.48 which was 1.46 times larger than that of 107-4 membrane. Apparently, SiO_2 could be well dispersed in the membrane when the addition was small and the bond of Si-OH in the nano-SiO_2 had affinities with the hydroxyl group and ether link in the PGME. These factors made PGME more easily to pass through, that is, the separation factor would increase in low content of SiO_2. However, when the SiO_2 content was larger, the separation factor decreased because of poor compatibility between SiO_2 and the membranes.

It was obvious from Fig. 8 that the flux increased directly with increasing SiO_2 content, both in 103-PDMS and 107-PDMS membranes. The reason may be that, the PGME molecules were firstly absorbed by SiO_2 when passed through the filled membrane. Then, the molecules spread down through the channel between SiO_2 and PDMS floor, subsequently released on the other side of the membrane. In other words, this fast spread channel made a great contribution to the increase of the flux and selectivity for organism. At the same SiO_2 content and PGME concentration, 103-PDMS membranes

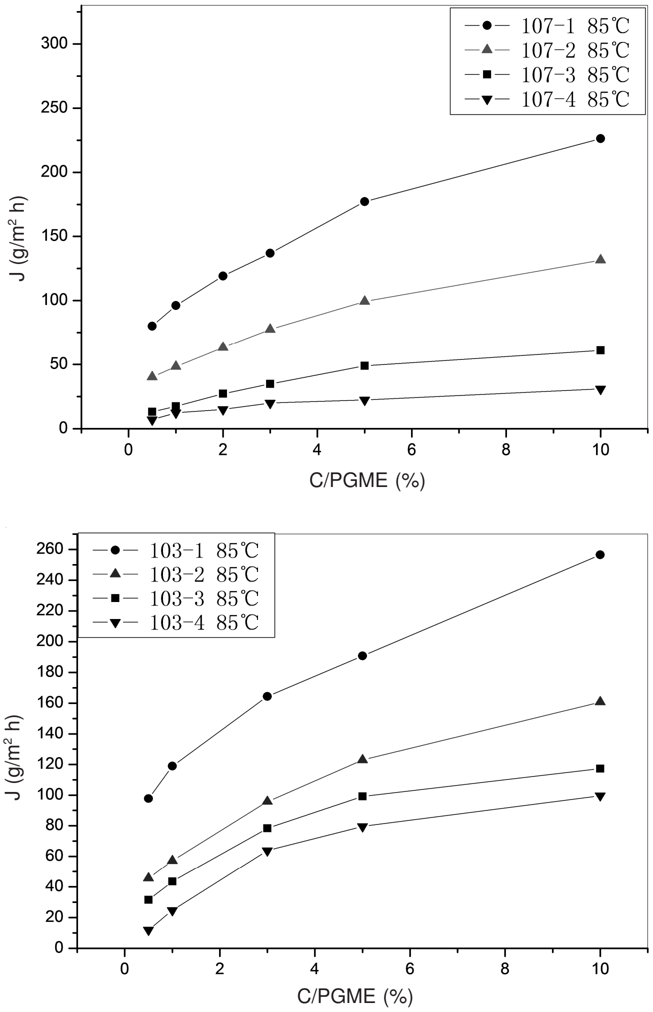


Fig. 8. Effect of PGME concentration on the permeation flux of 107-PDMS and 103-PDMS membranes

possessed a higher flux than 107-PDMS membranes, which was consistent with Fig. 6.

Conclusion

Compare with unfilled polydimethyl siloxane membranes, the permeation flux and selectivity of nano-SiO_2 filled polydimethyl siloxane membranes for propylene glycol monomethyl ether had been greatly improved. When the mass fraction of SiO_2 was 1.2 wt %, the separation effect was the best. Simultaneously, the highest separation factor of SiO_2 filled 103-PDMS membrane could reach to 16.88 and the corresponding flux was 45.55 g/m^2 h, which were superior to the performance of SiO_2 filled 107-PDMS membrane.

REFERENCES

1. T. Uragami, T. Ohshima and T. Miyata, *Macromolecules*, **36**, 9430 (2003).
2. K. Wojciech and O.G. Barbara, *Sep. Sci. Technol.*, **38**, 3669 (2003).
3. A. Hasanoglu, Y. Salt and S. Keleser, *Chem. Eng. Process.*, **44**, 375 (2005).
4. K.I. Okamoto, A. Butsuen, S. Tsuru and S. Nishioka, *Polym. J.*, **19**, 747 (1987).
5. T. Kashiwagi, K. Okabe and K. Okita, *J. Membr. Sci.*, **36**, 353 (1986).
6. K. Blume, J.G. Wijmans and R.W. Baker, *J. Membr. Sci.*, **49**, 253 (1990).
7. S. Takegami, H. Yamada and S. Tsujii, *J. Membr. Sci.*, **75**, 93 (1992).
8. K.C. Wu and Y.W. Chen, *Appl. Catal. A*, **257**, 42 (2004).
9. L. Liang, J.M. Dickson and J. Jiang, *J. Membr. Sci.*, **231**, 71 (2004).
10. B. Bettens and S. Dekeyzer, *J. Phys. Chem. B*, **109**, 5216 (2005).
11. A. Devanthery and M. Berode, *Int. Acta Occupa. Environ. Health*, **75**, 203 (2002).
12. X.H. Li and L.F. Wang, *Technol. Water Treat.*, **26**, 267 (2000).