



## Pervaporation of Acetic Acid-Water Mixture Using Silica Membrane Prepared by Sol-Gel Method

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**Abstract.** Silica membranes were developed and tested for the separation of acetic acid and water by pervaporation. Thin microporous silica membranes were prepared on a porous alumina tube by sol-gel method using tetraethyl orthosilicate (TEOS) as the silica precursor. Colloidal and polymeric silica sols were prepared by hydrolysis of TEOS. The pervaporation experiment results revealed that the silica membranes showed water selectivity towards acetic acid. The permeate flux and the separation factor were strongly influenced by the composition of the silica sols. For a feed concentration of 90 wt% acetic acid, the permeate flux varied between 0.016 to 0.91 kg/m<sup>2</sup> h, with the separation factor varying between 3.7 and 324.

**Keywords:** *acetic acid-water mixture; pervaporation; permeate flux; separation factor; silica membrane; sol-gel method; tetraethyl orthosilicate.*

### 1 Introduction

Membrane pervaporation is promising as an effective separation process for liquid mixtures with an azeotrope and/or small differences in boiling characteristics, which are difficult to separate using conventional distillation methods. Several researchers have developed pervaporation membranes from hydrophilic organic polymer materials – such as polyvinyl alcohol [1], polyacrylic acid [2], chitosan [3], polyperfluorsulfonic acid [4] – for the dehydration of aqueous organic mixtures. But recently, membranes made from inorganic materials have gained more and more interest because of their high chemical resistance and good thermal stability. Inorganic membranes made from zeolite, silica, zirconia and titania have been developed, showing a good separation performance for various liquid mixtures and gaseous mixtures [5-8]. The preparation of inorganic membranes is the most crucial factor in obtaining membranes with good separation performance.

Silica is one the most attractive materials for the development of inorganic membrane due to its good chemical stability against acids, good thermal

stability, low cost of the silica precursor, and ability to be shaped into a thin microporous film [9]. Due to these advantages, a number of researchers have developed silica membranes for use in gas separation. However, currently there are only few reports about the development of silica membranes for the separation of aqueous organic acids [10]. In this work, we have developed silica membranes by sol-gel method and tested them for the separation of acetic acid and water by pervaporation. The effect of the silica sol composition on the membrane microstructure and pervaporation performance was explored.

We tested the membranes for the dehydration of acetic acid, since acetic acid is one of the top 20 organic intermediates in the chemical industry, whereas the dehydration of acetic acid by conventional distillation is difficult and costly due to the small differences in the volatilities of acetic acid and water. Thus, the aim of this study was to develop a highly selective silica membrane that can be used for the separation of acetic acid-water mixtures.

## **2 Experimental Procedure**

### **2.1 Materials**

Tetraethyl orthosilicate (chemical structure:  $\text{Si}(\text{OC}_2\text{H}_5)_4$ , abbreviated name: TEOS) was obtained from Wako Pure Chem. Ind. Ltd. and used as the silica precursor. A porous alumina tube, supplied by Toshiba Ceramic Co. Ltd., was used as the supporting membrane. Ultra-pure deionized water was used. Methanol, acetic acid, ethanol, acetone, 1-3 butandediol, nitric acid, and sodium hydroxide were all supplied by Wako Pure Chem. Ind. Ltd.

### **2.2 Preparation of silica sols**

Two types of silica sols, colloidal and polymeric sols, were prepared. Colloidal silica sols were obtained by the hydrolysis of TEOS with water using a small amount of nitric acid ( $\text{HNO}_3$ ) as the catalyst, while polymeric silica sols were prepared by reacting TEOS with water and ethanol using nitric acid as the catalyst. Table 1 and Table 2 depict the compositions of the colloidal sols and polymeric sols, respectively. For all sols, the molar ratio of nitric acid to TEOS was 0.09 : 1. The reaction was carried out through stirring at room temperature for 3 hours. The viscosity of the sols was measured using a Cannon Rotary Viscosimeter model LV-2000.

**Table 1** Composition of Colloidal Silica Sols.

Sol	Molar Ratio	
	TEOS	H <sub>2</sub> O
Si-1	1	11.574
Si-2	1	115.74
Si-3	1	1157.4

**Table 2** Composition of Polymeric Silica Sols.

Sol	Molar Ratio		
	TEOS	C <sub>2</sub> H <sub>5</sub> OH	H <sub>2</sub> O
Si-4	1	3.8	6.5
Si-5	1	47.7	6.5
Si-6	1	179.6	6.5

### 2.3 Preparation of Silica Membranes

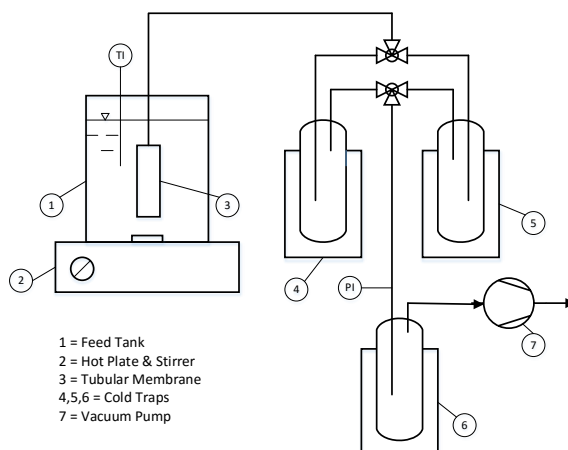
The silica membranes were prepared by coating a porous alumina tube with the sols using a dip-coating apparatus. The alumina tube had an outer diameter of 10 mm, an inner diameter of 7 mm and a length of 50 mm, while a pore size of 0.5  $\mu\text{m}$  was used for the supporting membrane. The coated membrane was then dried at 30°C for one hour and sintered by heating from room temperature to 200°C at a heating rate of 0.7°C/min. After a temperature of 200°C was reached, the temperature was kept constant at 200°C for one hour and then reduced to room temperature at a cooling rate of 0.7°C/min. This procedure was repeated 2-3 times to obtain a thin silica layer on the alumina tube.

### 2.4 Membrane Characterization using SEM and AFM

The microstructure of the membranes was studied using scanning electron microscopy (SEM) and atomic force microscopy (AFM). For the AFM measurements, silicon wafers were used as the substrates coated with the silica sols, dried and sintered under the same conditions as mentioned above.

### 2.5 Pervaporation Experiment

A schematic diagram of the pervaporation apparatus is shown in Figure 1. The feed was acetic acid-water mixture with a feed concentration varied between 10 and 90 wt% acetic acid. The feed temperature was kept constant at 298 K, whereas the permeate pressure was lowered using a vacuum pump and kept constant at 40 Pa. The effective membrane area was 9.8 cm<sup>2</sup>. The permeating component was collected in a cold trap using liquid nitrogen and the permeate flux was obtained by measuring the weight of the collected permeate during certain times at a steady-state condition.



**Figure 1** Schematic diagram of the pervaporation experiment.

To determine the selectivity of the membrane, the permeate concentration was measured by a titration method using sodium hydroxide. The separation factor  $\alpha$  was calculated using this equation:

$$\alpha = \frac{y_w/y_a}{x_w/x_a}$$

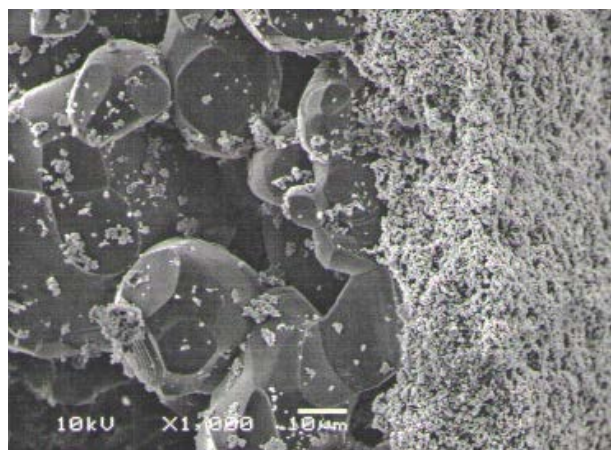
where  $y_w$  and  $y_a$  are the weight fraction of water and acetic acid in the permeate, respectively, while  $x_w$  and  $x_a$  are the weight fraction of water and acetic acid in the feed solution, respectively.

For the estimation of the pore size of the membranes, the permeate fluxes of various pure liquids of different molecular sizes (water, methanol, acetic acid, ethanol, and 1-3 butanediol) were measured.

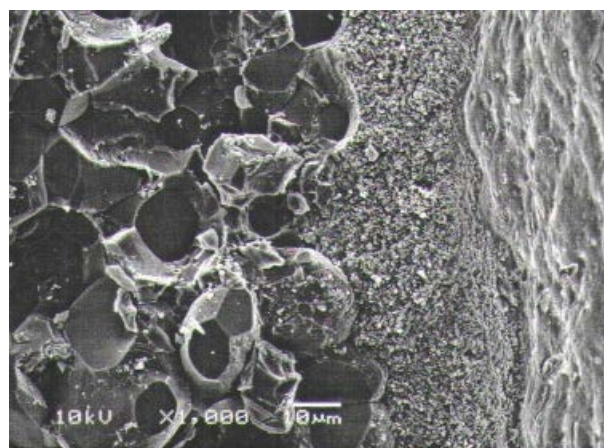
### 3 Results and Discussion

#### 3.1 Characteristics of the Membranes

An SEM image of a cross section of the porous alumina membrane before coating with the silica sol is shown in Figure 2. The alumina membrane consists of two layers: one is a macroporous layer constructed by large alumina particles with a size of more than 10  $\mu\text{m}$ , and the other one is a microporous layer constructed by smaller alumina particles with a size of less than 1  $\mu\text{m}$ . After coating the porous alumina membrane with the silica sol, a thin silica layer with a thickness of about 1  $\mu\text{m}$  was deposited on the alumina, as observed using SEM and shown in Figure 3.



**Figure 2** SEM image of a cross section of the porous alumina membrane as the supporting material.



↑  
nonporous silica layer

**Figure 3** SEM image of a cross section of the porous alumina membrane coated with silica membrane.

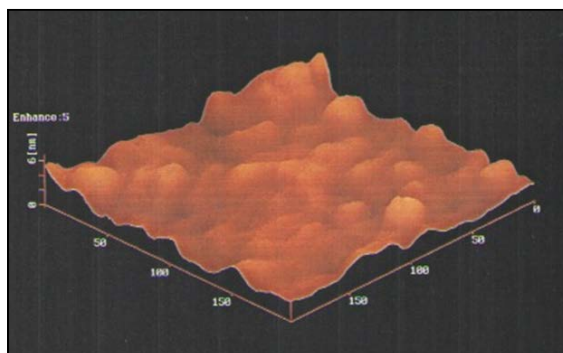
It was observed that the silica sols with high viscosity resulted in a thick silica layer, which easily formed cracks after drying. Table 3 depicts the appearance and viscosity of the silica sols with different compositions and the appearance of the silica membrane after drying. Si-1 membrane made from the Si-1 colloidal sol, which had high viscosity (6.97 cP), resulted in a cracked membrane. Dilution of the sol by adding more water resulted in the Si-2 and Si-3 membranes, which had no cracks.

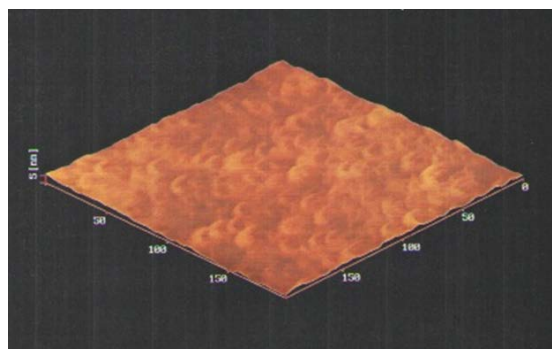
**Table 3** Sol appearance, sol viscosity and membrane appearance for various sol compositions.

Sol	Molar ratio				Sol appearance	Viscosity [cP]	Membrane Appearance After Drying
	TEOS	H <sub>2</sub> O	C <sub>2</sub> H <sub>5</sub> OH	HNO <sub>3</sub>			
Si-1	1	11.574	-	0.09	Opaque	6.97	Cracks
Si-2	1	115.74	-	0.045	Opaque	2.39	No cracks
Si-3	1	1157.4	-	0.023	Clear	1.99	No cracks
Si-4	1	6.5	3.8	0.09	Clear	4.48	Cracks
Si-5	1	6.5	47.7	0.09	Clear	2.19	No cracks
Si-6	1	6.5	179.6	0.09	Clear	1.89	No cracks

A polymeric silica sol was obtained by adding ethanol with a composition as shown in Table 3. Similar to the colloidal sols, a highly viscous sol such as the Si-4 sol resulted in a cracked membrane. No cracks were observed in the Si-5 and Si-6 membranes because the sols were diluted with ethanol. Because the goal was to produce crack-free membranes, sols Si-1 and Si-4, which both had high viscosity, were not used for membrane characterization.

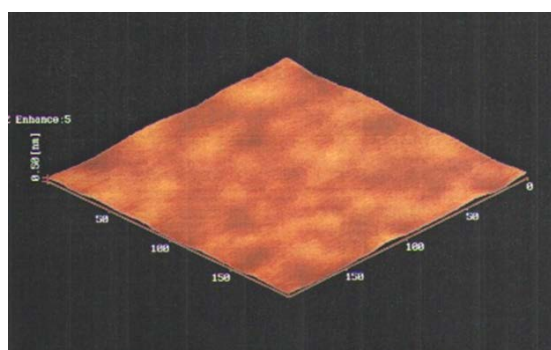
Figures 4 and 5 show AFM images of the Si-2 and Si-3 membrane surfaces respectively. Silica particles can be observed from the AFM image of each membrane. It can be seen that the average particle size of the Si-2 membrane is about 25 nm, whereas the Si-3 membrane shows an average particle size of about 10 nm, indicating that the particle size decreased with the decrease in viscosity.

**Figure 4** AFM image of the surface of silica membrane prepared using sol Si-2.

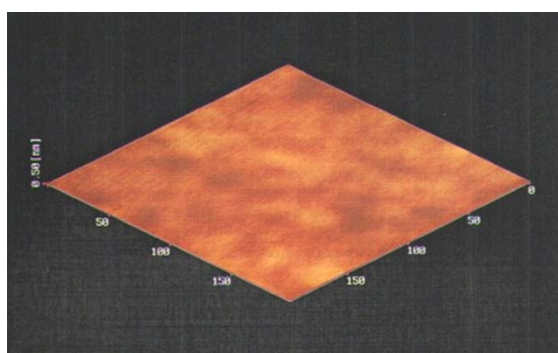


**Figure 5** AFM image of the surface of silica membrane prepared using sol Si-3.

A similar phenomenon was observed for the Si-5 and Si-6 membranes made from the polymeric silica sols Si-5 and Si-6, respectively. As can be seen in Figures 6 and 7, the AFM images show a particle size of about 15 nm for the Si-5 membrane and a smaller particle size of about 10 nm for the Si-6 membrane, which had a lower viscosity.



**Figure 6** AFM image of the surface of silica membrane prepared using sol Si-5.



**Figure 7** AFM image of the surface of silica membrane prepared using sol Si-6.

It was observed that sol Si-2, which had an intermediate viscosity and large particle size, easily deposited on the porous alumina membrane. On the other hand, when sols with lower viscosity and smaller particle size (such as Si-3, Si-5 and Si-6) were used, the dip-coating, drying and sintering process must be repeated many times to obtain a dense layer covering the whole surface of the porous alumina membrane. Therefore, sol Si-2 was used as the intermediate layer and on top of this layer a thin layer made from sols Si-3, Si-5 or Si-6 was deposited as the active layer.

### 3.2 Results of Pervaporation Experiment

Table 4 depicts the result of the pervaporation experiment. The Si-2 membrane showed a high flux of 0.91 kg/(m<sup>2</sup>h), however the separation factor was 3.7 only, indicating that the selectivity of the membrane was low. Interestingly, the pervaporation performance of the Si-3 membrane, which was prepared by depositing an Si-3 layer on top of the Si-2 intermediate layer, was different compared with that of the Si-2 membrane. Compared with the Si-2 membrane, the Si-3 membrane showed a lower permeate flux of 0.03 kg/(m<sup>2</sup>h), but a higher separation factor of 46.9 was achieved. A similar phenomenon was observed for the Si-5 and Si-6 membranes, as shown in Table 4. The Si-5 and Si-6 membranes were prepared by coating the Si-2 intermediate layer with the Si-5 sol and Si-6 sol, respectively, and showed a lower permeate flux and higher separation factor compared with the Si-2 membrane. The highest separation factor of 324 was achieved using the Si-6 membrane.

This phenomenon can be explained by using the AFM images of the membranes. Obviously, it was observed that the microstructures of the Si-3, Si-5 and Si-6 membranes were formed from silica particles with average particle sizes smaller than the Si-2 particle size. The smaller particle size resulted in a decrease in the pore size of the membrane, which strongly influences the pervaporation performance.

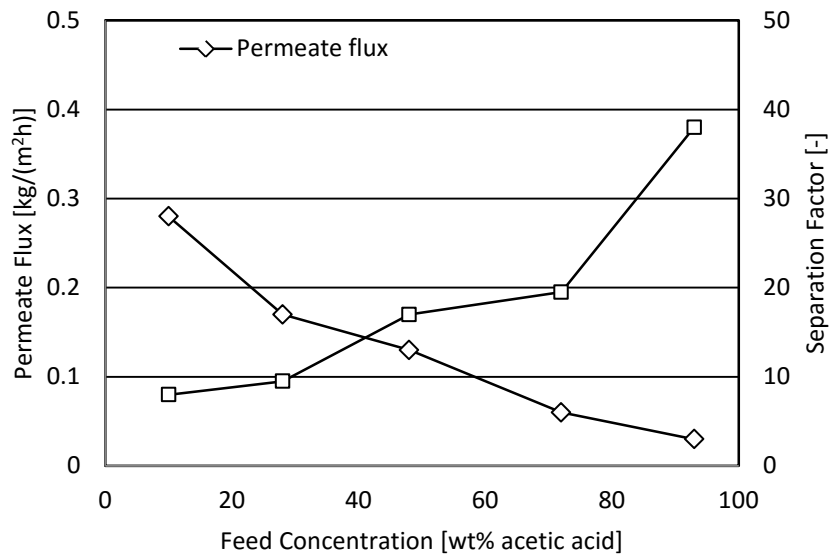
**Table 4** Permeate Flux and Separation Factor of Silica Membranes Prepared from Various Sols with Different Composition (feed concentration: 90 wt% acetic acid, feed temperature: 298 K).

Membrane	Permeate flux [kg/(m <sup>2</sup> h)]	Separation Factor [-]
Si-2	0.910	3.7
Si-3	0.030	46.9
Si-5	0.033	37.6
Si-6	0.016	324.0

To study the effect of the acetic acid concentration in the feed solution on the pervaporation performance, pervaporation experiments using the Si-5 and Si-6

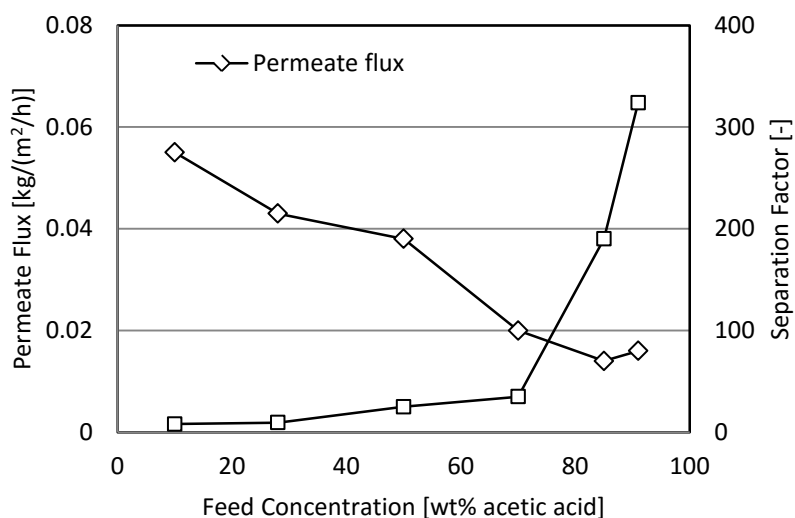


membranes were carried out at feed concentrations ranged between 10 to 90 wt% and a feed temperature of 298 K. Figures 8 and 9 show the pervaporation performance of the Si-5 and Si-6 membranes respectively. For both membranes, the permeate flux decreased with increasing acetic acid concentration in the feed, since water preferentially permeated through the membrane. As a result, the separation factor increased with increasing acetic acid concentration in the feed.



**Figure 8** Pervaporation performance of Si-5 membrane at different feed concentrations (feed temperature: 298 K).

It is interesting to note that for all feed concentrations, the Si-6 membrane showed higher selectivity but lower permeate flux compared to the Si-5 membrane. Both the Si-5 and Si-6 membranes were prepared from polymeric silica sols but with different compositions. The Si-6 sol contained more ethanol than the Si-5 sol, and more ethanol in the sol results in a smaller silica particle size, as shown in the AFM images (see Figures 6 and 7). As mentioned above, a smaller particle size will result in a more rigid and compact structure with a smaller pore size, which leads to a lower permeate flux and a higher separation factor.

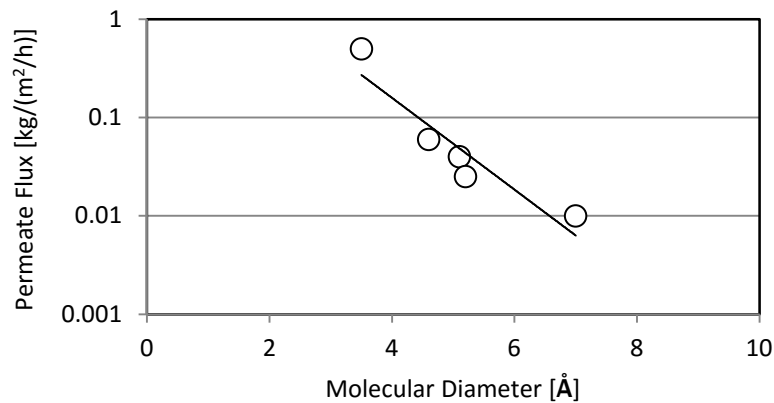


**Figure 9** Pervaporation performance of Si-6 membrane at different feed concentrations (feed temperature: 298 K).

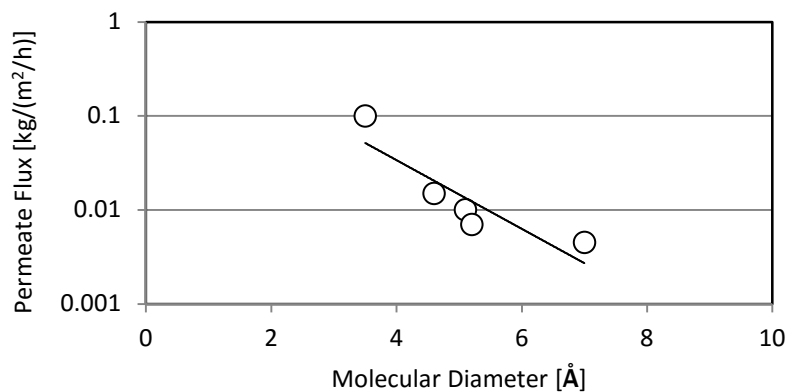
### 3.3 Estimation of Pore Size

Since it is not easy to measure the pore size of microporous membranes because of the very small size of the pores, in this work we measured the permeate fluxes of various pure liquids with known molecular diameters. The estimation of the pore size by this method is based on the Knudsen diffusivity theory that explains the dependency of the diffusivity on the molecular weight of the diffusing species [11]. Thus, assuming the diffusing species is a sphere with a certain diameter, we can suggest that the larger the molecular diameter of the species, the smaller the permeate flux. If the species has a molecular diameter larger than the pore size, the permeate flux will be zero. In this work, we used water, methanol, acetic acid, ethanol, and 1-3 butanediol, which are known to have average molecular diameters of 3.5 Å, 4.6 Å, 5.1 Å, 5.2 Å, and 7.0 Å, respectively.

Figures 10 and 11 show plots of the permeate fluxes of the pure substances vs the molecular diameter of the Si-3 and Si-5 membranes, respectively. As expected, it could be observed that the permeate fluxes decreased sharply with increasing molecular diameter, indicating that the permeation of the larger molecules was resisted by the small pores. The pore size of the membrane could then be estimated from the intersection of the line with the molecular diameter axis. Obviously, the pore sizes of both membranes were estimated as smaller than 1 nm.



**Figure 10** Plot of permeate flux vs. molecular diameter for Si-3 membrane.



**Figure 11** Plot of permeate flux vs. molecular diameter for Si-5 membrane.

#### 4 Conclusion

Inorganic membranes consisting of alumina as the supporting layer and silica as the active layer were prepared by sol-gel method using colloidal and polymeric silica sols with different compositions. It was found that diluted sol solutions were necessary to obtain crack-free silica membranes. The particle size of the silica membranes, as observed using AFM, was strongly influenced by the composition of the sols. This determined the pore size of the membranes and thus the pervaporation performance of the membranes. The pervaporation experiment showed that the selectivity of the membranes was improved by a bi-layer consisting of an intermediate silica layer made from the Si-2 sol and a skin silica layer made from diluted sols Si-3, Si-5 or Si-6. For a feed concentration

of 90 wt% acetic acid, the Si-6 membrane showed the highest separation factor of 324 with a permeate flux of 0.016 kg/(m<sup>2</sup>h). This work showed that silica membrane has a high potential for the dehydration of organic acids.

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