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# Permeation properties of organic compounds from aqueous solutions through hydrophobic silica membranes with different functional groups by pervaporation

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## ABSTRACT

In this work, hydrophobic silica membranes with phenyl groups were prepared by a sol-gel method using phenyltrimethoxysilane (PhTMS) as the silica precursor. The effect of the hydrolysis and condensation reaction of the PhTMS sol on the separation performance by pervaporation (PV) was investigated. To prepare a membrane for separation of ethyl acetate from water, the optimum reaction time for the silica sol was 3 h. Membranes were also prepared under the same conditions using ethyltrimethoxysilane (ETMS), *n*-propyltrimethoxysilane (PrTMS), isobutyltrimethoxysilane (BTMS), and hexyltrimethoxysilane (HTMS) as the silica precursors. PV was carried out using the ETMS, PrTMS BTMS, and HTMS membranes to separate organic compounds (5% mass fraction) from water at 295 K. The results indicated that the flux of an organic compound was related to the difference between the Hansen solubility parameters of the membrane and that of the organic compound.

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## 1. Introduction

Recently, many studies have reported on the separation of organic compounds from water by pervaporation (PV) [1–9]. PV is a membrane separation technique that is used to recover liquid organic compounds as vapors by reducing the pressure on the permeate side. This method can be used to separate azeotropes, thermally degradable mixtures, and low concentrations of organic compounds from water. For the recovery of low concentrations of organic compounds from water, it is expected that hydrophobic membranes will be effective [1]. However, membranes for PV need to have high flux, selectivity, and chemical and mechanical stability. To obtain high flux and selectivity, fine control of the membrane pore size is required to accommodate the large diameters of organic molecules [2]. Many studies have used hydrophobic polymer membranes [3–9]. However, polymer membranes are restricted to only certain feed mixtures because of their low chemical stability and thermal stability [2]. Alternatively, zeolite and microporous and mesoporous silica, titania, and zirconia inorganic membranes have been prepared for PV [10–17]. Recently, Kujawa et al. prepared hydrophobic alumina and titania membranes by grafting  $C_6F_{13}C_2H_4Si(OEt)_3$  (C6) molecules onto the membrane surface. A hydrophobic titania membrane treated with a C6 solution for 35 h showed separation factors of 30 and 91 for ethyl acetate (EA) and

methyl *tert*-butyl ether (MTBE) from water (organic content: 1% mass fraction), respectively [18]. Kujawa et al. concluded that the higher selectivity for MTBE compared with EA was related to the smaller distance between the Hansen solubility parameters (HSPs) of C6 and MTBE than that between C6 and EA while both fluxes are similar (MTBE flux:  $1.0 \text{ kg m}^{-2} \text{ h}^{-1}$ , EA flux:  $1.1 \text{ kg m}^{-2} \text{ h}^{-1}$ ). Liu and Shi also found that the HSP values affected the selectivity of the extraction of ethylbenzene and nitrobenzene by liquid membranes supported by a hollow fiber [19].

In a previous study, we prepared hydrophobic silica membranes on a porous alumina support with a  $\gamma$ -alumina interlayer using phenyltriethoxysilane (PhTES) and tetraethoxysilane (TEOS) as silica precursors. The membranes were prepared by a molecular template method using cetyltrimethylammonium bromide (CTAB) to form small pores of 1 nm that could separate organic compounds, such as EA, ethyl methyl ketone (MEK), and isopropyl alcohol, from water [11].

The interaction between membrane materials and the permeate will be an important factor in determining membrane separation performance. The EA flux of a phenyl-functionalized silica membrane prepared from PhTES and TEOS showed a two-fold increase in the flux for MEK despite the small kinetic diameter of MEK (0.504 nm) compared with EA (0.52) [11,13]. There is a high possibility that this difference between the fluxes was caused by differences in the interaction of phenyl-functionalized silica with EA and MEK. This suggests that functional groups on the membrane will be key to achieving high performance for the separation of the target compound.

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In the present work, we investigated the influence of functional groups on the hydrophobic silica membranes on the PV performance. First, the effects of the hydrolysis and condensation reaction time used in preparation of the silica sol on the membrane properties, such as pore diameter and membrane thickness, and PV performance for EA/water separation, were investigated. Phenyltrimethoxysilane (PhTMS) was used as a representative silicon alkoxide for preparation of phenyl-functionalized hydrophobic silica membranes (PhTMS membranes). The membranes were characterized by field emission scanning electron microscopy (FE-SEM) to evaluate the membrane thickness, permporometry was used to evaluate the pore size distribution, and contact angle measurements were used to evaluate the hydrophobicity of the membrane surface. The PV performance of the PhTMS membranes for separation of EA (5% mass fraction) from water was evaluated at 295 K. Silica membranes with ethyl, *n*-propyl, isobutyl, and *n*-hexyl groups were also prepared from ethyltrimethoxysilane (ETMS), *n*-propyltrimethoxysilane (PrTMS), isobutyltrimethoxysilane (BTMS), and *n*-hexyltrimethoxysilane (HTMS), respectively, and characterized. These membranes were used in PV for the separation of EA, MEK, acetone, and 1-butanol (1-BtOH) from water. In addition, we calculated the HSPs of the hydrophobic silica membrane with the different functional groups using a group contribution method. We discuss the prediction of organic flux for hydrophobic silica membranes based on the relationships among the HSPs of the hydrophobic silica membranes and organic compounds.

## 2. Experimental

### 2.1. Preparation of hydrophobic silica membranes

Hydrophobic silica membranes were prepared on tubular supports using a porous  $\alpha$ -alumina tube with a  $\gamma$ -alumina interlayer. The porous  $\alpha$ -alumina support (Noritake, Nagoya, Japan) had an average pore size 0.15  $\mu\text{m}$  and average porosity of 40%. The porous  $\alpha$ -alumina tube (length=35 mm) was joined to a dense  $\alpha$ -alumina tube (outer diameter=10 mm, inner diameter=6 mm, length=250 mm) and an  $\alpha$ -alumina disk ( $\phi$ =12 mm, thickness=2 mm) with a glass sealant (GA-13, Nippon Electric Glass) and then calcined at 1373 K [11].  $\gamma$ -Alumina interlayers are frequently used to form defect-free silica membranes [20–22]. If very thin silica layers with nanometer-sized pores form directly on the surface of a support with pores of about  $\phi$  0.15  $\mu\text{m}$ , there is a high probability that defects or cracks could form in the silica layer [11]. Hence, formation of a  $\gamma$ -alumina interlayer was proposed to obtain defect-free layers [20]. In this work, the  $\gamma$ -alumina interlayer was prepared using an established method [11].

To prepare the PhTMS membrane, first a PhTMS silica sol was prepared by hydrolysis and copolymerization of PhTMS (0.1 mol) in the presence of CTAB (0.008 mol) in 25 mL of ethanol with gentle stirring. This concentration of CTAB was higher than the critical micelle concentration of CTAB in ethanol (0.24 mol mL<sup>-1</sup>) [23]. The hydrolysis and condensation reactions of the PhTMS silica sol were promoted by adding 7.5 mL of 1 mol L<sup>-3</sup> HNO<sub>3</sub> dropwise to the mixture. Then, the mixture was stirred continuously at room temperature for 1, 3, 9, or 24 h. The alumina support was dipped into the silica sol for 60 s and then pulled out at a speed of 1 cm min<sup>-1</sup>. The support was dried at room temperature for 3 h and calcined at 453 K for 3 h. The membranes were then washed with ethanol to remove CTAB. ETMS, PrTMS, BTMS, and HTMS membranes were also prepared using the same method, with 3 h of stirring after addition of the HNO<sub>3</sub> solution.

### 2.2. Characterization of the hydrophobic silica membranes

The cross-sectional morphologies of the hydrophobic silica membranes were observed by FE-SEM (s-4800, Hitachi High-

Technologies Corp). Before the observation, membranes were coated with platinum using an ion sputtering device (JFC-1500, JEOL). The water contact angle on each membrane on a non-porous glass support was measured using an automatic contact angle meter (DMs-400, Kyowa Interface Science Co., Ltd.) to evaluate the hydrophobicity of the membrane. To prepare the samples for contact angle measurements, a non-porous glass plate was dipped into each silica sol prepared under the same conditions as the sols used for preparation of the hydrophobic silica membranes. The pore size distribution, including pinholes or cracks, for each hydrophobic silica membrane was estimated by permporometry. Permporometry is based on capillary condensation of a condensable vapor, which blocks the permeation of the non-condensable gas [12,13]. Capillary condensation of a vapor occurs in the membrane pores according to the Kelvin diameter. When vapor condenses in the pores at a certain pressure  $P$  that is lower than the saturated vapor pressure  $P_s$ , the membrane pores will be smaller than the Kelvin diameter as shown by the following equation:

$$D_p = \frac{-4\nu\sigma \cos \theta}{RT \ln(P/P_s)} \quad (1)$$

where  $D_p$  is the Kelvin diameter (m),  $\nu$  is the molar volume (m<sup>3</sup> mol<sup>-1</sup>),  $R$  is the gas constant (J mol<sup>-1</sup> K<sup>-1</sup>),  $T$  is temperature (K),  $\sigma$  is the surface tension (N m<sup>-1</sup>),  $\theta$  is the contact angle (°),  $P$  is the vapor pressure (Pa), and  $P_s$  is the saturated vapor pressure (Pa). Permporometry can be used to estimate the pore diameter distribution using the permeability of the non-condensable component in the presence of condensable vapor normalized to the permeability under dry conditions without the vapor [12,13]. The experimental apparatus for permporometry is illustrated in Fig. 1. EA was used as the condensable gas and He was used as the non-condensable gas. EA was fed by syringe pump and evaporated by heater. The gas mixture was provided at 100 mL min<sup>-1</sup> to the feed side of hydrophobic silica membrane at 0.2 MPa. The pressure on the permeate side was atmospheric pressure. The permeance was estimated using the flow rate measured with a soap-film flow meter. EA was provided by a syringe pump and vaporized at 393 K, and the vapor pressure was calculated using the above Kelvin equation.

### 2.3. Pervaporation

The PV separation properties of each hydrophobic silica membrane for various organic compounds (5% mass fraction in water) were measured. Each hydrophobic silica membrane was immersed in an aqueous solution of each organic compound as shown in Fig. 2. The

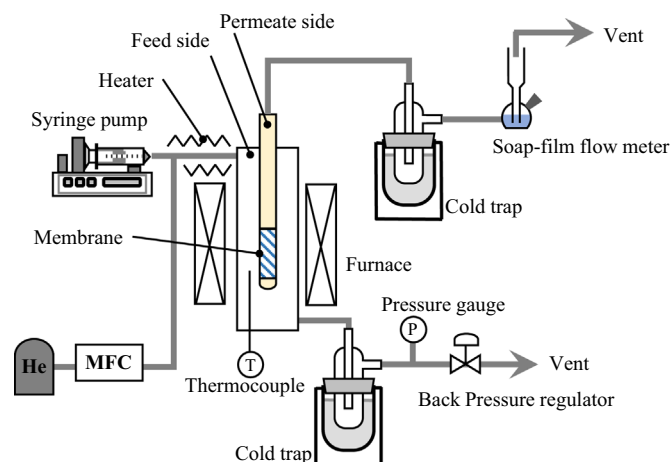


Fig. 1. Schematic of the apparatus for permporometry.

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