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Molecularly imprinted cellulose membranes for pervaporation separation of xylene isomers

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ABSTRACT

Molecularly imprinted polymeric membranes (MIPMs) were prepared from cellulose and 1,2- dihydroxybenzene as a print molecule with imprinting ratio of 0.5 and 1.0. Those membranes were applied to the separation of xylene isomers by pervaporation. The molecularly imprinted membranes selectively incorporated *o*-xylene from *o*-/*m*- and *o*-/*p*- mixtures at a low *o*-xylene concentration region, the adsorption selectivity toward *o*-xylene was determined to be 7.15 and 4.24, respectively, implying that 1,2-dihydroxybenzene worked well as the print molecule for *o*-xylene recognition; the pervaporation was carried out at 40 °C and at the downstream pressure of 0.5 kPa and showed permselectivity toward *o*-xylene at low *o*-xylene concentrations while toward *m*- and *p*-xylene at high *o*-xylene concentrations. The molecularly imprinted membranes gave higher flux than the control non-imprinted membrane. The results obtained in the present study revealed that molecular imprinting is one of promising methods to prepare separation membranes for pervaporation.

1. Introduction

Xylene is produced from crude oil as a mixture of all three isomers. Each of them is often used as intermediates and solvent, most industrial processes demand a single isomer. However, xylene isomers have very similar physicochemical properties, which makes the separation of isomer mixture not a simple matter. Distillation is ruled out because their boiling points differ by just a few degrees, for instance those for *o*-, *m*- and *p*-xylene is 144.4 °C, 139.1 °C, and 138.4 °C, respectively [1]. At present, industrial methods for xylene separation, such as crystallization or adsorption processes, involve slow, energy-intensive and complex processing [2,3]. Compared to conventional technologies, membrane separation technology has many advantages such as energy efficiency, environmentally benign technology with continuous operations and easy scale-up as well as a small footprint. Thus, as an alternative, membrane-based technologies have been gaining more interest in recent years.

A membrane is substantially a thin barrier that allows selective mass transport of permeants across the barrier [4–6]. The transport process is driven by a potential gradient such as concentration, pressure and electricity. The mechanism of pervaporation is explained by solution-diffusion mechanism. Diffusivity of permeants in the membrane is dominantly determined by their size and/or shape [7]. The performance of membrane separation refers to its permselectivity and flux (throughput).

The separation of xylene isomer has attracted a worldwide attention owing to its scientific and industrial importance. Pervaporation is a special membrane separation process with a phase change, the driving force for this process is the difference in the vapor pressure on the two sides of the membrane. Some studies of xylene separation by pervaporation were explored [8–35]. In the solution-diffusion mechanism, the permselectivity and flux of membrane separation are determined by the solubility and diffusivity selectivities of the permeants in the membrane. Since xylene isomers have similar size, it is difficult to separate them based on the diffusivity selectivity [7]. The utilization of their solubility difference is a viable strategy to enhance the separation performance. The solubility is a kind of affinity between the membrane and one isomer to be separated, which could be theoretically from naught to infinity. Therefore, people should design membrane materials with affinity that can molecularly recognize the target isomer. It is indispensable to introduce molecular recognition sites into a membrane so that the membrane recognizes the target isomer and incorporate it into a membrane.

Molecular imprinting is a versatile way to introduce molecular recognition sites into polymeric materials. The principle of molecular imprinting is as follows: a print molecule, usually the target or structurally related molecule, forms a complex with a functional monomer by covalent or non-covalent bonds. A cross-linking monomer leads to the formation of a three-dimensional polymer

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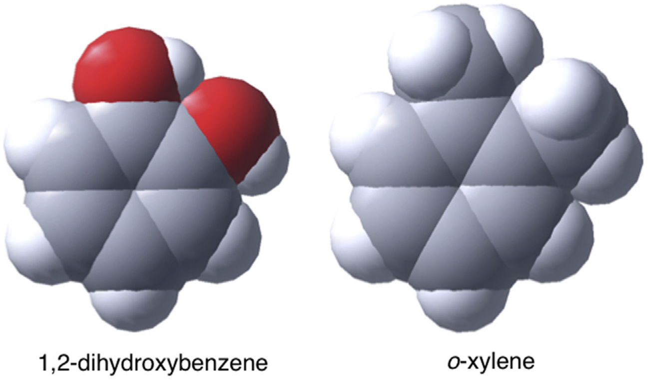
networks in which the print molecule is entrapped. The removal of the print molecule leaves a cavity working as molecular recognition sites where the target or structurally related molecule can bind the polymer, called molecularly imprinted polymers, with high selectivity [36–41]. However, conventional molecular imprinting results in highly cross-linked polymers, which are not regenerable. Another molecular imprinting technique, which is called an alternative molecular imprinting, directly converts polymeric materials to molecular recognition materials [42,43]. There is no polymerization process and mostly non-covalent bonds are formed in the imprinting procedure. The origin of this method can be traced back in 1962, when Michaels and his coworkers prepared pervaporation membranes using xylene isomer as the print molecule and polyethylene as the material to separate xylene mixture [8]. Utilizing the alternative molecular imprinting, many polymeric materials, such as synthetic polymers [44], oligopeptide derivatives [45], derivatives of natural polymer [46] and natural polymers [47], were directly adopted to prepare molecularly imprinted membranes. Michaels' study indicated that polymeric materials can be directly converted into membranes with molecular recognition sites [48–55].

The authors' group has used natural materials to prepare membranes [56–71]. Cellulose is abundant in nature and has strong hydrogen bonding network [72–74], which is expected to resist to be swollen by xylenes. Instead of xylenes, which are relatively volatile, benzenediol was adopted as a print molecule. Since benzenediol is a solid and has a similar structure to xylene. In the present study, 1,2-dihydroxybenzene molecularly imprinted cellulose membranes were prepared and their pervaporation of xylene mixtures was studied (Scheme 1).



Scheme 1

2. Experimental

2.1. Materials

Hardwood-based cellulose was purchased from Nacalai Tesque, Inc. and used as received. From the information from the supplier, the degree of polymerization of the cellulose was ca. 630 and the crystallinity was 85–90%. *N*, *N*-Dimethylacetamide (DMAc), LiCl, 1,2-dihydroxybenzene, *o*-xylene, *m*-xylene and *p*-xylene were obtained from Nacalai Tesque, Inc. and used without further purification.

2.2. Membrane preparation

Control cellulose membrane was prepared by dissolving cellulose in LiCl/DMAc solvent system [75]. 0.600 g of cellulose (mole number of anhydroglucose unit, 3.7×10^{-3} mol) was suspended in 20.0 cm^3 of DMAc at 100 °C for 30 min, 1.10 g of LiCl was then added and stirred. After cellulose was completely dissolved in LiCl/DMAc solution, the cellulose solution was stirred for additional 2 h and slowly cooled to room temperature. The cast solution thus prepared was poured into a flat laboratory dish and dried at 70 °C for 7 days. After peeled off, the membrane was dried again at 50 °C for 3 d ready to be used.

The 1,2-dihydroxybenzene molecularly imprinted cellulose membrane was prepared by adding 1,2-dihydroxybenzene into the cellulose solution as a print molecule. The amount of 1,2-dihydroxybenzene added is based on the imprinting ratio, the mole ratio of print molecule to that of anhydroglucose unit, (1,2-dihydroxybenzene)/(cellulose). We prepared molecularly imprinted membranes with imprint ratio of 0.50 (MIPM-05) and 1.0 (MIPM-10). 0.204 g or 0.408 g of 1,2-dihydroxybenzene (1.85×10^{-3} or 3.7×10^{-3} mol) was added to and dissolved in cellulose solution. After dried at 70 °C, the membrane was immersed in methanol to extract 1,2-dihydroxybenzene until the print molecule could be hardly detected in methanol by UV analysis. The membrane was dried again at 50 °C for 3 d ready to be used.

The average thickness of the control and imprinted membranes was determined to be ca. 90 μm.

2.3. Solubility experiments

The membrane samples were immersed in *o*-/*m*-xylene or *o*-/*p*-xylene mixtures at 40 °C. The weight fraction of *o*-xylene was ca. 0.1, 0.3, 0.5, 0.7 and 0.9 in both mixtures. Ten days later when the sorption equilibrium had been reached, xylene mixtures were extracted from the membrane [76]. The composition of the extracted xylene from the membrane was analyzed by Yanaco Gas Chromatograph G2800 with a 3.0 m-long column packed with Benton 34+DNP on Shimalite.

The solubility selectivity toward *o*-xylene, $S_{S(o/i)}$, is defined as

$$S_{S(o/i)} = (Z_o/Z_i)/(X_o/X_i) \tag{1}$$

where Z_o and Z_i are the weight fraction of *o*-xylene and *m*- or *p*-xylene in the membrane, and X_o and X_i are the weight fraction of *o*-xylene and *m*- or *p*-xylene in mixtures equilibrated with the membrane, respectively.

2.4. Pervaporation study

Pervaporation of *o*-/*m*-xylene and *o*-/*p*-xylene mixtures were carried out by a typical pervaporation technique [76,77]. The effective area of the membrane in the pervaporation cell was 17.3 cm^2. The downstream pressure was under vacuum which was kept at about 0.5 kPa and the operating temperature was maintained at 40 °C. The pervaporation was studied three times and the average values were adopted as experimental results. The composition of the feed and permeate sides was analyzed by the same gas chromatography as used for solubility experiments.

The separation factor toward *o*-xylene, $\alpha_{o/i}$, is defined as

$$\alpha_{o/i} = (Y_o/Y_i)/(X_o/X_i) \tag{2}$$

where Y_o and Y_i are the weight fraction of *o*-xylene and *m*- or *p*-xylene in permeate, X_o and X_i are the weight fraction of *o*-xylene and *m*- or *p*-xylene in feed, respectively.

3. Results and discussion

3.1. Solubility of o-xylene

Solubility is the dominant factor for molecular imprinting. As mentioned in Introduction, molecular imprinting was applied so that molecular recognition sites can be introduced into polymeric materials. The solubility results of control membrane, imprinted membranes with imprinting ratio of 0.5 (MIPM-05) and 1.0 (MIPM-10) in