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Vapor permeation of hydrocarbons through supported liquid membranes based on ionic liquids

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Abstract

Separation of benzene and cyclohexane is one of the most challenging processes in the chemical industry. In our previous paper, we examined the separation of a mixed solution of benzene and cyclohexane using a supported liquid membrane (SLM) based on ionic liquids. In this study, vapor permeation (VP) of benzene/cyclohexane through a SLM using ionic liquids based on 1-alkyl-3-methylimidazolium and quaternary ammonium salts was performed. We examined the effects of ionic liquids and the benzene fraction in the feed on the permeation flux and separation factor, and the stability of the SLM based on ionic liquid. It was found that the sorption step mainly affected the separation factor depending on the hydrophilicity of the ionic liquid. The hydrophilic liquid membrane that used *N*,*N*-diethyl-*N*-methyl-*N*-(2-methoxyethyl) ammonium tetrafluoroborate, which showed the highest selectivity of 47.1 for the mixed solution, gave the highest separation factor, 185 for 53 wt.% benzene and 950 for 11 wt.% benzene for the VP, which are superior to the previously reported values obtained by pervaporation. Over 1 month, a steady flux and separation factor were obtained, suggesting that the membrane was extremely stable.

Keywords: Ionic liquid; Supported liquid membrane; Benzene; Cyclohexane; Vapor permeation

1. Introduction

Ionic liquids as green solvents for separation processes have been extensively studied [1–4] because they basically have negligible vapor pressure, which makes them replacements for volatile organic solvents.

Supported liquid membranes (SLMs) are porous membranes whose pores are filled with liquids. SLMs are promising because they combine the processes of extraction and stripping, and the amount of solvent in the SLM process is also much lower than that in the solvent extraction process. However, the instability of SLMs had limited their commercial application [5]. Recently,

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it has been reported that SLMs based on ionic liquids were very stable because of negligible loss through vaporization [6]. After that, many studies on SLMs based on ionic liquids were performed. In our previous paper [7], we studied the separation of liquid benzene and liquid cyclohexane by using the SLMs based on ionic liquids and found selective permeation of benzene. In this paper, vapor permeation (VP) of benzene/cyclohexane through an SLM using ionic liquids based on 1-alkyl-3-methylimidazolium and quaternary ammonium salts was performed.

Currently, cyclohexane is produced by the catalytic hydrogenation of benzene at high temperature, and to produce high purity cyclohexane it must be separated from a mixture including unreacted benzene. Azeotropic distillation and extractive distillation are the processes currently available for the separation of benzene/cyclohexane mixtures due to their close boiling points [8]. Up to now, many researchers have developed alternative membrane separation processes, especially the membrane-based pervaporation (PV) and VP techniques because of the high separation costs of conventional techniques [9]. Numerous researchers have focused on this separation system to assess the PV and VP properties of membrane materials [9]. On the other hand, a few studies have been reported that use SLMs to separate benzene and cyclohexane in vapor [10].

In this study, we consider the application of ionic liquids to SLMs when separating benzene and cyclohexane in vapor to develop a reaction process with accompanying in situ separation at high reaction temperature.

2. Experimental

2.1. Materials

We prepared imidazolium-based ionic liquids, 1-butyl-3-methyl imidazolium hexafluorophosphate ($[C_4mim][PF_6]$), 1-hexyl-3-methyl imidazolium hexafluorophosphate ($[C_6mim][PF_6]$), and 1-octyl-3-methyl imidazolium hexafluorophosphate ($[C_8mim][PF_6]$) as described in a previous paper [11]. Diethyl (2-methoxyethyl) methylammonium bis(trifluoromethanesulfonyl) imide (T), and diethyl (2-methoxyethyl) methylammonium tetrafluoroborate (B) were kindly supplied by Nisshinbo Ind., Inc. (Tokyo, Japan). The structures of these ionic liquids are shown in Fig. 1. All remaining reagents were of analytical grade and were used without further purification.

2.2. Sorption experiment

In SLMs, vapors permeate the liquid in the pores of a polymer membrane. Therefore, we examined the distribution coefficient, K, of benzene and cyclohexane between the ionic liquid and hexadecane, which is inert solvent for the ionic liquids [11], as a measure of the degree of sorption. Ionic liquids (10 mL), hexadecane (10 mL) and benzene or cyclohexane (500 μL) were placed in a vial and shaken at a constant temperature (303 K) to attain equilibrium. After 2 h, the concentration of benzene in the hexadecane solution was determined by a

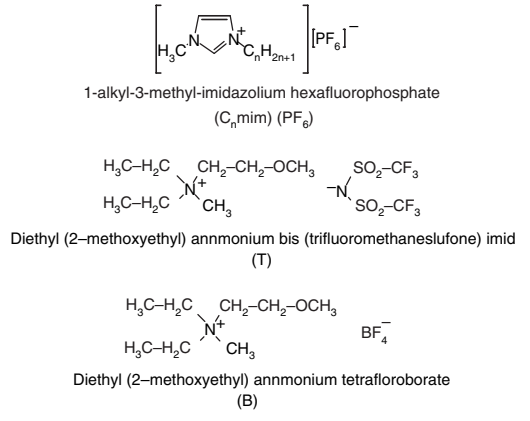

Fig. 1. Structure of imidazolium-based and quaternary ammonium-based ionic liquids: $n=4$, $[C_4mim][PF_6]$; $n=6$, $[C_6mim][PF_6]$; $n=8$, $[C_8mim][PF_6]$.