Pervaporation Permeation Behavior of a Series of Chlorinated Hydrocarbon/Water Mixtures Through PDMS Membranes

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Abstract: The permeation characteristics of a series of chlorinated hydrocarbons, which have different carbon and chlorine numbers, have been investigated through a poly(dimethylsiloxane) (PDMS) membrane in the pervaporation of pure hydrocarbon organics and dilute organic aqueous mixtures, respectively. The pervaporation of the dilute organic aqueous mixtures was performed at different feed compositions and feed temperatures. In particular, this study focused on examining the effects of both the chlorine and carbon numbers in the respective organic moieties on the permeation performance with respect to permeability, diffusivity, and solubility coefficients. The permeation behavior of the organic aqueous mixtures was analyzed in terms of their dependence on both the feed temperature and composition, and was compared with the permeations of the respective pure organic liquids. The permeation behavior of the chlorinated hydrocarbon aqueous solutions were interpreted in terms of the effects of the interaction between the organic permeant and the membrane material, and the interaction between the water and organic molecules absorbed in the membrane, resulting in a corresponding plasticization action on the membrane material. It was confirmed that the permeation of an organic permeant through the rubbery membrane is dominated by the sorption process rather than by a diffusion process.

Keywords: pervaporation, chlorinated hydrocarbon, PDMS, membranes, VOCs

Introduction

Water and air pollution from various organic compounds, which are used widely in industry, is causing serious environmental problems along with huge economic losses. To solve these problems, several conventional separation techniques, such as distillation, air stripping, aeration, and adsorption, have been suggested. However, because those techniques are complex and energy consuming, pervaporation has been widely investigated lately as a possible replacement process. Pervaporation is a membrane process that can offer significant opportunities for energy saving and reuse of valuable organics, when compared with conventional separation techniques. Furthermore, this membrane process can be integrated into conventional processes to enhance separation efficiency [1]. It is a very attractive method especially for the recovery of volatile organic compounds (VOCs) from waste mixtures containing trace VOCs. Much research has been conducted into the removal of trace VOCs from aqueous mixtures by pervaporation [2-6]. Baker and coworkers [7] investigated the separation of dissolved polar organic (ethanol) and non-polar organic solvents (ethyl acetate, chloroform, and 1,1,2-trichloroethane) from water using poly(dimethylsiloxane) (PDMS) and polyolefin composite membranes. In the case of the non-polar organic solvents, organic enrichment in the permeate of 50 ∼ 400-fold was obtained [7]. Nakagawa and coworkers [8] prepared a modified PDMS membrane by plasma grafting of fluoroalkyl methacrylates (FALMA) to enhance the affinity of PDMS to VOCs, and investigated the solution-diffusion mechanism of various VOCs in this modified PDMS membrane. They suggested that the permeation of VOCs through the rubbery membrane was characterized as a sorption-con-
controlled process in that a selectively permeating component VOC can only be larger in molecular size than water, but the rubbery polymeric membrane possesses a large free volume fraction, which may weaken the contribution of the permeant size to the diffusion property, resulting in the diffusion selectivity arising no big impact on the overall selectivity [8]. Yeom and coworkers [1] characterized the pervaporative permeation behavior of trace chlorinated hydrocarbons from water through PDMS membranes. They emphasized the formation of water clusters in the membrane depending on the hydrophilic circumstances established in the membrane by selectively absorbing VOC molecules. The formation of water clusters was claimed to suppress water permeation by increasing their diffusing size. A more fundamental understanding of the permeation, diffusion, and sorption effects will provide further insight into the transport of VOCs through rubbery membranes. However, to our knowledge, there have been no studies on the determination of permeation diffusion and sorption coefficients of VOC/water mixtures through rubbery membranes. Therefore, in this study, the permeations of both pure VOCs and VOC/water mixtures through a homogeneous PDMS membrane were carried out under various operating conditions, respectively, using a newly designed permeation apparatus that is able to evaluate the permeability, diffusivity, and solubility coefficients of the permeant simultaneously. In this paper, homologous series of chlorinated methanes and chlorinated ethanes were used as VOC components. The effects of both the chlorine and carbon numbers in the respective organic moieties were investigated on their permeability, diffusivity, and solubility coefficients. The permeation behavior of the organic aqueous mixtures was analyzed in terms of their dependence on both the feed temperature and composition, and compared with the permeations of the respective pure organic liquids. The permeation and separation behavior of the chlorinated hydrocarbon aqueous solutions are discussed in terms of the effects of the interactions between the organic permeant and the membrane material, and the interactions between the water and organic molecules absorbed in the membrane.

Experimental

Materials
Poly(dimethylsiloxane) (PDMS; GE655, General Electrics Co.) was generously provided by Dongyang Silicone (Seoul, Korea). n-Hexane used as a solvent, was purchased from Junsei Chemical Co. (Tokyo, Japan). The chlorinated hydrocarbons dichloromethane, chloroform, 1,2-dichloroethane, and 1,1,2-trichloroethane, used as VOCs, were purchased from Aldrich Chemical Co. (Milwaukee, USA). All organic solvents were of reagent grade and used without further purification. Water was ultrapure and deionized.

PDMS Membrane Preparation
The PDMS used in this study consists of two parts. Part A was mainly PDMS oligomers terminated with vinyl groups and part B was a mixture of Pt catalyst and PDMS oligomer with active hydrogens. A casting solution was prepared by dissolving parts A and B at a ratio of 9 : 1 in n-hexane. The casting solution was poured into a glass petri dish and then allowed to dry in a fume hood. After being cured at room temperature for 24 h, the membrane was placed in an oven at 100 °C for 2 h to ensure complete crosslinking. The crosslinking reaction took place through addition reactions in which the active hydrogens in part B attacked the vinyl groups in part A under Pt catalysis. The membrane thickness was 203 ~ 210 µm.

Swelling Measurements
To determine the amount of pure organics absorbed in the PDMS membranes, swelling measurements of the membranes were performed in each pure organics material. Dry membrane strips were immersed in pure organics thermostated at 25 °C for 72 h to allow the strips to reach equilibrium sorption. The dimension of a membrane strip were 7 × 2 cm. After measuring the swollen length of a strip at equilibrium sorption, the strip was dried for 30 h at room temperature under vacuum and then the dry length was measured. The swelling ratio, R, for an isotropic material is defined as [1]

$$ R = \frac{(L_S - L_D)}{L_D} $$

where L_S and L_D are the swollen and dry lengths of a strip, respectively.

All measurements were repeated 4 or 5 times; the resulting data had standard deviations of ±5 %. In addition, considering the vapor pressures of each pure organic compound, normalized swelling ratios were obtained from the swelling ratios obtained experimentally by normalizing by the vapor pressure of each pure organics compound.

Permeation Apparatus
The pervaporation apparatus used in this study is described elsewhere [9,10]. This apparatus can perform on-line measurements of both the permeation transient and the permeate composition during pervaporation. In addition, the permeability, diffusivity, and solubility coefficients from the permeation transient curves were determined simultaneously. This apparatus consists of three parts: a) feeding system, b) membrane cell, and c)
measurement and data acquisition system. The feed mixture was circulated from the feed tank, which could be controlled in a range of 5 to 150 °C with an accuracy of ±0.2 °C, through the membrane cell by a pump with an adjustment function of the flow rate. The rotor meter monitored the flow rate. The membrane cell was made of stainless steel with an effective area of 18 cm². The membrane cell was placed in a heating oven to control the feed temperature from room temperature up to 150 °C. The measuring system of the permeation properties, which was connected with the permeate side of the membrane cell, consisted of a mass flow meter (MFM), a precise pressure transducer (PT), and a gas chromatograph (GC). The MFM (Brooks, Japan) used in this study had a capacity of 1000 cm³ (STP)/min. The PT (Labovac Piza 2000, Saskia, German) equipped with pirani and piezo dual sensors could measure permeate pressures ranging from 1 × 10⁻⁵ to 1999.9 mbar. The MFM and PT were connected with a computer through a 21-bit interface module for analog-to-digital conversion at a sampling rate. When permeation happened through the membrane, the MFM and PT produced voltages corresponding to the permeation, respectively. The voltages produced could be monitored and displayed in real time by the computer, performing data acquisition. The GC (HP 5890 Series II plus) was equipped with an integrator (HP 3396 Series II), a sample injector (6-port valve) actuated by air, a TCD detector, and a packed column. The column was 6-ft long with a 1/8 in. inside diameter and included a Porapak Q packing material. Evacuation of the permeate was provided by the vacuum pump (GLD-201 B, Ulvac Kiko Co., Japan); a cold trap (Jeiotech Ltd., Seoul, Korea) was installed before the vacuum pump. The line in this system was wrapped with a heating band to control the inner temperature and, thereby, prevent the condensation of the permeate vapor on the inner wall of the line.

**Pervaporation Permeation**

In this study the permeations of pure organics and/or organic/water mixtures through poly(dimethylsiloxane) membranes were carried out under different operating conditions by using the novel permeation apparatus, which could measure both the permeation transients and

### Results and Discussion

#### Permeation Properties of Chlorinated Hydrocarbons in PDMS Membrane

The physical properties of the chlorinated hydrocarbons are shown in Table 1. As the number of chlorine atoms increases in a moiety with a given number of carbon atoms and/or the number of carbon atoms increases in an organic with a given number of chlorine atoms, it molar volume increases, its saturated vapor pressure decreases, and its solubility in water decreases. Thus, when the organic compound has more chlorine or carbon atoms, it becomes more hydrophobic, and the molar volume of the chlorinated hydrocarbons increases.

Figure 1 shows the permeation properties of the pure organics through PDMS membranes at 35 °C. The permeability coefficients of the pure organics increased with...
Table 2. Solubility Parameters of Chlorinated Hydrocarbons and Their Swelling Ratios (SR, NSR) in the PDMS Membrane at 25 °C

<table>
<thead>
<tr>
<th>Organics</th>
<th>Solubility Parameter (MPa)$^{1/2}$, $\delta t$</th>
<th>Swelling Ratio (SR)</th>
<th>Normalized Swelling Ratio at 25 °C ($\times 10^3$, SR/mmHg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₂Cl₂</td>
<td>20.3</td>
<td>0.424</td>
<td>0.99</td>
</tr>
<tr>
<td>CHCl₃</td>
<td>19.0</td>
<td>0.521</td>
<td>2.62</td>
</tr>
<tr>
<td>C₂H₄Cl₂</td>
<td>20.9</td>
<td>0.211</td>
<td>1.83</td>
</tr>
<tr>
<td>C₂H₅Cl₃</td>
<td>19.6</td>
<td>0.272</td>
<td>6.80</td>
</tr>
</tbody>
</table>

* $\delta t$: Total solubility parameter
* Normalized swelling ratio (NSR) = swelling ratio/saturated vapor pressure
* Solubility parameter of PDMS = 15 ∼ 16 Mpa$^{1/2}$

Figure 2. Total permeability coefficients of various organic solutions through a PDMS membrane plotted with respect to the VOC concentration in the feed at 35 °C.

increasing number of chlorine atoms or molar volume. According to the so-called solution-diffusion model, by which the pervaporation process is most often expressed, permeation is the combined effect of diffusion and sorption steps; thus, analysis of diffusion and solubility coefficient data could help to understand the permeation behavior of the VOC molecules. The solubility coefficients of the VOCs show a similar tendency to their permeability coefficients. This tendency of increasing the solubility with molar volume is commonly known, i.e., solubility increases with the boiling or critical point of the permeant; in other words, solubility increases with the condensability of the permeant [11]. In addition, this trend of the solubility coefficients is consistent with the results of the normalized swelling ratios of the VOCs absorbed in the swollen membrane, as shown in Table 2. The normalized swelling ratio of a VOC is parametrically identical with the solubility coefficient shown in Figure 1. The only difference between them is that the volume in the normalized swelling ratio refers to the net liquid volume absorbed, while that in the solubility coefficient indicates the vaporized volume of the absorbed liquid. Generally, the diffusivity of a permeant through a polymeric membrane is expressed as a function of both its molecular size and its affinity toward the membrane material [1]. These two factors affect the diffusion coefficient in the opposite way, as described below. Large molecules interact with more segments of the polymeric chains than do small molecules, favoring the passage of small molecules. In addition, absorbed VOC molecules can plasticize a polymeric membrane, depending on the affinity of the VOC to the membrane. The plasticization action of the absorbed VOC enhances the mobility of the polymeric chains and, thereby, increases the diffusivity of the VOC in the membrane. As can be seen in Figure 1, the diffusion coefficient of the permeant obviously decreases with its molar volume. However, a deviation from this trend was found for dichloroethane; its diffusion coefficient is not greater than that of chloroform, although its molar volume is smaller. This situation arises because the lower solubility or affinity of dichloroethane toward the PDMS membrane causes a smaller degree of plasticization on the membrane and, consequently, yields a smaller value of the diffusion coefficient. Thus, we see from Figure 1 that the diffusion coefficients between the VOC species are not much different, going reversely in the order of permeant size, but the VOC solubility coefficients follow distinctly their molecular size order. Also, the permeability coefficient is observed to change in the same manner as the solubility coefficient does with respect to the VOC molecular size, confirming that the overall permeation of VOCs is controlled to a greater degree by the sorption process.

Effect of Feed Composition on Permeation Performance of Chlorinated Hydrocarbon Aqueous Mixtures through PDMS Membrane

The permeations of the organic aqueous mixtures were carried out at concentrations ranging from 1.30 to 5.20 × 10⁻³ mol at 35 °C; the results are shown Figure 2. The total permeability coefficients of all the mixtures increased with increasing VOC concentration in the feed aqueous mixture. Also, like the permeability of the pure VOCs, the total permeability coefficients increased with increa-
The permeations of the VOC aqueous mixtures were analyzed, and it was found that the permeability coefficient increased with increasing VOC concentration. This result indicates that the amount of the VOC absorbed in the organophilic PDMS membrane increases with increasing VOC concentration in the feed aqueous mixture. On the other hand, the diffusion coefficient remained almost constant with respect to the VOC concentration in the feed aqueous mixture. It is very interesting to note that the diffusion coefficient of the mixture in the membrane decreased with increasing VOC molar volume, unlike the permeation of the pure VOCs, in which the diffusion coefficient of dichloroethane did not follow the trend; with a larger molar volume, the diffusion coefficient had a value higher than that of dichloroethane. This result could be explained in terms of the competing effects of the permeant molecular size and its plasticization action on the membrane material.

Temperature Effect on Permeation Performance of Chlorinated Hydrocarbon Aqueous Mixtures through PDMS Membrane

The permeations of the VOC aqueous mixtures were analyzed, and it was found that the permeability coefficient increased with increasing VOC concentration. This result indicates that the amount of the VOC absorbed in the organophilic PDMS membrane increases with increasing VOC concentration in the feed aqueous mixture. On the other hand, the diffusion coefficient remained almost constant with respect to the VOC concentration in the feed aqueous mixture. It is very interesting to note that the diffusion coefficient of the mixture in the membrane decreased with increasing VOC molar volume, unlike the permeation of the pure VOCs, in which the diffusion coefficient of dichloroethane did not follow the trend; with a larger molar volume, the diffusion coefficient had a value higher than that of dichloroethane. This result could be explained in terms of the competing effects of the permeant molecular size and its plasticization action on the membrane material.
carried out at temperatures ranging from 35 (3.3 K⁻¹) to 65 °C (30 K⁻¹); the results are described by the Arrhenius plots shown in Figure 5. Because the plots were not too distinguished to illustrate in a single graph, two typical VOC aqueous solutions, that is, chloroform and dichloroethane, were selected to present the feed temperature effect. These VOCs have similar molar volumes and solubilities in water. Usually, in an amorphous polymer such as PDMS, the thermal motion of polymer chains randomly produces free volume. That is, as the operating temperature increases, the vibration frequency and amplitude of the polymer chain both increase, and the resulting free volume becomes larger. In pervaporation, the permeating molecules can diffuse through these free volumes. Thus, the tendency of increasing permeation rate with increasing operating temperature is commonly observed. However, it is found in this study that all of the total permeability coefficients that were normalized by the permeant vapor pressure slightly decreased with increasing feed temperature. This observation could not be explained by considering only the effect of the free volume in terms of the operating temperature. In the pervaporation process, the permeation mechanism can be explained using a solution-diffusion model. Therefore, from this point of view, more details on these results could be obtained through the analysis of solubility and diffusivity coefficients, as shown in Figure 6. The solubility coefficients of the two solutions decreased with increasing operating temperature. In addition, the membrane selectivity to the VOC decreased [12], as shown in Figure 7. This result indicates that the solubility coefficient of the VOC component decreases with temperature. Actually, the selective absorption of the VOC component into the PDMS membrane is attributed to the strong attractive interaction between the VOC molecules and the membrane material. Because the interaction tends to weaken at higher temperature, the selective sorption of the VOC component is reduced correspondingly. At the same time, the repulsive interaction acting on the water component also weakens, so that the relative water
sorption to VOC sorption will be more significant. This result implies that the affinity of the VOC toward the membrane material decreases with increasing operating temperature. The slope of each plot represents the respective activation energy. In the diffusion process [1], the activation energy is generally related to the interaction among the permeating molecules and to the plasticization action of the permeant in the membrane. That is, weak interactions among permeating molecules or strong plasticization action of the permeant in the membrane results in a low activation energy. On the contrary, strong interactions among permeating molecules, causing a bigger size of the permeating unit by associated or coupled permeating molecules, or a small plasticization action gives, consequently, a high activation energy. Consequently, a large molar volume of chloroform leads to a large activation energy in the diffusion process. Thus, it is normal that chloroform, with its larger molar volume, has a larger diffusional activation energy and a lower sorptional energy, as can be found in Figure 6. Because the permeation activation energy is defined as the sum of the diffusional and sorptional activations, these two VOC aqueous solutions have similar permeational activation energies, as can be seen in Figure 5.

Conclusions

The permeation behavior of pure chlorinated hydrocarbons, which have similar physical-chemical properties, and of chlorinated hydrocarbon/water mixtures have been examined through a PDMS membrane in a pervaporation process. This study concentrated on a comparison of the permeation, sorption, and diffusion behavior of a series of chlorinated hydrocarbons with different numbers of chlorine and carbon atoms. The permeation behavior of the chlorinated hydrocarbons as a function of the concentration in the feed aqueous mixtures and the operating temperature was compared with that of the pure chlorinated hydrocarbons.

In the case of pure organics, the physical-chemical properties of the chlorinated hydrocarbons selected were observed to influence the permeation properties. That is, as the molar volumes of organics increased and/or the saturated vapor pressures decreased, the permeability and solubility coefficients increased, while the diffusion coefficients decreased. The reason why the solubility coefficients increased with the molar volumes of organics is that the organics become more hydrophobic; that is, if the molar volume of the organic compound is large, its affinity toward PDMS membranes having hydrophobic characteristics is enhanced. On the other hand, in the case of diffusion of a larger permeant through a PDMS membrane, the permeant can have a higher degree of interaction with the membrane material so that the permeant resistance increases, the permeant would then undergo slower permeation than would a smaller permeant. In the case of organic aqueous mixtures, although the permeation properties show a similar trend to those of the pure organics, this trend is not consistent with the results of the pure organics because of the interactions of organic-water in the feed and of organic-water-sorbed in the membrane. In the organic aqueous mixtures, the solubility coefficients decrease while the diffusion coefficients increase with the operating temperature, resulting in a decrease in both the total permeability coefficients and the selectivities for two organics. Consequently, permeation of organic compounds through an organophilic membrane, such as PDMS, is a solubility-selective process.

References