

# Spectroscopic Characterization of Cellulose Acetate Polymer Membranes Containing Cu(1,3-butadiene)OTf as a Facilitated Olefin Transport Carrier

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Polymer–metal complexes composed of Cu(1,3-butadiene)OTf and cellulose acetate (CA), Cu–CA, have been successfully applied to facilitated olefin transport membranes for the olefin/paraffin separation, and the reversible solid-state interactions of Cu<sup>+</sup> ions with cellulose acetate (CA) and olefins have been observed using FT-IR and UV spectroscopy. FT-IR study clearly shows that the Cu<sup>+</sup> ions in the Cu–CA membrane are coordinated by the carbonyl groups of CA. Upon incorporation of Cu(1,3-butadiene)OTf into CA, the carbonyl stretching frequency of CA at 1753 cm<sup>-1</sup> shifts to a lower frequency at around 1702 cm<sup>-1</sup> and the degree of coordination increases with increasing amounts of Cu(1,3-butadiene)OTf. The Cu<sup>+</sup>–carbonyl interaction is found to be significantly affected by the coordination of an olefin, suggesting that the olefin and carbonyl group compete with each other for the coordination to Cu<sup>+</sup> ions. Reversible olefin coordination to Cu<sup>+</sup> ions in the Cu–CA membranes has been observed by FT-IR and UV studies. Treatment of the Cu–CA membrane with propylene, ethylene, or 1,3-butadiene produces a corresponding olefin-coordinated membrane in which the coordinated olefin is easily replaced by another olefin.

## Introduction

Olefin/paraffin separation by facilitated transport membranes using transition metal complexes as carriers has attracted much interest as the most promising alternative to energy-intensive low-temperature distillation because of their low energy consumption, compact unit, and simple operation.<sup>1–6</sup> The basis for the separation is the formation of a reversible  $\pi$ -complex between metal ions, like Ag<sup>+</sup> or Cu<sup>+</sup>, and the olefins.<sup>6–9</sup> There have been many reports on the facilitated transport of olefins by using supported liquid membranes, ion-exchange membranes, or dense polymer membranes

containing Ag<sup>+</sup> ions as carriers.<sup>10</sup> Cuprous salts have been widely used as adsorbents in the adsorptive separation of olefin/paraffin mixtures, but the studies on the Cu<sup>+</sup> ion-mediated facilitated transport membranes have been extremely limited even though the separation by facilitated membranes is more desirable than adsorptive separation in terms of energy efficiency as well as simplicity.<sup>11–13</sup>

Recently, we have communicated that the dense polymer membrane consisting of poly(vinyl pyrrolidone) and CuBF<sub>4</sub> is effective for the separation of ethylene/ethane and propylene/propane mixtures.<sup>14</sup> During the course of our study on the development of facilitated transport membranes containing cuprous complexes, we have found that Cu(1,3-butadiene)OTf, a relatively stable cuprous complex, can also be applied to the dense polymer membrane as a transport carrier. Since the understanding of the phenomena occurring on the solid polymer membrane is of pivotal importance in developing membranes of better performance,<sup>6,15</sup> we have investigated the interaction of Cu<sup>+</sup> ions with cellulose acetate (CA) and olefins in the polymer membrane

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consisting of Cu(1,3-butadiene)OTf and CA, Cu-CA. We report here the spectroscopic observation of the reversible solid-state interactions of Cu<sup>+</sup> with olefins and CA as well as the performance of Cu-CA membranes for the olefin/paraffin separation.

### Experimental Section

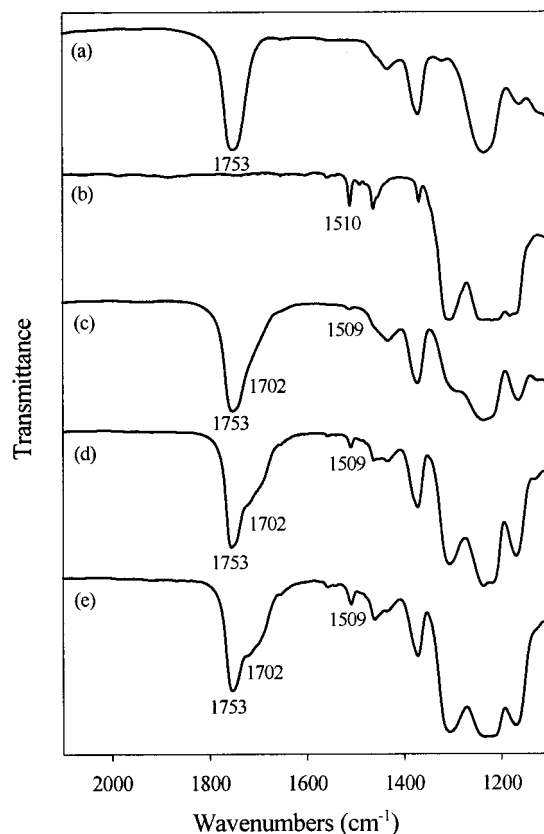
**General.** All operations were carried out under an atmosphere of purified argon using standard Schlenk techniques or in a drybox. All solvents were freshly distilled according to the literature. CA (acetyl content: 39.8 wt %), cuprous oxide, 1,3-butadiene, and trifluoromethanesulfonic anhydride were purchased from Aldrich. Cu(1,3-butadiene)OTf was prepared according to the literature procedure.<sup>16</sup>

**Cu-CA Membrane for IR and UV Measurements.** Cu(1,3-butadiene)OTf (0.15 g) was mixed with 2 wt % CA (0.1 g, molar ratio of Cu/CA = 3) in THF solution. The solution was dropped onto a 25 mm × 3 mm CaF<sub>2</sub> (IR) or quartz window (UV). The coated window was dried and placed in a specially designed gas cell.<sup>17</sup> IR and UV spectra were recorded on a Perkin-Elmer Spectrum GX I and Sinco UV S-2100 spectrometer, respectively.

**Cu-CA Membrane for Permeation Measurements.** The polymer membranes with varying molar ratio of Cu/CA for permeation test were prepared as follows: Cu(1,3-butadiene)OTf (0.24 g) was mixed with 8 wt % CA (0.16 g) in THF solution (Cu/CA = 3). The solution was cast onto a polyester membrane filter (Whatman, 0.1 μm) and dried in a vacuum for 1 h. Separation measurements were performed with the prepared membrane placed in a stainless steel separation module with an olefin/paraffin (v/v = 50/50) mixture.<sup>18</sup> The flow rates of the mixed gas were controlled using a mass flow controller. The total feed pressure of the mixed gas was set at 20 psig by a back pressure regulator. A feed mixture at a flow rate of 3 mL/min was introduced into the upper chamber of the measurement cell until the desired pressure was reached. Only steady-state samples were collected. The permeation properties of pure and mixture gas were measured at 25 °C and at feed pressure between 5 and 85 psig. Volumetric gas flow rates were determined by using a soap-bubble flowmeter. The feed and permeated gases were analyzed using a Gow-Mac gas chromatography equipped with a thermal conductivity detector and a unibead 2S 60/80 column.

### Results and Discussion

In a carrier-mediated facilitated transport membrane, it is reported that the reversible reaction between carriers and penetrants cause concentration fluctuation in the membrane. Based on this concept, Kang et al. proposed a concentration fluctuation model where facilitated transport increases with the increase of equilibrium constant, *K*, and backward reaction rate constant, *k*<sub>2</sub>, between the carrier and the penetrant.<sup>19</sup> In this respect, it is extremely important to study the interaction between the carrier and the penetrant in the solid polymer membrane for the better understanding of facilitated transport phenomenon and for the development of high permeance facilitated transport membranes as well. Since the degree of interaction between the carrier and the penetrant is likely to be largely affected by the presence of polymer, the interaction between the carrier and the polymer is also investigated.



**Figure 1.** IR spectral changes of C=O in CA upon interaction with Cu(1,3-butadiene)OTf: (a) CA; (b) Cu(1,3-butadiene)OTf; (c) Cu-CA membrane (Cu/CA = 1); (d) Cu-CA membrane (Cu/CA = 3); and (e) Cu-CA membrane (Cu/CA = 6).

Figure 1 shows the IR spectra of CA, Cu(1,3-butadiene)OTf, and Cu-CA membranes with varying molar ratio of Cu/CA. The peak at 1510 cm<sup>-1</sup> in Figure 1b can be assigned to the C=C stretching frequency of the coordinated 1,3-butadiene in Cu(1,3-butadiene)OTf. The presence of the peak at 1509 cm<sup>-1</sup> (Figure 1c-e) demonstrates that the coordinated 1,3-butadiene is not removed by the interaction with CA. The incorporation of Cu(1,3-butadiene)OTf into CA results in the appearance of a new carbonyl peak at around 1702 cm<sup>-1</sup> at the sacrifice of the free carbonyl peak of CA at 1753 cm<sup>-1</sup> (Figure 1c-e). This result indicates that some of the carbonyl groups of CA coordinate to Cu<sup>+</sup> ions, probably through the electron donation from oxygen atom to the vacant 4s orbital of Cu<sup>+</sup> ion. The degree of coordination of carbonyl groups to Cu<sup>+</sup> ions increases with increasing the molar ratio of Cu/CA. Two carbonyl peaks at 1753 and 1702 cm<sup>-1</sup> in Figure 1c-e can be associated with free and coordinated carbonyl groups, respectively.

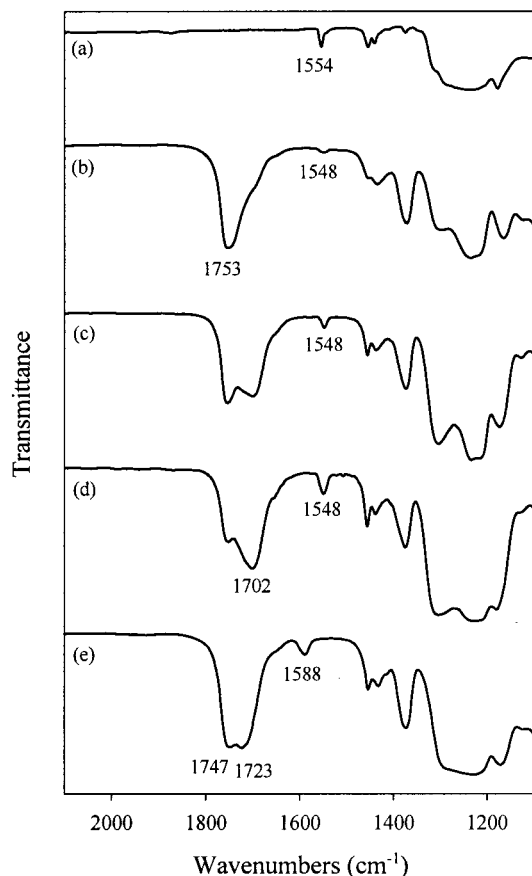
Figure 2 shows the IR spectra of Cu(propylene)OTf and propylene-coordinated Cu-CA membranes with varying molar ratio of Cu/CA. Cu(propylene)OTf and the propylene-coordinated Cu-CA membranes were obtained by the in situ reaction of Cu(1,3-butadiene)OTf or Cu(1,3-butadiene)OTf-CA membranes with propylene in the gas cell. The peak at 1554 and 1548 cm<sup>-1</sup> (Figure 2a,b-d) can be assigned to the stretching frequency of the coordinated propylene in Cu and Cu-CA membranes, respectively. The peak shift to a lower frequency by 6 cm<sup>-1</sup> can be attributed to the increased

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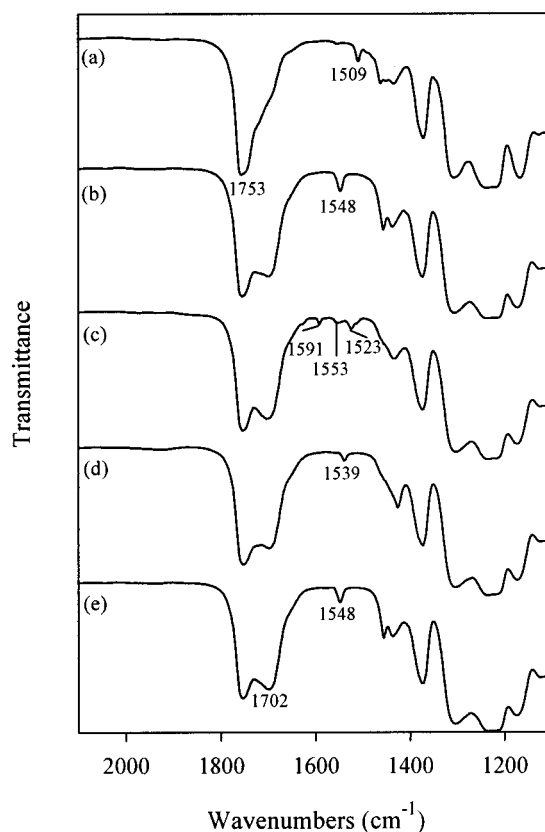
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**Figure 2.** IR spectral changes of C=O in CA and propylene-coordinated membranes. The membrane has been exposed to 30 psig of propylene for 2 min followed by N<sub>2</sub> purge for 3 min: (a) Cu(propylene)OTf; (b) Cu(propylene)OTf-CA membrane (Cu/CA = 1); (c) Cu(propylene)OTf-CA membrane (Cu/CA = 3); (d) Cu(propylene)OTf-CA membrane (Cu/CA = 6); and (e) Ag(propylene)OTf-CA membrane (AgOTf/CA = 3).

electron density on Cu<sup>+</sup> ions by the electron donation from carbonyl groups of CA, which in turn causes the increased electron donation from Cu<sup>+</sup> ions to the empty  $\pi^*$  orbital of the coordinated propylene. As of 1,3-butadiene-coordinated Cu-CA membranes, the intensities of the peaks corresponding to coordinated carbonyl groups and coordinated propylene in propylene-coordinated Cu-CA membranes increase with increasing molar ratio of Cu/CA. The degree of coordination of carbonyl groups to Cu<sup>+</sup> ions seems to be largely influenced by the coordination of olefins, suggesting that the olefin and carbonyl group compete with each other for the coordination to Cu<sup>+</sup> ions. As can be seen in Figure 1c-e and Figure 2b-d, the peak intensity ratio of coordinated to uncoordinated carbonyl is considerably higher for propylene-coordinated membranes in comparison with that for 1,3-butadiene-coordinated membranes. This can be ascribed to the difference in bonding modes of olefins to Cu<sup>+</sup> ions. It is likely that 1,3-butadiene in the starting Cu-CA membrane is more strongly coordinated to Cu<sup>+</sup> ions probably in a  $\eta^4$ -fashion and, therefore, the available coordination sites for carbonyl groups become limited. While, on the other hand, propylene seems to be much weakly coordinated in a  $\eta^2$ -fashion, giving more chances for carbonyl groups to interact with Cu<sup>+</sup> ions.



**Figure 3.** IR spectral changes for the reversible olefin coordination in the Cu-CA membrane. The membrane has been exposed to 30 psig of olefin for 2 min followed by N<sub>2</sub> purge for 3 min (Cu/CA = 3): (a) Cu(1,3-butadiene)OTf-CA membrane; (b) Cu(propylene)OTf-CA membrane; (c) Cu(1,3-butadiene)OTf-CA membrane; (d) Cu(ethylene)OTf-CA membrane; and (e) Cu(propylene)OTf-CA membrane.

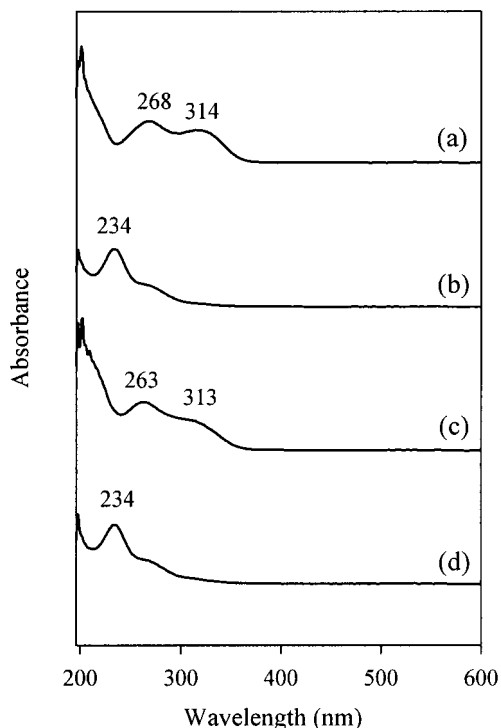
Bonding strength between metal ion and propylene in Ag(propylene)OTf-CA and Cu(propylene)OTf-CA membranes has been compared by the IR spectral change of C=C stretching frequency. Figure 2d-e shows that the C=C stretching frequency of the coordinated propylene in the Cu(propylene)OTf-CA membrane is 40 cm<sup>-1</sup> lower than that in the Ag(propylene)OTf-CA membrane, indicating that propylene is more strongly bound to Cu<sup>+</sup> ions than to Ag<sup>+</sup> ions. Accordingly, the dissociation of the coordinated propylene in the Cu-CA membrane would be more difficult compared with that in the Ag-CA membrane and this is probably one of the reasons why Cu-CA membranes exhibit lower selectivity for olefin over paraffin than those of Ag-CA membranes.<sup>20</sup>

A series of FT-IR spectra in Figure 3 demonstrate the rapid and reversible olefin coordination to Cu<sup>+</sup> ions dissolved in the solid Cu(1,3-butadiene)OTf-CA membrane.

Figure 3a is the IR spectrum of the Cu-CA membrane with the molar ratio of Cu(1,3-butadiene)OTf/CA = 3. When the membrane was exposed to 30 psig of propylene for 2 min and then purged with N<sub>2</sub> for 3 min, a new IR absorption peak at 1548 cm<sup>-1</sup> appeared (Figure 3b). This new peak represents the C=C stretching frequency for the coordinated propylene. The peak

(20) The selectivity for propylene over propane was around 200 with the AgOTf-CA membrane at the molar ratio of Ag/CA = 3.



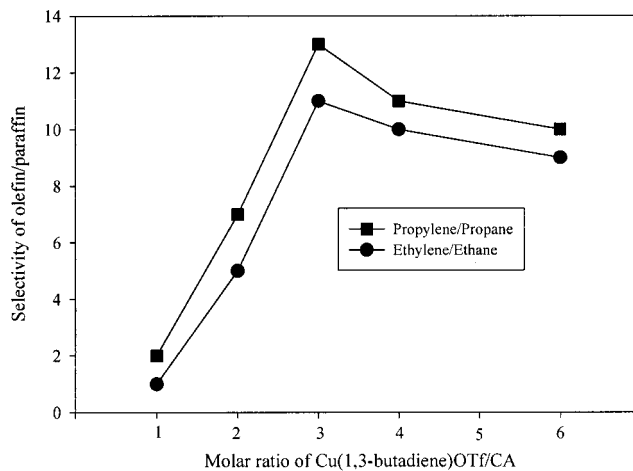


**Figure 4.** UV spectral changes for the reversible olefin coordination in the Cu-CA membrane. The membrane has been exposed to 30 psig of olefin for 2 min followed by N<sub>2</sub> purge for 3 min (Cu/CA = 3): (a) Cu(1,3-butadiene)OTf-CA membrane; (b) Cu(propylene)OTf-CA membrane; (c) Cu(1,3-butadiene)OTf-CA membrane; and (d) Cu(propylene)OTf-CA membrane.

at 1548 cm<sup>-1</sup> remains even after outgassing at 10<sup>-5</sup> Torr for 4 h at room temperature. Interestingly, however, exposure of the propylene coordinated membrane to 30 psig of 1,3-butadiene for 2 min and subsequent treatment with N<sub>2</sub> for 3 min gives three new peaks at 1591, 1553, and 1523 cm<sup>-1</sup> with the concomitant disappearance of the peak at 1548 cm<sup>-1</sup> (Figure 3c), indicating that the coordination mode of 1,3-butadiene is different from that of the starting membrane, Cu(1,3-butadiene)OTf-CA (Figure 3a). The peak at 1591 cm<sup>-1</sup> has been identified as for free, dissolved 1,3-butadiene. The two other peaks for the coordinated 1,3-butadiene can be ascribed to the difference in bonding mode of 1,3-butadiene. Once the 1,3-butadiene ligand in the starting membrane, Cu(1,3-butadiene)OTf-CA, is removed, the vacant sites are likely to be occupied by carbonyl groups of CA and, thereby, prohibiting the coordination of the incoming 1,3-butadiene in a η<sup>4</sup>-fashion.

Likewise, the three peaks disappeared and a new peak at 1539 cm<sup>-1</sup> corresponding to coordinated ethylene appeared when ethylene was introduced into the cell containing a 1,3-butadiene-coordinated Cu-CA membrane (Figure 3d). When the ethylene-coordinated membrane was exposed to 30 psig of propylene and then purged with N<sub>2</sub>, the peak representing the coordinated propylene reappeared at 1548 cm<sup>-1</sup> (Figure 3e).

The reversible olefin coordination has also been observed by the spectral changes in the UV absorption as shown in Figure 4. Figure 4a shows broad absorption bands centered at 268 and 314 nm for the Cu(1,3-butadiene)OTf-CA membrane (Cu/CA = 3). When the membrane was exposed to propylene atmosphere for 2

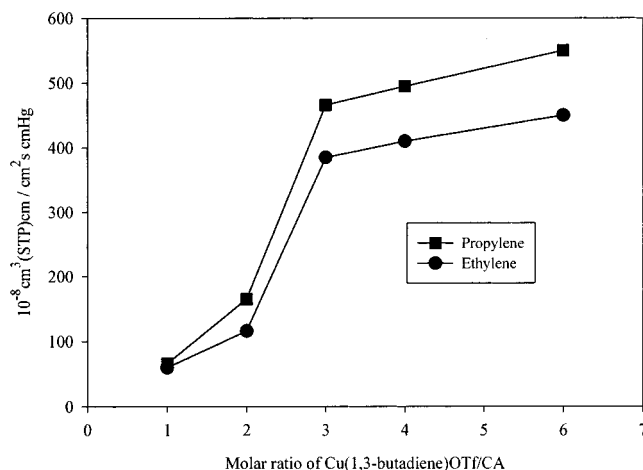


**Figure 5.** Effect of the molar ratio of Cu(1,3-butadiene)OTf/CA on the selectivity for olefin over paraffin at 25 °C and 20 psig of feed pressure.

min and followed by N<sub>2</sub> purge for 3 min, the absorption bands centered at 268 and 314 nm disappeared and a new band appeared at 234 nm for the coordinated propylene (Figure 4b). In the same manner, the absorption band of coordinated 1,3-butadiene centered at 263 and 313 nm appeared with the disappearance of the absorption band at 234 nm upon exposure of the membrane to 1,3-butadiene atmosphere and subsequent N<sub>2</sub> purge (Figure 4c). These results again indicate that the coordinated olefin is not rigidly held to the Cu<sup>+</sup> ions, thus the coordinated olefin is labile enough to be easily replaced by another olefin. The coordinated propylene at 234 nm reappeared when propylene was introduced into the cell containing the 1,3-butadiene-coordinated membrane (Figure 4d).

Such a reversible olefin coordination to Cu<sup>+</sup> ions has been applied to the separation of the olefin/paraffin mixture to evaluate the facilitated olefin transport effect of Cu<sup>+</sup> ions in the cellulose acetate membranes. Figure 5 shows the effect of the molar ratio of Cu(1,3-butadiene)OTf/CA on the selectivity for olefin over paraffin. The selectivity for propylene over propane and ethylene over ethane increased with increasing molar ratio of Cu/CA up to 3 and thereafter gradually decreased with further increase in the molar ratio. The maximum selectivity at the molar ratio of Cu/CA = 3 implies that the coordination environment of Cu<sup>+</sup> ions in the Cu-CA membranes has a significant effect on the performance of the membrane. The monomer unit of CA (acetyl content: 39.8 wt %) has approximately 4.9 carbonyl groups and thus, in principle, each Cu<sup>+</sup> ion in the membrane (Cu/CA = 3) can be coordinated by about 1.6 carbonyl groups. From the following permeation results and the above spectroscopic data, it is likely that the Cu<sup>+</sup> ions in Cu-CA membrane should be in around a 2-fold carbonyl coordinated state for the membrane to be highly selective in the facilitated transport of ethylene and propylene.

Pure-gas permeation properties of Cu-CA membranes as a function of Cu(1,3-butadiene)OTf contents were investigated in order to find out the origin of the selectivity maximum in Figure 5. As can be seen in Figure 6, the pressure-normalized ethylene and propylene flux rapidly increased with the increasing molar



**Figure 6.** Effect of the molar ratio of Cu(1,3-butadiene)OTf/CA on the pure-olefin permeation properties of the Cu-CA membrane at 25 °C and 20 psig of feed pressure.

**Table 1. Pressure-Normalized Pure Ethylene and Propylene Fluxes as a Function of Feed Pressure for the Cu-CA Membrane (Cu/CA = 3) at 25 °C**

feed pressure (psig)	pressure-normalized flux <sup>a</sup> (10 <sup>-8</sup> cm <sup>3</sup> (STP)/cm <sup>2</sup> ·s·cmHg)	
	C <sub>2</sub> H <sub>4</sub>	C <sub>3</sub> H <sub>6</sub>
5	703	810
10	505	628
20	385	466
35	284	366
60	171	354
85	177	345

<sup>a</sup> The paraffin flux was too small to be measured.

ratio up to Cu(1,3-butadiene)OTf/CA = 3 but thereafter increased in a much reduced rate. This result again demonstrates the importance of the molar ratio of Cu/CA = 3. The pure ethane and propane fluxes, however, were too small to be measured with our equipment. Upon introduction of an olefin onto the membrane, the membrane is plasticized to a certain extent, which may enhance the copermeation of paraffin in the olefin/paraffin mixture. The mixed gas selectivity, therefore, is like to be affected by the amount of the copermeated paraffin. Considering the results described above, it is concluded that the selectivity maximum behavior is mainly originated from the change in accessibility of propylene to the binding sites of Cu<sup>+</sup> ions and the plasticization effect of olefins. Such a selectivity maximum behavior has been previously reported by Nishide et al. for oxygen transport using Co porphyrin compounds incorporated into a polymer matrix.<sup>21</sup>

The pure ethylene and propylene permeation properties of a solid polymer membrane with a molar ratio of Cu(1,3-butadiene)OTf/CA = 3 as a function of feed pressure is shown in Table 1. The pressure-normalized ethylene and propylene flux decreases as the feed pressure rises from 5 to 85 psig. This behavior occurs because the transport of olefins is controlled by the complexation reaction of olefins with the Cu<sup>+</sup> ions, not by diffusion through the CA matrix. Once all available Cu<sup>+</sup> ions are complexed, a higher olefin pressure does

**Table 2. Pressure-Normalized Mixed Gas (Propylene/Propane) Flux at 25 °C as a Function of Feed Pressure for the Cu-CA Membrane (Cu/CA = 3)**

feed pressure (psig)	pressure-normalized flux <sup>a</sup> (10 <sup>-8</sup> cm <sup>3</sup> (STP)/cm <sup>2</sup> ·s·cmHg)		mixed-gas selectivity (C <sub>3</sub> H <sub>6</sub> /C <sub>3</sub> H <sub>8</sub> )
	C <sub>3</sub> H <sub>6</sub>	C <sub>3</sub> H <sub>8</sub>	
5	588	44	13.4
10	521	39	13.4
20	397	30	13.2
35	260	23	11.2
60	193	21	9.2
85	184	23	7.9

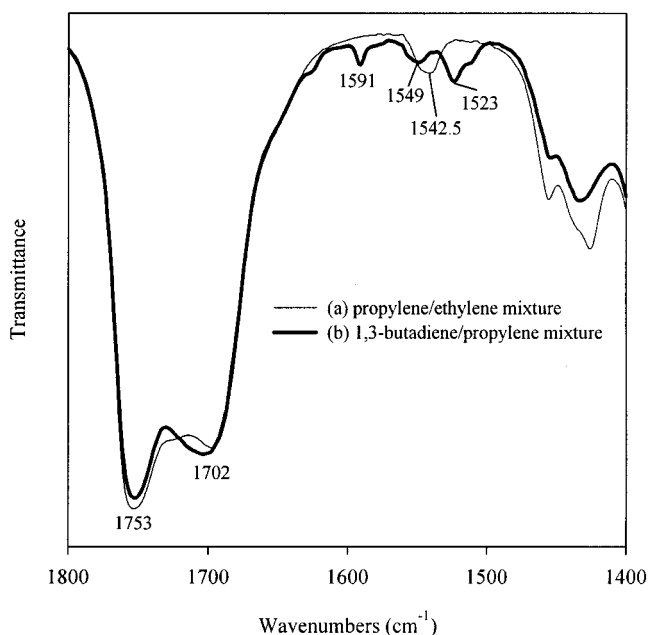
<sup>a</sup> The pressure-normalized propane flux was calculated from the measurement of the total flux of the propylene/propane mixture gas and GC area analysis.

not increase the transport of the olefin, thereby, decreasing the pressure-normalized olefin flux.<sup>21</sup>

The permeation properties of the Cu(1,3-butadiene)-OTf-CA membrane (Cu/CA = 3) were evaluated with a propylene/propane (v/v = 50/50) mixture at a feed pressure between 5 and 85 psig. The pressure-normalized propane flux was calculated from the measurement of total flux of propylene/propane mixture gas and GC area analysis. The experimental results are given in Table 2. Increasing the feed pressure from 5 to 85 psig lowers the propylene/propane selectivity from 13.5 to 7.9. The reduction in selectivity is caused by the decrease in propylene flux resulting from the carrier saturation.<sup>22</sup> The mixed-gas propane fluxes were significantly higher than those obtained in the pure-gas measurements. The increase in propane flux is probably due to increased propane solubility in the membrane because of the plasticization of the membrane by the copermeation of propylene. A series of IR spectra in Figure 7 demonstrate olefin binding affinity to Cu<sup>+</sup> ions in the Cu-CA membrane (Cu/CA = 3) (see Figure 3b-d for the stretching frequency of coordinated propylene, 1,3-butadiene, ethylene). When the membrane was exposed to 30 psig of propylene/ethylene (v/v = 50/50) mixture for 2 min and followed by a N<sub>2</sub> purge for 3 min, IR spectra (Figure 7a) showed a rather broad peak centered at 1542.5 cm<sup>-1</sup>. The peak is most likely to correspond to the mixture of coordinated ethylene and propylene, suggesting that ethylene and propylene have similar binding affinity to Cu<sup>+</sup> ions. While, on the other hand, exposure of the membrane to 30 psig of 1,3-butadiene/propylene (v/v = 50/50) mixture for 2 min and subsequent treatment with N<sub>2</sub> for 3 min, 1,3-butadiene coordinated species were predominant (Figure 7b), indicating that 1,3-butadiene has higher binding affinity than propylene. To link the binding affinity of olefins to Cu<sup>+</sup> ions in the membrane with facilitated olefin transport, the separation of propylene/ethylene (v/v = 50/50) and 1,3-butadiene/propylene (v/v = 50/50) were carried out at 25 °C and 20 psig of feed pressure. As shown in Table 3, the mixture-gas selectivities were found to be around 1 for propylene/ethylene and 2 for 1,3-butadiene/propylene mixture. The order of facilitated olefin transport is 1,3-butadiene > propylene ≈

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**Figure 7.** IR spectra of the Cu-CA membrane (Cu/CA = 3) treated with (a) a propylene/ethylene mixture and (b) a 1,3-butadiene/propylene mixture. The membrane has been exposed to 30 psig of propylene/ethylene (v/v = 50/50) or 1,3-butadiene/propylene (v/v = 50/50) for 2 min followed by N<sub>2</sub> purge for 3 min.

**Table 3. Mixed Gas Selectivities for C<sub>3</sub>H<sub>6</sub>/C<sub>2</sub>H<sub>4</sub> (v/v = 50/50) and C<sub>4</sub>H<sub>6</sub>/C<sub>3</sub>H<sub>6</sub> (v/v = 50/50) for the Cu-CA Membrane (Cu/CA = 3) Used for the Permeation Test at 25 °C and 20 psig of Feed Pressure**

pressure-normalized flux <sup>a</sup> (10 <sup>-8</sup> cm <sup>3</sup> (STP)/cm <sup>2</sup> ·s·cmHg)			mixed-gas selectivity	
C <sub>2</sub> H <sub>4</sub>	C <sub>3</sub> H <sub>6</sub>	C <sub>4</sub> H <sub>6</sub>	C <sub>3</sub> H <sub>6</sub> /C <sub>2</sub> H <sub>4</sub>	C <sub>4</sub> H <sub>6</sub> /C <sub>3</sub> H <sub>6</sub>
444	518 489	1192	1.1	2.3

<sup>a</sup> The pressure-normalized propane flux was calculated from the measurement of the total flux of the propylene/propane mixture gas and GC area analysis.

ethylene, which is in agreement with the order of olefin binding affinity to Cu<sup>+</sup> ions. From the results in Figure 7 and Table 3, it is concluded that the facilitated olefin transport can be related to the binding affinity of olefins to metal ions.

Further experiments are under progress to propose a model equation.

### Conclusions

Polymer-metal complexes composed of Cu(1,3-butadiene)OTf and cellulose acetate (CA), Cu-CA, have been prepared and applied to the facilitated transport solid polymer membrane for the olefin/paraffin separation. FT-IR and UV studies show that coordinated olefins to Cu<sup>+</sup> ions in Cu-CA membranes are easily replaced by other olefins. Therefore, olefins can permeate the membrane, resulting in selective separation of olefins from the olefin/paraffin mixture.

The coordination of carbonyl groups to Cu<sup>+</sup> ions is found to be influenced by the coordination of olefins, indicating that olefins and carbonyl groups compete with each other for coordination to Cu<sup>+</sup> ions.

The bonding mode of coordinated 1,3-butadiene in the starting membrane, Cu(1,3-butadiene)-CA is quite different from that in the membrane after exposure of the starting membrane with 1,3-butadiene. Once the 1,3-butadiene in the starting membrane is removed, the vacant sites are likely to be occupied by the carbonyl groups of CA, thereby prohibiting the coordination of the incoming 1,3-butadiene in a η<sup>4</sup>-fashion.

The pressure-normalized ethylene and propylene flux rapidly increased with the increasing molar ratio up to Cu(1,3-butadiene)OTf/CA = 3 but thereafter increased in a much reduced rate, demonstrating the importance of the molar ratio of Cu/CA = 3. The selectivity maximum behavior is mainly originated from the change in accessibility of propylene to the binding sites of Cu<sup>+</sup> ions and the plasticization effect of olefins, not from the morphological changes of the membranes.

From the IR spectroscopic results, it is found that 1,3-butadiene has the highest binding affinity to Cu<sup>+</sup> ions among ethylene, propylene, and 1,3-butadiene. The order of facilitated olefin transport is 1,3-butadiene > propylene ≈ ethylene, which is in agreement with that of the olefin binding affinity to Cu<sup>+</sup> ions.

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