일반강연 A-9

Poly(n-butylmethacrylate)막을 이용한 은이온과 올레핀 복합체의 거동에 관한 연구

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Complexation Behavior of Olefin with Silver Ions Dissolved in Poly(n-butylmethacrylate)

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1. Introduction

Olefin/paraffin separation by the facilitated transport membrane using silver salts as carriers has been considered as a promising alternative to the conventional energy intensive distillation process. The basis for the separation is the ability of silver ions to react reversibly with olefin forming silver-olefin complexes. Because of such reversible and specific interaction of silver ions with olefin molecules, silver ions can act as olefin carriers for facilitated transport in the membrane and then lead a carrier-mediated transport in addition to a normal Fickian transport. In this study, we report the effect of silver ions concentration on solubilities of propane and propylene measured by quartz crystal microbalance (QCM). The QCM offers a rapid and efficient approach to gravimetric sorption measurements. The crystal can be used effectively as a microbalance, because the small change in mass results in a

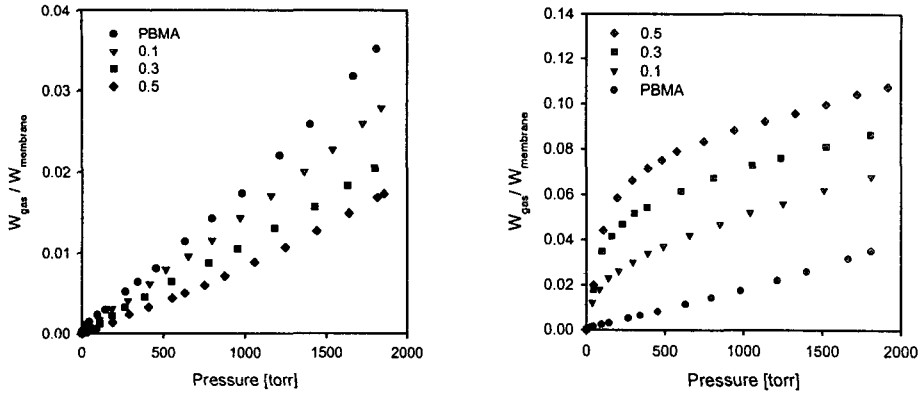
proportional shift of resonant frequency. Monitoring the concentration of the olefin-silver ion complexes by IR and Raman spectroscopy also gave us information for the complexation. From these results, the equilibrium constant (K) and coordination number (n) of the reversible complexation reaction between olefin and silver ion were obtained.

2.Experimental

Poly (n-butyl metacrylate) (PBMA) (MW=337,000) and silver triflate ($AgCF_3SO_3$, 99.9+%) (AgTf) were purchased from Aldrich Chemical Co. All chemicals were used as received without further purification. An appropriate amount of the silver salt was dissolved in the 10 wt.% PBMA solution in Tetrahydrofuran (THF) and stirred for several minutes at room temperature. The mole fraction of a silver ion to carbonyl oxygen in the solution was 0.1, 0.3 and 0.5. The solution was then coated onto a quartz crystal. Film was dried in a vacuum state at room temperature for overnight. After drying, gas was introduced into sample cell. Experiment was in progress according to the pressure change.

3.Results and discussion

As shown in Figure 1 (a), the amount of propane sorption into membrane decreased with salt concentration. The increase of the salt concentration means that relative ratio of polymer matrix in membrane is reduced. When the amounts of sorbed propane per polymer matrix are compared, they showed the almost same sorption isotherm representing that propane is dissolved only in polymer matrix but not in silver salts. Figure 1 (b) presents propylene sorption isotherm according to the change of the silver ion concentration. As the salt concentration increased, the amount of propylene sorption into membrane also increased due to additional propylene sorption by silver ion-propylene complexation.



(a) (b)

Figure 1. Gas sorption equilibrium into PBMA/$AgCF_3SO_3$ (a) propane sorption isotherm (b) propylene sorption isotherm.

Dual sorption model is introduced to analyze the propylene solubility in PBMA/$AgCF_3SO_3$ membranes.

$$C = k_D p + \frac{C_H K p}{1 + K p}$$

C_H is the concentration of coordinated propylene and K is equilibrium constant.

First, Henry constant (k_D) was obtained by using graphical method from isotherm slope. Henry constants for PBMA/$AgCF_3SO_3$ membranes with 0.1, 0.3 and 0.5 of silver mole fraction are 0.104, 0.105 and 0.106 $cm^3(STP)/cm^3cmHg$, respectively. It represents the Henry constants are not so sensitive to the concentration of silver salt but to the polymer matrix. Secondly, original equation was converted to calculate Langmuir parameters as following.

$$\frac{p}{y} = \frac{1}{C_H K} + \frac{p}{C_H} \qquad \text{where, } y = C - k_D p$$

In the plot of p/y vs p, C_H and K were determined from the slope and the intercept, respectively. The value of C_H increased from 7.1, to $18.6*10^{-4}$ mol/cm^3 with increasing silver salt concentration, whereas k_D and K value were not changed significantly. Figure 2 shows the model

prediction using evaluated parameters. They show good agreement with experimental data points.

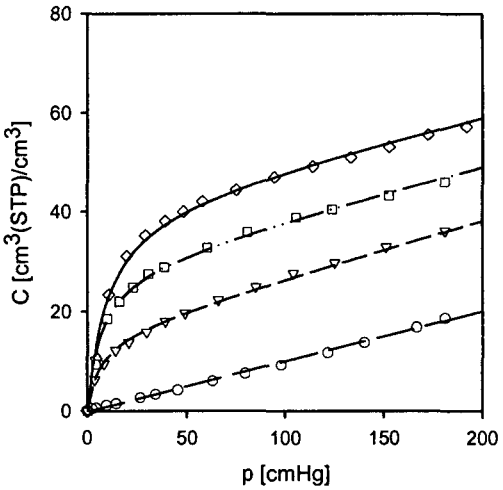


Figure 2. Comparison of the experimental data with model prediction.

It is also found that the coordination number of silver ions for propylene, i.e. the concentration ratio of propylene to silver ions is approximately one at silver mole fraction of 0.1 and reaches 0.7 above 0.3.