P-9

Insight into Complexation of Olefin with Silver Ions Dissolved in Poly(n-butyl methacrylate)

Dongkyun Ko, Kyung Min Lee, Kwi Jong Lee, Yong Soo Kang

Center for Facilitated transport Membranes, Korea Institute of Science and Technology

P. O. Box 131, Cheongryang, Seoul 130-650, South Korea

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 UV 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 obtatined.

2. Experimental

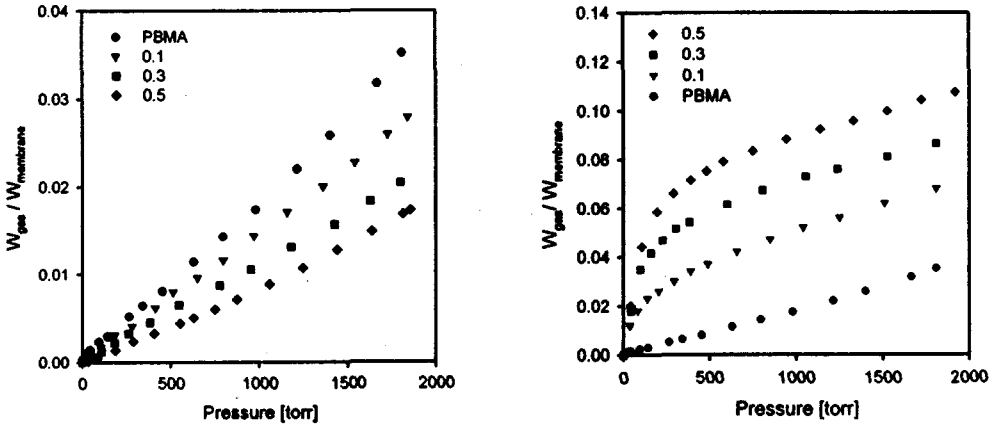
Poly (n-butyl methacrylate) (PBMA) (Mw=337,000) silver triflate ($AgCF_3SO_3$, 99.9+%) (AgTf) and silver perchlorate ($AgClO_4$, 98%) were purchased from Aldrich Chemical Co. All chemicals were used as received without further purification. An appropriate amount of the silver salt was dissolved in the 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.

IR spectra were obtained with a Mattson Galaxy 6030 spectrometer; 64-200 scans were signal-averaged at a resolution 2 cm^{-1}. Spectroscopic characterization was performed using a home-made pressure cell equipped with CaF_2 windows because samples are sensitive to water in air. The polymer solution was coated onto a silicone plate and its absorbance was then measured.

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.

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

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

First, Henry constant (k_D) was obtained by using graphical method form 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.

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

In the plot of p/y vs p, C_H and K were determined from the slope and the intercept, respectively. The value of CH 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.

The sorption isotherms of propane and propylene in PBMA/AgTf complex membranes are reported. The sorption of propane gas is processed through polymer matrix only. The propylene sorption, however, is processed through both polymer matrix and silver salt carrier. Regardless of silver salt concentration, the sorption amount of propane gas into polymer is almost same as function of applied gas pressure. Because propylene molecules make complex with silver ion, propylene can be dissolved into electrolytes in addition to sorption into polymer matrix. The solubility into polymer matrix is same, confirmed by similar Henry's constants.