O-B5

Effect of Amino Acids in Silver Polymer Electrolyte Membranes on Facilitated Olefin Transport

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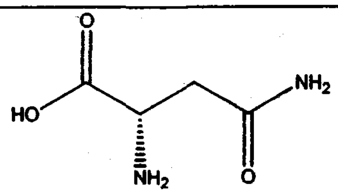
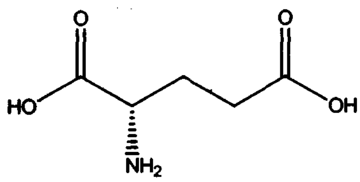
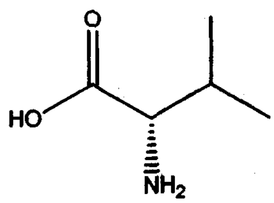
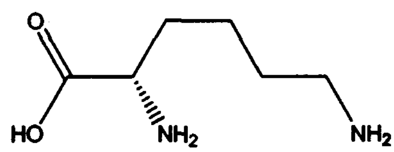
Here the effect of various amino acids on the separation performance for these two contrastive membranes is investigated. It was especially focused on the structures of amino acids, and their effects on the silver ion activity as well as the interaction between polymer electrolytes and amino acid. The amino acids studied include asparagine, valine, glutamic acid and lysine. Table 1 presents the chemical structures of the amino acids. All amino acids contain carboxylic group (-COOH) as well as amine group (NH_2). The amino acids shown in Table 1 were chosen to compare the effect of various functional groups. Especially, asparagine, valine, glutamic acid and lysine will give insight to the role of amide (CON), isopropyl ($CH(CH_3)_2$), carboxylic (COOH) and amine group (NH_2), respectively.

Separation Performance

Figures 1 and 2 show the selectivity of propylene over propane and the mixed gas permeance through POZ/$AgBF_4$ and POZ/$AgNO_3$ membranes containing various concentrations of amino acids, respectively. The mole ratio of monomeric unit of POZ to silver ion was fixed to unity, i.e. [C=O]:[Ag]=1:1. The presence of amino acids in POZ/$AgBF_4$ and POZ/$AgNO_3$ membranes gives an increase in both the selectivity and the permeance for all kinds of amino acids selected in this study. Amino acids contain NH_3^+ cations because the silver polymer electrolyte solutions, e.g. POZ/$AgBF_4$ or POZ/$AgNO_3$ in water, are measured to be a strong acid ranging from pH 3-4 (Suntex Industries Inc., Taiwan). The positive charge of NH_3^+ may interact with the counteranion of silver salt in silver polymer electrolytes. Thus, the interaction between silver ion and counteranion will be reduced upon the addition of amino acids and consequently causes the silver ions to be more active for olefin coordination. It is furthermore found that its enhancement is strongly sensitive to the kind of amino acids. The separation performance of membrane containing amino acids is arranged in the order; asparagines > valine ≈ glutamic acid > lysine. This result represents the other group in amino acids besides NH_3^+ and COOH is of pivotal importance in determinig silver ion activity. It is demonstrated that the amide group (CON) in asparagine is the most effective in improving the separation performance and amine (NH_2) in lysine is the least effective among them. The groups of $CH(CH_3)_2$ in valine and COOH in glutamic acid are intermediate. The asparagine possesses the amide carbonyl group (C=O) to coordinate to the silver ions. The silver ion in POZ/Ag salt complexes containing asparagine can interact with both carbonyl oxygens of POZ and asparagine, and thus becomes more free from its counteranion in the silver polymer electrolytes. As a result, the activity of silver ion as an olefin carrier increases more significantly on addition of asparagine. The selectivity of propylene/propane and the mixed gas permeance increased up to 65.5 and 18.0 GPU, respectively, for the POZ/$AgBF_4$/asparagine membrane, and the corresponding values increased up to 34.0 and 1.4 GPU, respectively, for the POZ/$AgNO_3$/asparagine membrane. It should be noted that inactive $AgNO_3$ becomes an active olefin carrier for facilitated olefin transport upon addition of amino acids. Another intriguing feature is that the membrane performance always shows a maximum at a mole ratio of amino acid of 0.01. This may be considered to be caused by the heterogeneity or defect formation due to the miscibility limitation between three components including polymer, silver salt and amino acid.

Table 1. The Chemical Structure of Amino Acids Selected for Study

Amino acid	Chemical Structure	Amino acid	Chemical Structure
Asparagine		Glutamic acid	
Valine		Lysine	

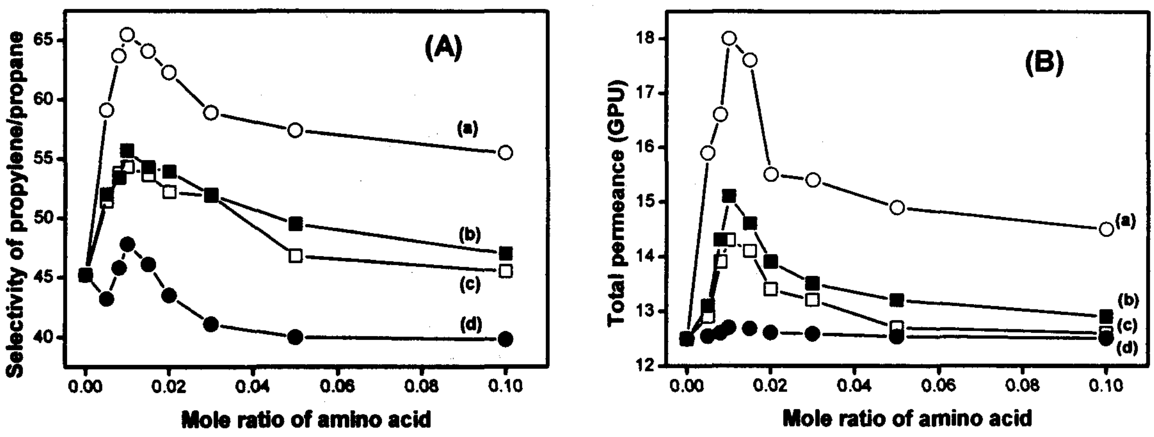


Figure 1. Separation performance (A) mixed-gas selectivity and (B) total permeance of POZ/$AgBF_4$ membranes with various mole ratios of amino acids: (a) asparagine, (b) valine, (c) glutamic acid and (d) lysine.

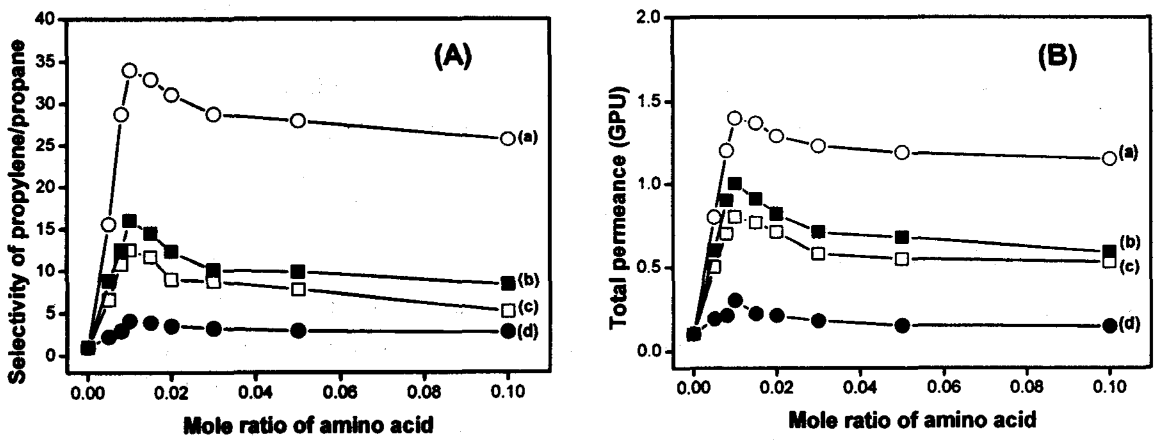


Figure 2. Separation performance (A) mixed-gas selectivity and (B) total permeance of POZ/$AgNO_3$ membranes with various mole ratios of amino acids: (a) asparagine, (b) valine, (c) glutamic acid and (d) lysine.