Pervaporation separation of polyion complex composite membranes for the separation of water/alcohol mixtures: characterization of permeation behavior by using molecular modeling techniques

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ABSTRACT

In this work, the physicochemical properties for permeant molecules and polyion complex membrane prepared by complexation between SA and chitosan were determined by using molecular modeling methods, and the permeation behaviors of water and alcohol molecules through the PIC membrane have been investigated. In the case of penetrant molecule, the experimental results showed that the prepared membrane was excellent pervaporation performance result in most solution, and the selectivity and permeability of the membrane were dependent on the molecular size, the polarity and the hydrophilic surface of permeant organics. However, the separation behavior of methanol aqueous solution exhibited other permeation tendency with other feed solutions and contradictory result. That is, the membrane were preferentially permeable to methanol over water despite water molecule has stronger polarity and small molecular size than methanol molecule. In this study, the results were discussed from the viewpoint of chemical and physical properties between permeant molecules and membrane in the diffusion state.

INTRODUCTION

Polyelectrolyte complexes have gained special interest as one of the membrane materials for the separation of organic mixture in recent years. The reason is because they have showed the highest flux and selectivity for the pervaporation dehydration[1-3]. In general, polyelectoryte complex is formed when macromolecules of opposite charge are allowed to interest. The interaction usually involves a polymeric acid or its salt with a polymeric base or its salt. Electrostatic interactions constitute the main attractive forces, but hydrogen bonding, ion dipole forces, and hydrophobic interactions frequently play a significant role in determining the ultimate structures. In addition, permeabilities and permselectivities of permeants through membranes made from these complexes are controlled by these properties. Accordingly, water affinity depends on the chemical structure of the polymer components, charge density, ratio of cationic to anionic charge, pH, presence of microions, and the procedures employed in the

complex preparation. The water molecules in the polymer matrix may be free or strongly bound. However, they can often be solubilized in a ternary solvent system of water, a polar organic solvent, and a strongly ionized, simple electrolyte. By the reason, polyelectrolyte complexes have to form by the interaction of polyacids and polybases with pK values below 2.0 or from macromolecules of high charge density. Accordingly, ionic polysaccharide polymers such as sodium alginate (SA) and chitosan, were used as complex materials for the separation of water–alcohol mixtures in this study, and also in order to made the more stable complex membrane, a strong acid was used to induce the interaction between them. We aim to characterize the permeation behavior of water-alcohol mixtures through polyelectrolyte complex composite membranes, based on the sodium alginate (SA) polyanion and chitosan polycation, using molecular modeling techniques.

RESULTS AND DISCUSSION

Figure 1 and 2 show the effect of the composition of feed mixture on the permeation rate and the separation factor of PIC composite membrane composed of sodium alginate and chitosan for the separation of various water-alcohol mixtures. In the case of water-methanol mixture, as the alcohol concentration in the feed mixture increases, the permeation rate increased gradually while the separation factor was no change almost as 0.77 to 0.46. However, in most other water-alcohol mixtures the separation behavior exhibited a decrease in the permeation rate and an increase in the separation factor according to feed composition. Also, the permselectivity and permeability for water molecule increased gradually with increasing the difference of molecular size and polarity between water and alcohol. To consider above results more concretely, the physicochemical relationship between complex structure and permeants, which was has been surveyed by using molecular moldering techniques, such as energy minimization methods and molecular dynamics method. As a result, as can be seen from Figure 3, the complex structure calculated from simple and double helix structure was 6.5944 Å~5.49606 Å according to backbone chain atom under 2D wire frame condition, and appeared interatomic distance of 4.9593 Å ~3.8179 Å under 3D space filling condition. In the case of two-fold helix chain conformer, the atomic distance of 7.4094 Å ~8.3509 Å (under 2D wire frame condition) and 4.4996 Å ~ 5.5256 Å (under 3D space filling condition.) observed. On the other hand, as the alkyl chain of alcohol molecule becomes long, their polarity and hydrogen bonding ability were dwindling as shown in Table 1, respectively. Most of the size of alcohol molecule was more than 3Å while methanol was smaller than complex structure's ion-hole volume and hydrogen bond ability also was level about half than water. Accordingly, it can be considered that the retention time of methanol molecule at diffusion step, which was short relatively, because physicochemical properties of methanol molecule such as hydrophilic surface and hydrogen

bonding ability is smaller than water molecule, as can be seen in Table 1. By conclusion methanol molecule could permeate more preferentially than water molecule.

REFERENCES

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3. S.G. Kim, Y.I. Kim, G.T. Lim, J. Jegal and K.H. Lee, J. *Appl. Polym. Sci.*, **85**, 714 (2002).

Figure 1. Pervaporation results on the permeation rate of the prepared membrane as a function of feed composition for the separation of water-alcohol mixtures; operating temp.=40℃

Figure 2. Pervaporation results on the separation factors of the prepared membrane as a function of feed composition for the separation of water-alcohol mixtures; operating temp.=40 ℃

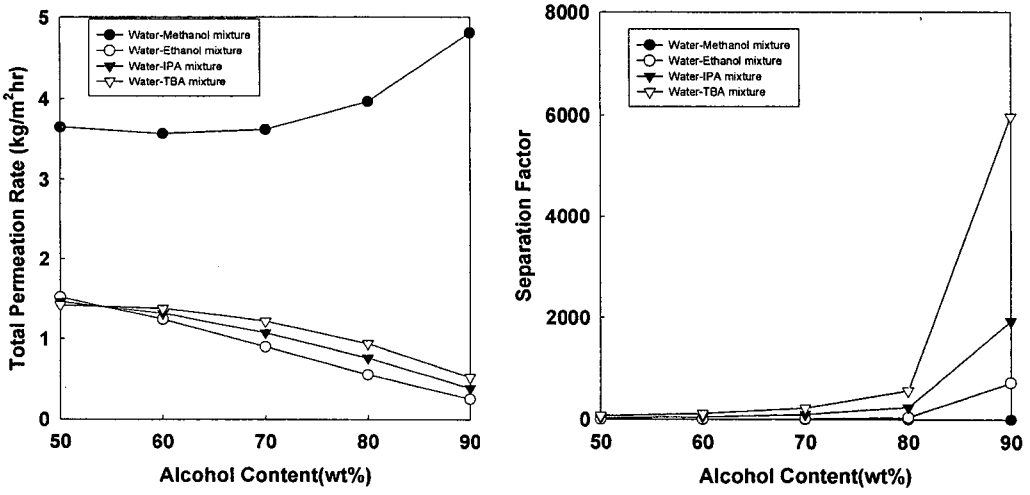


Figure 3 Molecular Modeling Results for Simple Ladder Structure (a) and Two-Fold Helix Chain Conformer

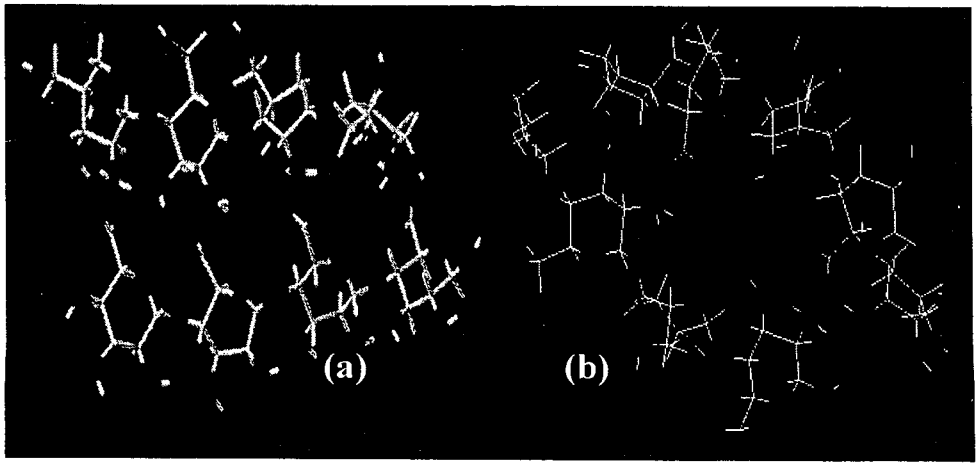
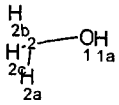
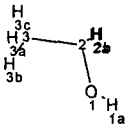
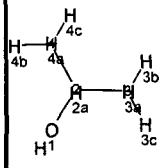
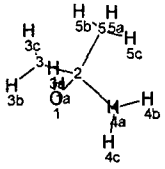


Table 1. Physicochemical Properties calculated from Molecular Modeling

Name / Property	H_2O	Methanol	Ethanol	Propan-2-ol	t-butylalcohol
Structure					
Interatomic distance (Å)	(1a-1b): 1.5179 (O1-1b): .9601	(2a-1a): 2.8325 (2b-2a): 1.7967	(3c-1a): 4.0565 (3b-2b): 3.0574	(4b-3c): 4.2960 (1a-3b): 3.8727	(3c-4c): 4.2978 (5a-1a): 3.4932
Molecular Weight	18.0153	32.0422	46.0691	60.0959	74.1228
Molecular volume	11.2197	21.6731	31.612	41.5624	51.5311
Surface area	2.1758	3.61524	4.96094	6.30816	7.78356
Lop P	-1.15	-.768	-.325	.074	.473
Solubility parameter	47.8	29.6107	26.4947	23.5076	21.6694
Dispersion	15.6	15.1106	15.7607	15.7552	15.3518
Hydrogen bonding	42.3	22.3057	19.3925	16.3379	14.2323
Polarity	16	12.285	8.80342	6.11979	5.59701
Hydrophilic surface %	100	60.8798	38.0249	22.0229	17.8596
H bond acceptor	.573684	.327753	.332134	.335396	.33794
H bond donor	.523684	.227141	.226308	.225637	.225148
Dipole moment	2.0032	1.65069	1.61491	1.66502	1.70173