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SEPARATION OF XYLENE ISOMERS BY PERVAPORATION THROUGH A HIGHLY PERMSELECTIVE POLYMER MEMBRANE HAVING DINITROPHENYL GROUP

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The separation of xylene isomers was carried out by pervaporation through a polymer membrane having a dinitrophenyl group. The polymer membrane was effective for selective permeation of m-xylene from the mixture of xylene isomers. This selectivity can be attributed to the difference in the charge-transfer complexing ability between xylene isomers and the dinitrophenyl group.

The separation of xylene isomers continues to interest researchers throughout the world. Recent commercial processes use techniques of selective adsorption on moleculer sieves and liquid extraction to effect the desired separation between p- and m-xylene. Among the experimental techniques that have been investigated are included the separation of xylene isomers by liquid permeation through polymer membranes and by clathration.

Pervaporation through a polymer membrane is one of the most attractive techniques for specific and selective separation of organic liquid mixtures since it does not require isolation of the permeate and can be applied to various organic mixtures including an azeotropic mixture or a close-boiling mixture.1) The separation of xylene isomers by pervaporation has been investigated using the polymer membrane containing Werner complexes or cyclodextrin, and cellulose ester membranes.2-4) However, the permselectivity of these membranes was below 1.5. It is known that the selective permeation of liquid mixture through a polymer membrane is a function of the difference in solubility and/or diffusivity of a permeate in polymer matrix.1,4) Therefore, effective separation of the liquid mixture through the membrane may be realized by introducing a group that may strongly interact with the specific component of the mixture into the membrane.

The interaction between an electron acceptor and an electron donor is well known as the charge-transfer interaction. Xylene molecule is an electron donor since it has two electron donating methyl groups. Foster et al. investigated the interaction between xylene isomer and electron accepting 1,4-dinitrobenzene by NMR and found that the charge-transfer interaction exsists between them.5) Thus, it is expected that the use of a polymer membrane containing electron acceptor will enable the separation of xylene isomers based on the charge-transfer interaction.

In this communication, we will describe the separation of xylene isomers by pervaporation through a highly permselective polymer membrane having dinitrophenyl group which is a typical electron accepting group, on the basis of the charge-transfer interaction. The use of this interaction is unprecedented at membrane separation.

The polymers containing dinitrophenyl groups were synthesized by the condensation between 2-hydroxyethyl acrylate(HEA) - 2-hydroxyethyl methacrylate (HEMA) copolymer and 3,4- or 3,5-dinitrobenzoyl chloride in N,N-dimethylformamide/ pyridine mixture.[6)] The degree of 3,4-dinitrophenyl group and 3,5-dinitrophenyl group introduction in copolymers were 0.48 and 0.69 mole fraction, respectively. The structure of these polymers is shown in Fig. 1.

Polymer membranes for the pervaporation experiments were prepared by casting a tetrahydrofuran(THF) solution of the polymer on Teflon plate. The THF was evaporated completely in vacuo at 40 °C for 2 d. The membrane thickness was about 50 - 70 μm.

Pervaporation of xylene isomer was carried out at 30 °C using a stainless steel cell described previously.[1)] The permeation area of the membrane is 11.4 cm^2. The composition and flux of xylene isomer permeated were determined by a gas chromatography. The pervaporation rate, $P(g{\cdot}m/m^2{\cdot}h)$, was calculated by the correction of flux with the membrane thickness, and the separation factor, $\alpha_{A/B}$, which was a measure of the preferential permeation of component A, was defined as the concentration ratio A/B in the permeate divided by the concentration ratio A/B in the feed.

The results of pervaporation of the mixture of xylene isomers through P(3,4-DNP) membrane, P(3,5-DNP) membrane and HEA-HEMA copolymer membrane are shown in Table 1. In the case of the HEA-HEMA copolymer membrane which was lacking for the dinitrophenyl groups, the separation factor for the mixture of o-xylene and p-xylene was 1.02 and no selective permeation was observed. On the other hand, in the case of the polymer membranes containing the dinitrophenyl groups, the separation factors were above 1.3 and selective permeation through the membrane

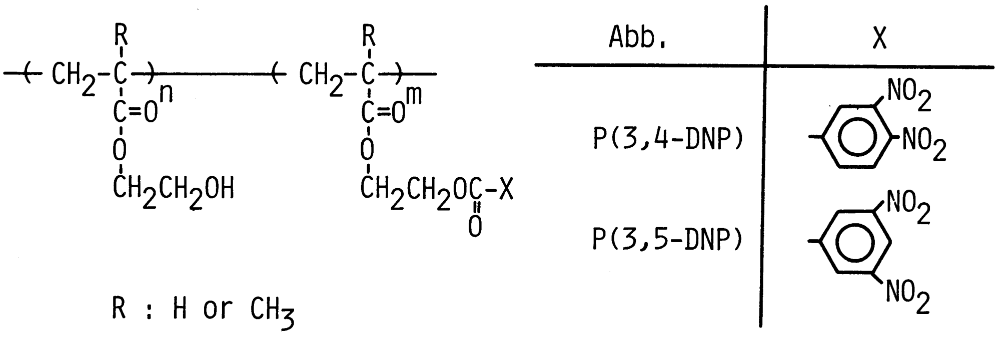

Fig. 1. Structure and abbreviation of polymer having dinitrophenyl group.

Table 1. Pervaporation of the mixture of xylene isomers through polymer membranes at 30 °C

Membrane	Composition of xylene isomers			P	$\alpha_{A/B}$
	A/B	in feed	in permeate	10^{-3} g·m·m^{-2}·h^{-1}	
P(3,4-DNP)	m-/o-	50.3/49.7	74.0/26.0	3.57	2.82
	m-/p-	48.9/51.1	69.7/30.3	2.33	2.39
	o-/p-	49.5/50.5	62.6/37.4	4.72	1.71
P(3,5-DNP)	m-/o-	50.5/49.5	58.1/41.9	3.64	1.37
	m-/p-	51.8/48.2	67.7/32.3	1.32	1.95
	o-/p-	49.8/50.2	64.4/35.6	2.88	1.82
HEA-HEMA	o-/p-	49.3/50.7	50.4/49.6	3.15	1.02

could be realized. Especially, the separation factor of P(3,4-DNP) membrane for the mixture of m-xylene and o-xylene exceeded 2.8. Table 1 also shows that the order of the permselectivity of P(3,4-DNP) membrane for xylene isomers was p-xylene < o-xylene < m-xylene. This tendency was the same as that of P(3,5-DNP) membrane. In general, it is known that selective permeation by pervaporation through the polymer membrane is based on the difference of the solubility of each molecule into the membrane and/or the diffusivity in the membrane. Michaels et al. reported that the order of the diffusivity of xylene molecule in polyethylene membrane was o-xylene < m-xylene < p-xylene and this order was agreed with the opposite order of the cross-sectional area of xylene molecules.7) However, the order of the permeability of the polymer membranes having the dinitrophenyl groups did not fit it. This indicates that the selectivity of the polymer membrane having the dinitrophenyl groups for xylene isomers can be attributed to the different factor, presumably, the difference in the solubility into the polymer membrane between xylene isomers. For confirming this reasoning, the order of the strength

Table 2. Association constant of charge-transfer complexes between xylene isomers and dinitrophenyl compounds

	Association constant / kg mol^{-1}		
	3,4-EDB	3,5-EDB	1,4-dinitrobenzene[a)]
p-Xylene	0.178	0.379	0.35
o-Xylene	0.285	0.465	0.42
m-Xylene	0.305	0.504	0.41

a) These values were obtained by Emslie et al., in Ref. 5.

of the charge-transfer interaction was investigated by using ethyl 3,4-dinitrobenzoate(3,4-EDB) or ethyl 3,5-dinitrobenzoate(3,5-EDB), which are low-molecular weight compound model of the dinitrophenyl groups in the polymer membrane. Thus, the association constants of the charge-transfer complex between xylene isomers and dinitrophenyl compounds were calculated by the method according to Foster et al.5) Table 2 shows the association constants of the charge-transfer complexes. The order of the association constants is p-xylene < o-xylene < m-xylene in both cases. This result indicates that the strength of the charge-transfer interaction between the electron donating xylene molecule and the electron accepting dinitrophenyl compound is in the order of p-xylene < o-xylene < m-xylene. This order is coincident to the order of the permselectivity of the membrane. Therefore, it is considered that xylene molecule forms a complex with the dinitrophenyl group by the charge-transfer interaction in the membrane and the observed permselectivity can be attributed to the different ability of the complex formation.

In conclusion, it is possible to separate the mixture of xylene isomers by pervaporation through the polymer membrane having an electron accepting group based on the charge-transfer interaction between xylene molecule and the electron accepting group, such as dinitrophenyl group.

The detailed permeation mechanism of xylene molecule through the polymer membrane with an electron acceptor is now undergoing.

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