

PERVAPORATION OF ETHANOL AND WATER THROUGH POLYMERIC MEMBRANES WITH INCORPORATED *N*-(HALOGENOPHENYL)MALEIMIDE UNITS

Jan LOKAJ and Jitka BILA

Institute of Macromolecular Chemistry,

Academy of Sciences of the Czech Republic, 162 06 Prague 6, The Czech Republic

Received May 16, 1993

Accepted June 15, 1993

Styrene-*N*-(chloro- or bromophenyl)maleimide and methyl methacrylate-*N*-(chloro- or bromophenyl)maleimide copolymers were synthesized. Membranes casted from the copolymer solutions were used for the pervaporation of ethanol-water mixtures at 35 °C. The membranes were characterized by the separation factor related to the preferentially transported water and by the permeate flux. The pervaporation characteristics were dependent on the hydrophilicity or polarity of the polymer chains, on the kind and position of the halogen and on the composition of the mixture to be separated. Membranes made from the copolymers of styrene with *N*-(2-chlorophenyl)maleimide or *N*-(2-bromophenyl)maleimide show the highest separation factors in the separation of concentrated ethanol solutions. The permeate flux through membranes made from the copolymers of methyl methacrylate with *N*-(halogenophenyl)maleimide was by one order of magnitude higher than through membranes made from similar styrene copolymers.

Separation of liquid mixtures by pervaporation is one of the important applications of membrane technology¹. This method is based on permeation of the components through a membrane and their subsequent evaporation; chemical composition and physical properties of the membrane are important factors. Thus, determination of the relationship between the structure and transport properties of membrane materials is the essential part of study of a pervaporation process.

In an earlier work² we described the separation of ethanol-water mixtures by pervaporation through membranes based on the copolymers of styrene with *N*-phenylmaleimides, substituted on the phenyl ring by three or five chlorine or bromine atoms, or the dimethylamino and methyl groups. Similarly to membranes of copolymers of styrene with unsubstituted *N*-phenylmaleimide³, water passed preferentially through these membranes; however, the separation efficiency was much greater. Their separation factors depended on the imide structure and increased with increasing concentration of ethanol in the feed.

This study describes the membranes prepared from the copolymers of styrene or methyl methacrylate with *N*-(2-, 3-, or 4-chlorophenyl)maleimide or *N*-(2-, 3-, or

4-bromophenyl)maleimide and evaluates the effect of various *N*-(monohalogenophenyl)maleimide units incorporated in polymer membranes of varying polarity or hydrophilicity on their pervaporation properties in the separation of water and ethanol.

EXPERIMENTAL

Materials

The following *N*-(halogenophenyl)maleimides were prepared⁴ by cyclodehydration of the corresponding maleamic acids: 2-chloro- (2-Cl-PMI), m.p. 74 °C; 3-chloro- (3-Cl-PMI), m.p. 93 °C; 4-chloro- (4-Cl-PMI), m.p. 108 °C; 2-bromo- (2-Br-PMI), m.p. 91 °C; 3-bromo- (3-Br-PMI), m.p. 135 °C; and 4-bromo- (4-Br-PMI), m.p. 110 °C. Styrene (S) (b.p. 36 °C/1.56 kPa), methyl methacrylate (MMA) (b.p. 42 °C/10.4 kPa) and 2,2'-azobis(isobutyronitrile) (AIBN) (m.p. 105 °C) were purified by the procedure described in an earlier work⁵. The ethanol-water mixtures were prepared from ethanol for UV spectroscopy and redistilled water. The solvents were chromatographically pure (GC).

Synthesis of Styrene or Methyl Methacrylate-*N*-(Halogenophenyl)maleimide Copolymers

Reaction mixtures containing styrene (24.4 g), *N*-(halogenophenyl)maleimide (0.4 g) and AIBN (0.06 g) were heated at 50 °C in an inert atmosphere in sealed glass ampoules. After 6 h, the copolymers were precipitated with ethanol and reprecipitated from benzene solutions. The composition of the copolymers was determined from the C and N contents. The conversions of the monomers (approximately 10 %) were calculated from the composition and weight of the copolymers.

The copolymers of methyl methacrylate with *N*-(halogenophenyl)maleimides were prepared in a similar manner from a mixture of MMA (3.60 g), *N*-(halogenophenyl)maleimide (0.90 g), AIBN (0.045 g) and benzene (12 ml). The polymerization time was 20 h.

Preparation of Membranes

The membranes were obtained by casting chloroform solutions of the copolymers (0.1 g/ml) onto glass plates to form a 0.35 mm layer. The solvent was evaporated at room temperature and, after immersing the plate in water, a membrane with a thickness of approximately 30 μm was released.

Methods

Pervaporation properties of the membranes were studied using the apparatus described in an earlier work². The EtOH-H₂O mixture (200 ml) circulated in the cell of the apparatus at 35 °C over the membrane with a working area of 49 cm². The composition of the mixture was determined pycnometrically. The pressure on the permeate side of the membrane was maintained at approximately 400 Pa. The permeate was collected in an ampoule cooled with liquid nitrogen and analyzed by GC (Porapak Q, 1-propanol as an internal standard).

The membranes were characterized by the permeate flux and the separation factor $\alpha_{\text{H}_2\text{O}}$ related to the preferentially permeating water. The separation factor is defined by Eq. (1):

$$\alpha_{\text{H}_2\text{O}} = \frac{w_{\text{H}_2\text{O}}^{\text{P}} w_{\text{EtOH}}^{\text{F}}}{w_{\text{EtOH}}^{\text{P}} w_{\text{H}_2\text{O}}^{\text{F}}}, \quad (1)$$

where w^{P} and w^{F} are the weight fractions in the permeate and feed, respectively.

RESULTS AND DISCUSSION

Styrene or Methyl Methacrylate-N-(Halogenophenyl)maleimide Copolymers

In the radical copolymerization of the monomer pairs styrene-*N*-(chlorophenyl)maleimide and styrene-*N*-(bromophenyl)maleimide, the initial monomer mixtures contained 0.8 and 0.7 mole % of substituted maleimide, respectively. As a consequence of a strong tendency of the comonomers to alternating copolymerization⁴, its content in the obtained copolymers increased 10 to 13-fold (Table I). The copolymers were film-forming; their chloroform solutions were employed in the casting of compact transparent membranes. As the number of incorporated maleimide units increased, the membranes became more brittle.

Solution radical copolymerization of methyl methacrylate with 10.8 mole % *N*-(chlorophenyl)maleimide or 9.0 mole % *N*-(bromophenyl)maleimide in the initial comonomer mixture occurred with preferential addition of the radicals of both comonomers to MMA, which was reflected in a lower content of the incorporated maleimide compared to its amount in the original monomer mixture (Table I). This phenomenon is associated with the formation of a more reactive and less polar radical

TABLE I

Composition and limiting viscosity numbers of styrene or methyl methacrylate-*N*-(halogenophenyl)-maleimide copolymers

Copolymer	Comonomers	X-PMI Content, mole %		$[\eta]^a$, ml g ⁻¹
		feed	copolymer	
<i>I</i>	S, 2-Cl-PMI	0.8	9.4	92.0
<i>II</i>	S, 3-Cl-PMI	0.8	10.0	91.0
<i>III</i>	S, 4-Cl-PMI	0.8	8.5	91.0
<i>IV</i>	S, 2-Br-PMI	0.7	8.9	96.5
<i>V</i>	S, 3-Br-PMI	0.7	8.7	87.5
<i>VI</i>	S, 4-Br-PMI	0.7	8.5	95.0
<i>VII</i>	MMA, 2-Cl-PMI	10.8	6.5	51.0
<i>VIII</i>	MMA, 3-Cl-PMI	10.8	9.4	51.2
<i>IX</i>	MMA, 4-Cl-PMI	10.8	6.7	48.0
<i>X</i>	MMA, 2-Br-PMI	9.0	5.5	48.4
<i>XI</i>	MMA, 3-Br-PMI	9.0	7.6	52.2
<i>XII</i>	MMA, 4-Br-PMI	9.0	5.3	48.6

S styrene, MMA methyl methacrylate, PMI *N*-phenylmaleimide. ^a In benzene at 20 °C.

from MMA, compared to that obtained from the substituted maleimide⁶. The copolymerization was carried out in benzene solution to avoid the unfavourable gel effect.

Dilution of the initial monomer mixture with benzene was the main reason for the lower limiting viscosity numbers of the copolymers of methyl methacrylate compared to those shown by the copolymers of styrene with *N*-(halogenophenyl)maleimides. Because of the presence of ester groups in the polymer chains, membranes made from the copolymers of methyl methacrylate are far more polar than those made from the styrene copolymers.

Pervaporation of EtOH–H₂O Mixtures through Styrene or Methyl Methacrylate–N-(Halogenophenyl)maleimide Copolymer Membranes

The results of the pervaporation experiments are listed in Table II. The separation characteristics of membranes of copolymers *I* – *XII* were determined using two different EtOH–H₂O mixtures (61.2 – 66.3 wt.% and 82.6 – 84.7 wt.% EtOH in the feed).

Membranes based on styrene–*N*-(halogenophenyl)maleimide copolymers *I* – *VI* behaved similarly as the above described² membranes of the copolymers of styrene with substituted *N*-phenylmaleimides. The permeate flux was in the range 9 – 14 g m⁻² h⁻¹ and the separation factors increased with increasing EtOH concentration in the feed. Membranes with incorporated *N*-(2-chlorophenyl)maleimide and *N*-(2-bromophenyl)maleimide units showed the highest $\alpha_{\text{H}_2\text{O}}$ values ($\alpha_{\text{H}_2\text{O}} = 57.7$ at $w_{\text{EtOH}}^{\text{F}} = 82.6\%$ and $\alpha_{\text{H}_2\text{O}} = 48.2$ at $w_{\text{EtOH}}^{\text{F}} = 84.7\%$, respectively). In comparison with them, membranes containing *N*-(3- or 4-halogenophenyl)maleimide showed lower $\alpha_{\text{H}_2\text{O}}$ values at higher EtOH concentrations, but higher values at lower EtOH concentrations. At the same time, the separation of more concentrated ethanol solutions was more efficient using membranes with *N*-(chlorophenyl)maleimide units in the polymer chains than in the case of membranes containing *N*-(bromophenyl)maleimide units.

The selectivity towards water in the pervaporation of a mixture with the higher EtOH content is apparently associated with the electronegativity of the halogen and its distance from the carbonyl groups which act as carriers facilitating permeation of water³. While no great differences were observed between the $\alpha_{\text{H}_2\text{O}}$ values for membranes of the copolymers of *N*-(3- or 4-halogenophenyl)maleimides (*II*, *III* or *V*, *VI*), the separation factors for membranes with incorporated *N*-(2-chlorophenyl)- or *N*-(2-bromophenyl)maleimide were approximately by 33% or 47% higher than those for the former membranes. The $\alpha_{\text{H}_2\text{O}}$ values for the membrane made from *I* containing 2-chlorophenyl groups exceeded the values for membrane made from *IV* with 2-bromophenyl groups by about 20%. Because of small differences in the composition and chain lengths of copolymers *I* – *III* (Table I), the main reason for the high separation efficiency of the membrane from *I* is probably the activation of the carbonyl groups of the *N*-(2-chlorophenyl)maleimide unit by electronegative chlorine atoms, which assists in the preferential transport of water. The bromine atom in the *N*-(2-bromophenyl)maleimide unit

apparently has a similar, though smaller activating effect. However, the lower separation factors in pervaporation of mixtures with higher water contents indicate a dependence of interactions and transport processes in the membranes on the composition of the separated solutions.

TABLE II
Pervaporation of EtOH-H₂O mixtures through styrene or methyl methacrylate-*N*-(halogenophenyl)-maleimide copolymer membranes at 35 °C

Copolymer ^a	EtOH Content, wt. %		Permeate flux g m ⁻² h ⁻¹	Separation factor $\alpha_{\text{H}_2\text{O}}$
	feed	permeate		
<i>I</i>	63.6	10.0	12	15.7
	82.6	7.6	10	57.7
<i>II</i>	64.8	9.0	12	18.6
	82.6	9.4	10	45.7
<i>III</i>	61.2	7.8	11	18.6
	82.6	10.3	10	41.1
<i>IV</i>	62.5	12.4	14	11.8
	84.7	10.3	9	48.2
<i>V</i>	61.6	6.4	9	23.5
	84.7	15.0	9	31.4
<i>VI</i>	62.7	8.9	12	17.2
	84.2	13.4	10	34.4
<i>VII</i>	62.6	11.5	155	12.9
	84.2	45.1	186	6.5
<i>VIII</i>	66.3	7.4	92	24.6
	83.8	34.5	118	9.8
<i>IX</i>	64.1	7.3	110	22.7
	83.4	35.3	108	9.2
<i>X</i>	62.4	11.9	184	12.3
	83.3	59.4	298	3.4
<i>XI</i>	65.6	7.8	116	22.5
	83.3	36.6	108	8.6
<i>XII</i>	64.8	7.3	124	23.4
	83.4	36.8	110	8.6

^a See Table I.

It is apparent that, of the series of styrene copolymers *I* – *VI*, copolymers *I* and *IV* are most suitable for the preparation of membranes for removal of water from concentrated ethanol solutions.

The membranes made from the copolymers of methyl methacrylate with *N*-(halogenophenyl)maleimides *VII* – *XII* are characterized by permeate flux values that are by one order of magnitude higher and by decreasing $\alpha_{\text{H}_2\text{O}}$ values with increasing EtOH content in the feed. The high permeate flux values are in accordance with a higher polarity or hydrophilicity of these copolymers, due to the presence of ester groups in the polymer chains. Permeation was easiest through the membranes with incorporated *N*-(2-halogenophenyl)maleimides. In the pervaporation of more concentrated ethanol solutions, the permeate flux through these membranes made from copolymers *X* and *VII* reached the values of 298 and 186 g m⁻² h⁻¹, respectively; the corresponding separation factors decreased to 3.4 and 6.5, respectively. Similarly to membranes made from copolymers of styrene with *N*-phenylmaleimide, described by Yoshikawa et al.³, the increase in the permeate flux with the simultaneous decrease in $\alpha_{\text{H}_2\text{O}}$ can be a consequence of swelling of the membrane by ethanol.

In the pervaporation of EtOH–H₂O mixtures of the lower EtOH concentration, the separation factors for membranes based on the copolymers of methyl methacrylate with *N*-(3- or 4-halogenophenyl)maleimides were greater than 20; the permeate flux was about 10 times greater than for membranes made from similar styrene copolymers. Thus, considering the determined separation factor values, the copolymers of methyl methacrylate with *N*-(halogenophenyl)maleimides are much more useful than the analogous styrene copolymers for the separation of ethanol–water mixtures.

CONCLUSIONS

The following factors are important for the pervaporation of aqueous ethanol through polymer membranes with incorporated *N*-(halogenophenyl)maleimides at 35 °C:

- polarity or hydrophilicity of the polymer chain
- kind and position of halogen
- composition of EtOH–H₂O mixtures to be separated.

In the case of hydrophobic membranes based on the copolymers of styrene with *N*-(halogenophenyl)maleimide, the separation factors $\alpha_{\text{H}_2\text{O}}$ increased with increasing EtOH content in the feed, whereas, when using more polar (hydrophilic) membranes based on the corresponding methyl methacrylate copolymers, the separation factors decreased. The former membranes showed permeate flux values that were by one order lower. In the separation of concentrated ethanol solutions, the membranes made from the styrene–*N*-(chlorophenyl)maleimide copolymers were more effective than those containing *N*-(bromophenyl)maleimide, the membranes made from the copolymers of

styrene with *N*-(2-halogenophenyl)maleimide showing the highest selectivity towards water. In the separation of dilute EtOH solutions, membranes made from methyl methacrylate-*N*-(3- or 4-halogenophenyl)maleimide copolymers were more effective than those from styrene-*N*-(3- or 4-halogenophenyl)maleimide copolymers, the permeate flux values being by one order of magnitude higher at the same or slightly higher separation factors.

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Translated by M. Stulikova.