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PERVAPORATIVE REMOVAL OF VOLATILE ORGANIC COMPOUNDS FROM MULTICOMPONENT AQUEOUS MIXTURES

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ABSTRACT

The present study concerns with the separation of binary and ternary water–organics mixtures by pervaporation using different organophilic membranes (i.e., PERVAP-1060—polydimethylsiloxane, PERVAP-1070—zeolite filled polydimethylsiloxane, PEBAX-4033—polyether block amide). The following binary and ternary liquid mixtures were investigated: water–methyl acetate; water–ethyl acetate; water–butyl acetate, water–methyl *t*-butyl ether (MTBE), and water–methanol–MTBE. The organic components of these mixtures can be found in the wastewaters from textile, pharmaceutical, and petrochemical industries.

The experiments were focused on the efficiency of investigated membranes used for the removal of organics from water. During the experiments, the following parameters characterizing system

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were determined: the separation factor (α), the permeate flux (J), and the degree of the removal of organics from water (D_r) in the batch mode pervaporation. The influence of the feed temperature, the initial content of organics in the feed, and the feed volume to the membrane area (V/S) ratio were investigated. It was proved that all membranes were selective in the removal of volatile organic compounds from water. The selectivity and transport properties as well as the efficiency parameters were dependent strongly not only on the kind of the membrane and the kind of the separated feed mixture but also on the process parameters.

The PERVAP-1060 membrane showed the best efficiency in the removal of organics from water, whereas the PERVAP-1070 membrane was the most selective one. Much lower efficiencies found for PEBAX-4033 membrane were caused by the fact that the selective layer of PEBAX-4033 membrane contained both the hydrophobic and hydrophilic blocks. Comparing the properties of a given membrane in contact with binary and ternary mixtures, it was stated that the selectivities and permeate fluxes were lower in contact with the latter ones.

Key Words: Pervaporation; Multicomponent mixtures; Organophilic membranes; VOCs removal

INTRODUCTION

In many industrial processes, substances leak into the wastewater. Membrane processes appear to be well qualified for the separation, purification, and concentration of these substances.[1–6] The most commonly used technologies for removing volatile organic compounds (VOCs) from water, like air stripping or carbon adsorption, generate the secondary wastes. This coupled with a growing interest in recycling both for economical and environmental reasons, opens up new opportunities for such membrane technologies like pervaporation.[6–10]

Pervaporation is the membrane separation technique in which the liquid feed mixture is in contact with one side of a membrane whereas the permeate in a vapor state is continuously removed from the other side of membrane into the vacuum or sweeping gas.[7–9] Pervaporation can be applied for the dehydration of organics (e.g., ethanol, isopropanol, and amines), for the extraction of organics from aqueous solutions and/or for the separation of the components of nonaqueous mixtures (e.g., methanol/methyl *t*-butyl ether (MTBE), ethanol/cyclohexane, and

C_8 isomers).[6–10] Pervaporation appears to be promising especially when the preferentially permeable component is present in the feed at low concentration. Therefore, the removal of low contents of organic solvents from aqueous solutions through organophilic membranes presents a large opportunity for the application of pervaporation in wastewater treatment and solvent recovery. Possible applications are to be found in the food, chemical, and pharmaceutical industries.

We have recently presented the selective and transport properties of organophilic membranes in contact with the chosen binary water–organics mixtures.[11] The present study concerns with the efficiency of the pervaporation process in the separation of binary and ternary water–organics mixtures using organophilic membranes.

EXPERIMENTAL

Systems Investigated

Experiments were performed for the following binary and ternary mixtures: water–methyl acetate (H_2O–MeAc), water–ethyl acetate (H_2O–EtAc), water–butyl acetate (H_2O–BuAc), water–MTBE (H_2O–MTBE), and water–methanol–MTBE (H_2O–MeOH–MTBE). The chosen physicochemical data of investigated solvents are given in Table 1.

Membranes

Three types of hydrophobic membranes were used in this study, namely PERVAP-1060, PERVAP-1070 (Sulzer Chemtech, Neunkirchen, Germany) and PEBA-4033 (GKSS, Geesthact, Germany). All these membranes are composite. The PERVAP-1060 membrane possesses a selective layer made of

Table 1. Chosen Physicochemical Data of Investigated Solvents[12,13]

Solvent	Molecular Weight (g/mol)	Molar Volume (cm^3/mol)	Solubility in Water (g/100 g H_2O)	Dielectric Constant, ε [−]	Solubility Parameter, δ ($[cal/cm^3]^{0.5}$)
Water	18	18.0	—	81.0	23.4
MeOH	32	40.5	∞	31.2	14.3
MeAc	74	92.5	31.9	7.1	9.6
EtAc	88	98.0	7.9	6.1	9.1
BuAc	116	132.0	0.7	5.0	8.5
MTBE	88	119.0	5.1	≈3	—

polydimethylsiloxane (PDMS). The PERVAP-1070 membrane is composed of a thin PDMS layer with hydrophobic ZSM-5 zeolite particles incorporated into it to increase selectivity.[14]

The selective top layer of PEBAX-4033 membrane is made of the polyether–polyamide block copolymer (PEBA). The PEBA is a thermoplastic elastomer, which consists of rigid polyamide linear blocks and flexible polyether linear blocks.[15,16] The characteristics of the investigated membranes are given in Table 2.

Pervaporation Measurements

Pervaporation experiments were carried out in the laboratory-scale pervaporation system presented elsewhere.[11] The thermostated feed solution was circulated over the membrane with an area of $170\,\mathrm{cm}^2$. The permeate was collected in cold traps cooled by liquid nitrogen. During experiments, the upstream pressure was maintained at the atmospheric pressure, while the downstream pressure was kept below 1 mbar by using a vacuum pump. The permeate flux was determined by weight, whereas the feed and permeate compositions were determined by using a gas chromatograph (VARIAN 3300 Varian Analytical Instruments, Walnut Creek, USA).

The efficiency of the pervaporation process was determined on the basis of the permeate fluxes (J), permeate composition, and the degree of removal of the organic compound from water (D_r), according to the following equation:

$$D_\mathrm{r} = \frac{m_t}{m_0} 100\% \tag{1}$$

where D_r is the degree of removal, m_t the amount of the organics removed from the feed after time t, and m_0 is the total amount of organics to be removed.

A half-time parameter $t_{1/2}$, defined as the time needed to reach by a system $D_\mathrm{r} = 50\%$ was also introduced to describe the efficiency of a given membrane.

The effect of feed temperature, feed composition, and a feed volume to membrane area ratio (V/S) on the permeate fluxes (J), D_r and $t_{1/2}$ were determined for each membrane in contact with the binary and ternary water–organics mixtures. Experiments were performed for V/S in the range 60–$180\,\mathrm{cm}^3/\mathrm{cm}^2$ and for temperatures ranging from 313 to 333K.

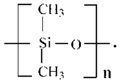
RESULTS AND DISCUSSION

Water–Ester Binary Mixtures

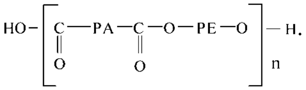
The efficiency of the pervaporation process in the removal of esters from water using investigated membranes is shown in Fig. 1. It is seen that for each

Table 2. Characteristics of Pervaporation Membranes Investigated

Membrane	Skin Layer	Producer
PERVAP-1060	PDMS[a]	SULZER Chemtech Membrane System (Germany)
PERVAP-1070	PDMS filled with ZSM-5[b] zeolite	SULZER Chemtech Membrane System (Germany)
PEBAX-4033	PEBA[c]	GKSS (Germany)

[a] Polydimethylsiloxane (PDMS) 
$$\left[-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{\overset{|}{\underset{|}{Si}}}}-O- \right]_n .$$

[b] ZSM-5 zeolite $Na_n[Al_nSi_{(96-n)}O_{192}] \sim 16H_2O$, $n < 27$.

[c] Poly(ether block amide) (PEBA) 
$$HO-\left[\underset{\displaystyle O}{\underset{\|}{C}}-PA-\underset{\displaystyle O}{\underset{\|}{C}}-O-PE-O \right]_n -H.$$

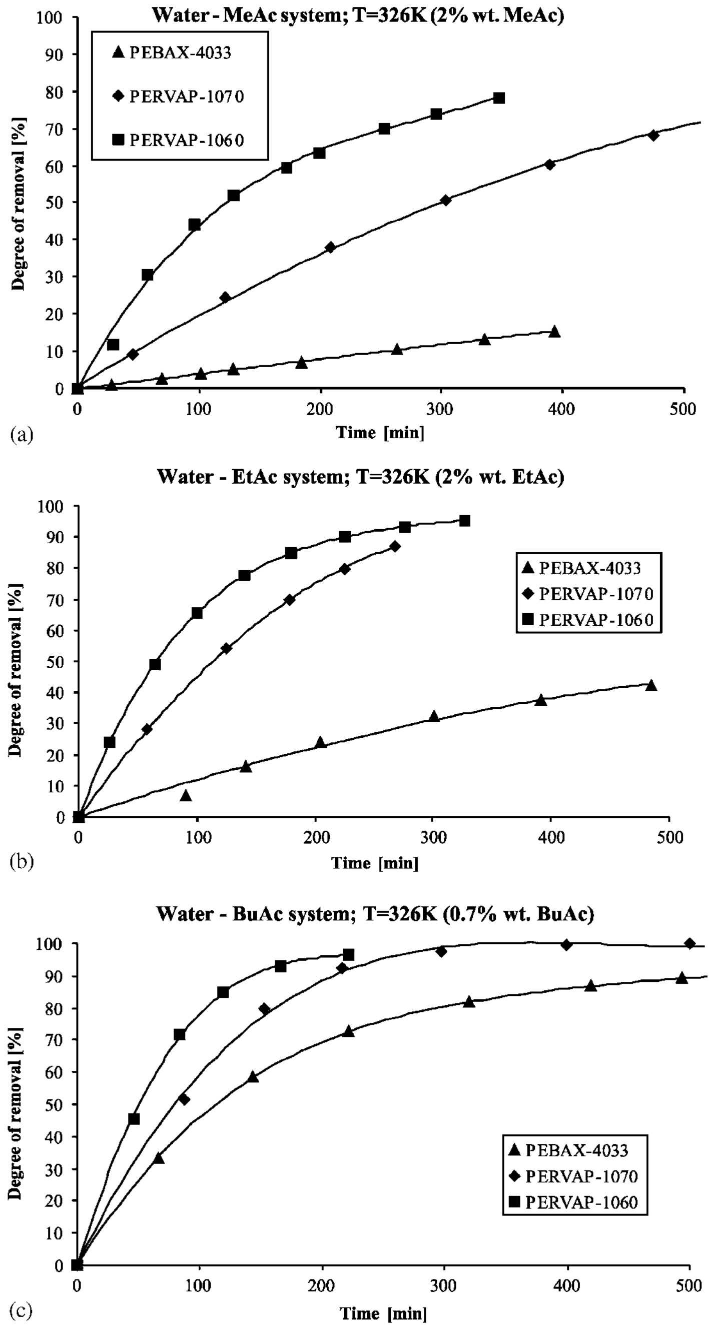


Figure 1. Degree of removal of acetate esters in contact with hydrophobic membranes.

ester, the fastest separation was obtained with PERVAP-1060 membrane, regardless of the fact that selectivity of PERVAP-1070 membrane exceeds that of the PERVAP-1060 one (Table 3). However, one should remember that for all investigated systems, the permeate fluxes through PERVAP-1060 membrane are higher that those through the PERVAP-1070 membrane (Table 3). Much lower D_r values found for PEBAX-4033 membrane are caused by the fact that the selective layer of PEBAX-4033 membrane contains both the hydrophobic and hydrophilic blocks.[15,16]

Comparing the efficiency of removal of different esters (Fig. 1) from water through a given membrane, it is seen that D_r increases with increasing hydrophobicity of ester, following the order:

$$D_r(\text{MeAc}) < D_r(\text{EtAc}) < D_r(\text{BuAc}).$$

These results are well consistent with the results on the selectivity and permeate fluxes, presented in our previous work.[11]

Figure 2 shows the influence of both the temperature and V/S on the $t_{1/2}$ for water–BuAc mixture and investigated membranes. For all V/S values and temperatures investigated, PERVAP-1060 membrane is the most efficient one. It is seen that with increasing temperature, the separation proceeds faster. As the selectivity of membrane does not depend strongly on temperature, the increase in the efficiency of the separation process is caused mainly by the permeate flux increase. For a given membrane, $t_{1/2}$ is proportional to V/S. It was found that within the range of V/S investigated, this relation was linear.

Figure 3 shows permeate fluxes vs. time for BuAc in contact with PEBAX-4033 membrane. The flux of BuAc decreases with time as the content of BuAc in the feed decreases, whereas the water flux remains practically at a constant level (60–80 $\mathrm{g\,m^{-2}\,hr^{-1}}$).

Butyl acetate is widely used in the pharmaceutical industry and partially recycled using distillation. The high efficiency of pervaporation for BuAc

Table 3. Selective and Transport Properties of Investigated Membranes in Contact with Water–Ester Binary Mixtures

	PERVAP-1060		PERVAP-1070		PEBAX-4033	
Feed Composition (wt% of Organics)	α	J ($\mathrm{g\,m^{-2}\,hr^{-1}}$)	α	J ($\mathrm{g\,m^{-2}\,hr^{-1}}$)	α	J ($\mathrm{g\,m^{-2}\,hr^{-1}}$)
MeAc (0.5 wt%)	180	258	330	94	15	28
EtAc (0.5 wt%)	315	315	460	126	20	35
BuAc (0.5 wt%)	480	550	950	300	380	175

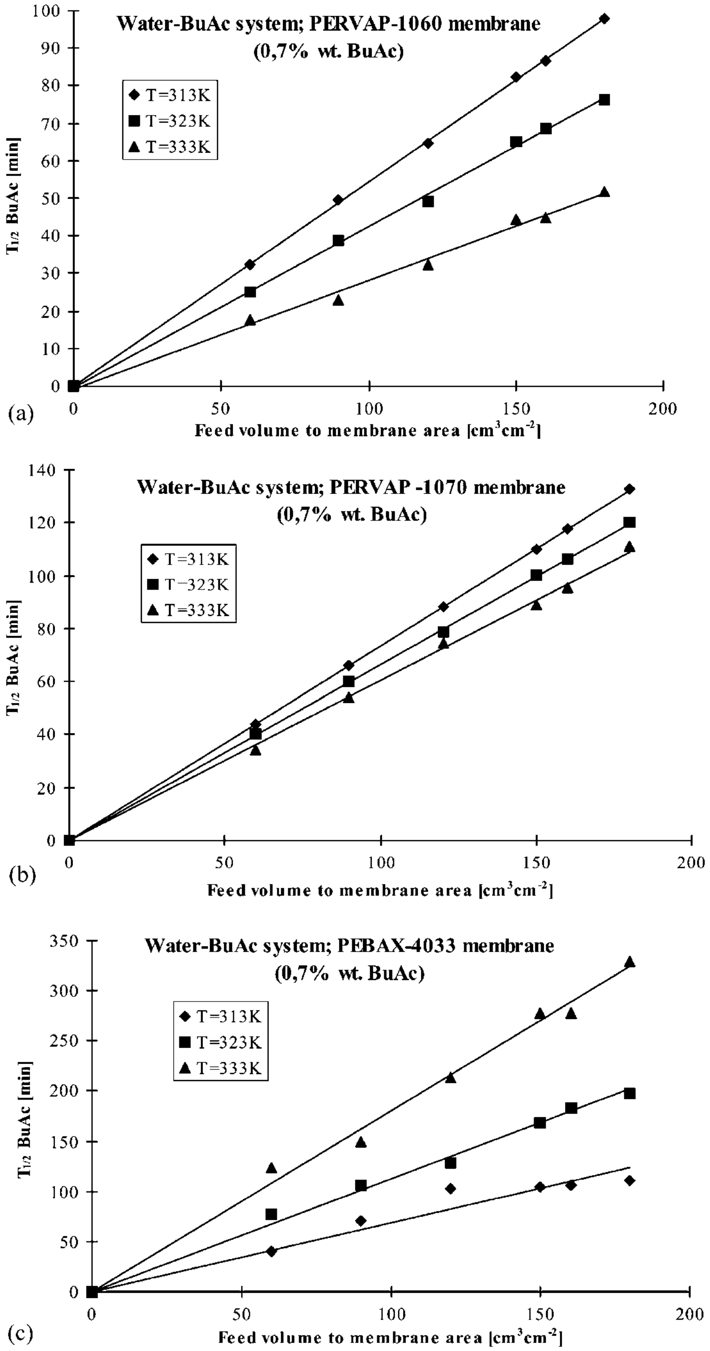


Figure 2. The influence of temperature and V/S on $t_{1/2}$ for BuAc.

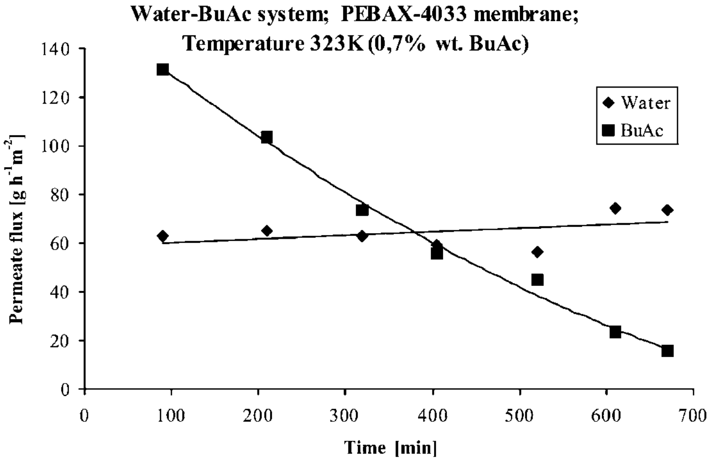


Figure 3. The pervaporation permeate fluxes of water and BuAc through PEBAX-4033 membrane.

removal from water suggests that this technique can also be applied for the BuAc recycling. In a batch-wise pervaporation removal of 95% BuAc from the saturated solution and with $V/S = 117\,\mathrm{cm}^3/\mathrm{cm}^2$ would need no more than 180 min at 323K (Fig. 4). It should also be pointed out that pervaporation is much more flexible than other techniques and any assumed degree of organic removal can be obtained simply by increasing the separation time, by increasing the process temperature, or by decreasing the *V*/*S* ratio.

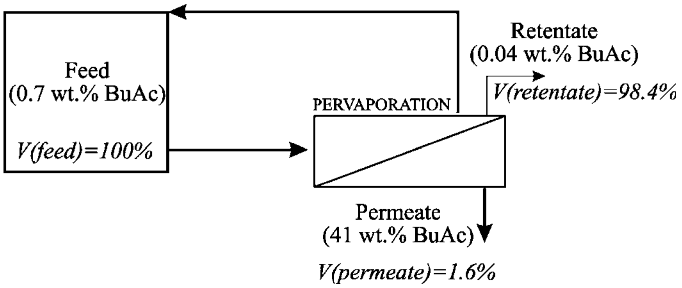


Figure 4. Removal of BuAc from the saturated water solution by the batch-mode pervaporation. Duration of the batch process: 180 min ($D_r = 95\%$), $V/S = 117\,\mathrm{cm}^3/\mathrm{cm}^2$, $T = 326\mathrm{K}$.

Water–MTBE Binary Mixture

Similarly like for water–esters mixtures, the pervaporation experiments were performed for H_2O–MTBE system. MTBE is produced on a large scale from isobutylene and methanol and is used as a fuel enhancer. Nowadays it turned out that MTBE, appreciated for its proecological properties as a lead alkyls replacer, can also cause severe air and water pollution and became suspected as a carcinogenic chemical.[17,18]

Efficiency of the investigated membranes in the removal of MTBE from water is shown in Fig. 5. From these data, one can see that the fastest separation is obtained with PERVAP-1060 membrane, but the degree of removal of MTBE from water (D_r) is lower than that for water–ester mixtures (Fig. 1). It is caused by the fact that MTBE is quite polar solvent and possesses relatively high solubility in water (Table 1).

The influence of temperature and V/S on the $t_{1/2}$ parameter for all investigated membranes in contact with H_2O–MTBE mixture is shown in Fig. 6. The temperature increase causes decrease in the time needed to reach the assumed degree of removal of MTBE from water. These results are well consistent with the results obtained for the water–ester systems.

Water–MeOH–MTBE Ternary Mixtures

When a given membrane contacts ternary mixture (e.g., H_2O–MeOH–MTBE), its selective and transport properties are usually different from those found for binary mixtures. This is caused by the interactions between all species presented in the separating solution and between them and the membrane matrix. Table 4 presents the comparison of selective and transport properties of investigated membranes in contact with H_2O–MTBE, H_2O–MeOH binary mixtures, and H_2O–MeOH–MTBE ternary mixture. MTBE, as the most hydrophobic component of investigated ternary mixture is transported preferentially, however, both the selectivities and permeate fluxes of organic components are much smaller when compared to binary mixtures (Table 4).

The selectivity of hydrophobic membranes in contact with H_2O–MeOH–MTBE ternary mixture (Fig. 7) shows that the PERVAP-1070 membrane is the most selective one. However, similar to it was found for binary mixtures, the PERVAP-1060 membrane is the most effective one in the removal of MTBE from ternary mixture (Fig. 8). During the separation process, both organic components are removed from the ternary mixture although the more hydrophobic one, i.e., MTBE is removed preferentially (Fig. 9). The permeate fluxes of all the components vs. time of the separation process are shown in Fig. 10. The MTBE flux decreases with time as the amount of MTBE in the

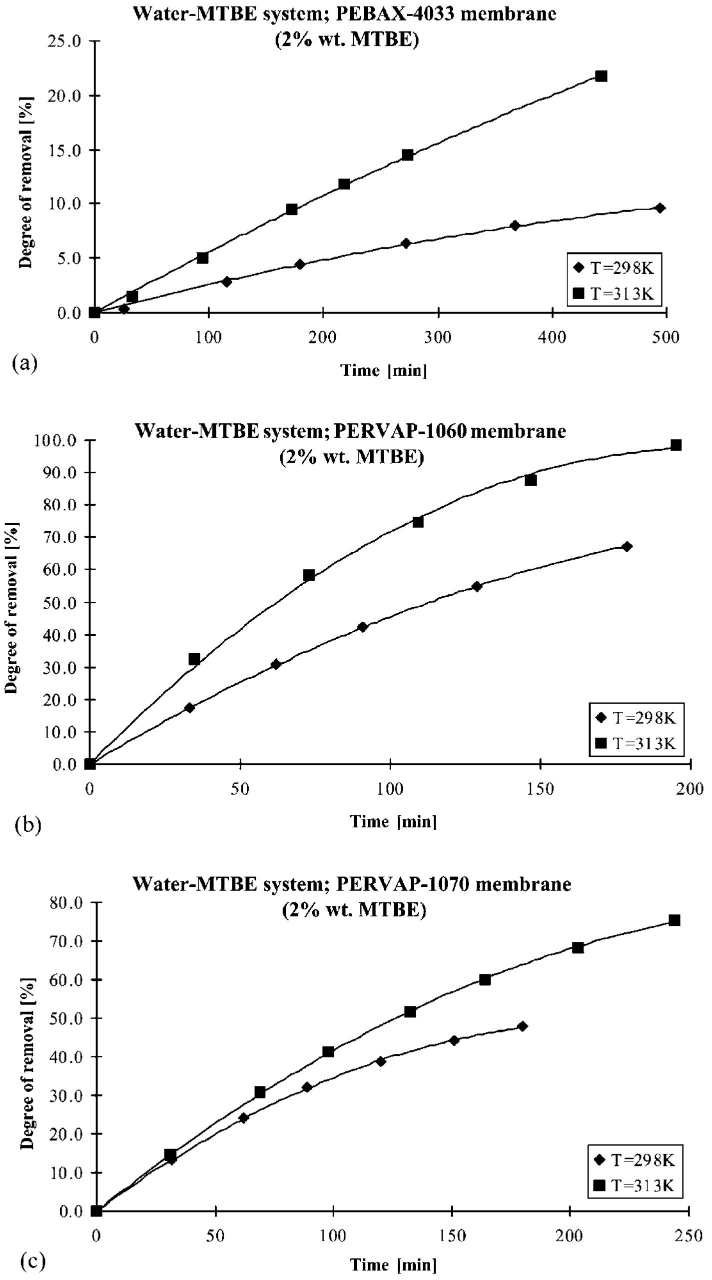


Figure 5. Degree of removal of MTBE from water using hydrophobic membranes.

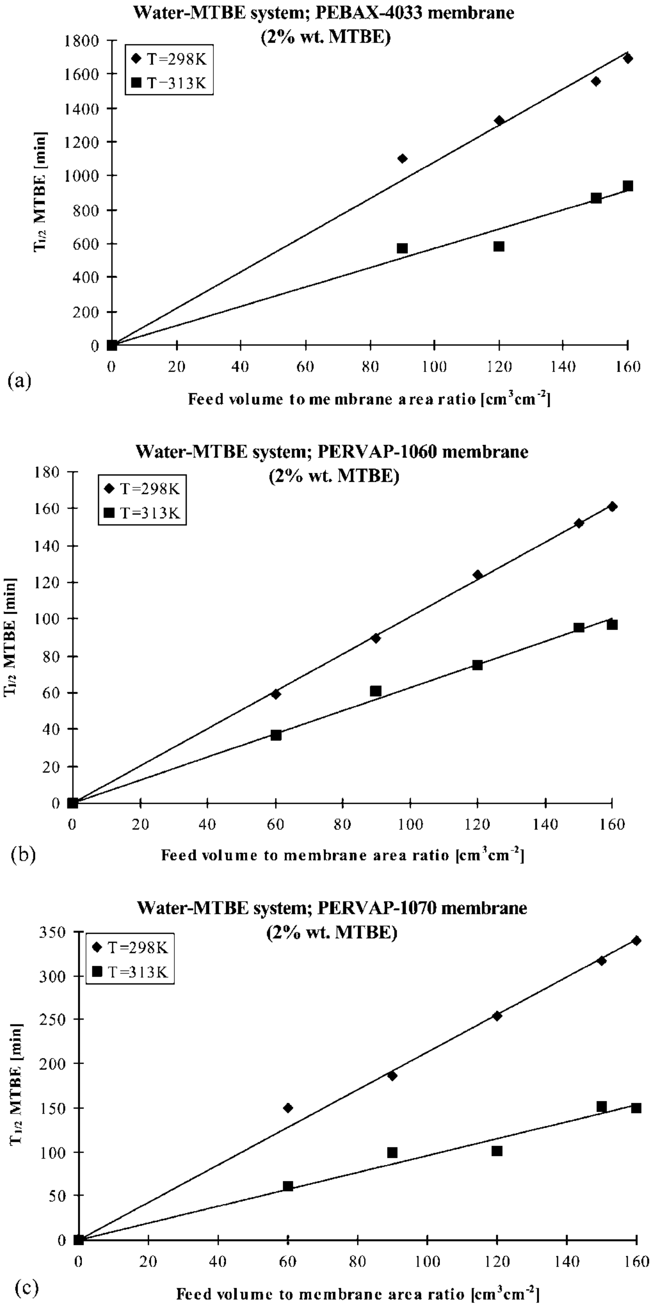


Figure 6. The influence of temperature and V/S on $t_{1/2}$ for MTBE.

Table 4. Comparison of Selective and Transport Properties of Investigated Membranes in Contact with Water–Organics Binary and Ternary Mixtures

	PERVAP-1060		PERVAP-1070		PEBAX-4033	
Feed Composition (wt% of Organics)	α	J (g m^{-2} hr^{-1})	α	J (g m^{-2} hr^{-1})	α	J (g m^{-2} hr^{-1})
Binary mixture (H_2O–MeOH)						
MeOH (2 wt%)	7	210	3	80	2	20
Binary mixture (H_2O–MTBE)						
MTBE (1 wt%)	270	700	280	250	33	10
Ternary mixture (H_2O–MeOH–MTBE)						
MeOH (2 wt%)	3	20	2	10	2	2
MTBE (1 wt%)	160	150	250	130	56	10

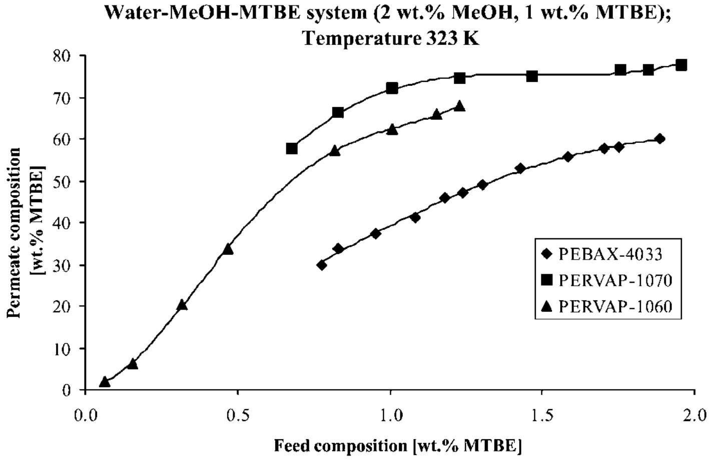


Figure 7. McCabe–Thiele separation diagram for the ternary H_2O–MeOH–MTBE system.

separated mixture decreases. The permeate fluxes of water and MeOH are practically constant during the whole experiment.

Pervaporation results obtained with water–MTBE and water–MeOH–MTBE mixtures suggest that for the efficient removal of MTBE from wastewater, pervaporation should be coupled with another separation method, like carbon adsorption into a hybrid system. In such a case, pervaporation could also be used for the regeneration of carbon adsorbent.[1]

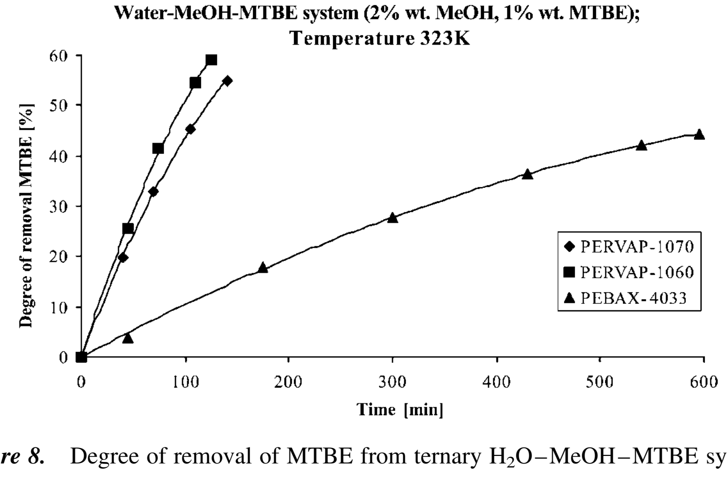


Figure 8. Degree of removal of MTBE from ternary H_2O–MeOH–MTBE system.

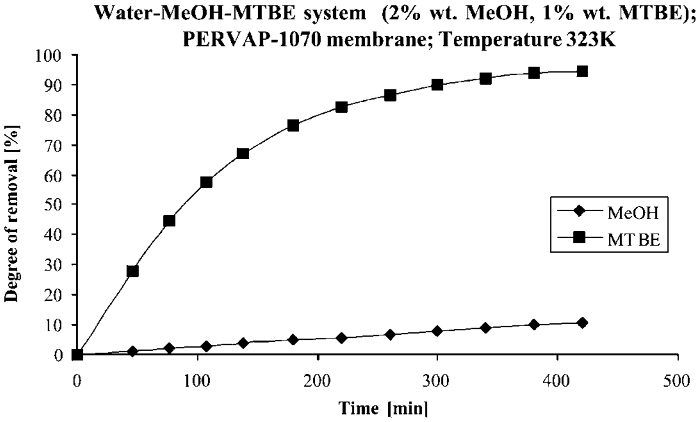


Figure 9. Degree of removal of MeOH and MTBE from ternary H_2O–MeOH–MTBE system.

CONCLUSIONS

Organophilic membranes used in these investigations showed high selectivity towards organic solvents of low polarity. The PERVAP-1060 membrane showed the best efficiency in the removal of organics from water, although the PERVAP-1070 membrane was the most selective one. Much lower

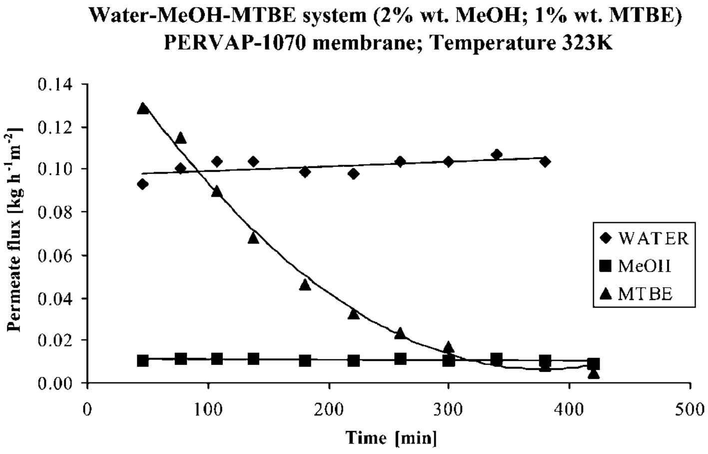


Figure 10. Pervaporation permeate fluxes of water, MeOH, and MTBE through PERVAP-1070 membrane.

efficiencies found for PEBAX-4033 membrane were caused by the fact that the selective layer of PEBAX-4033 membrane contained both the hydrophobic and hydrophilic blocks. Comparing the properties of a given membrane in contact with binary and ternary mixtures one can state that the selectivities and permeate fluxes were lower in contact with ternary mixtures.

Pervaporation seems to be an effective method for the removal of organic solvents from binary and ternary aqueous solutions. However, the practical application of pervaporation to the treatment of process water and/or wastewater will depend on: investment and operation costs, final organics concentration in the clean water, and the effectiveness of the competitive separation methods.

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