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Dehydration of Water–Pyridine Mixtures by Pervaporation*

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Abstract

Several ion-exchange and neutral membranes were examined in the pervaporation of water–pyridine mixtures. Carboxylic and sulfonic ion-exchange membranes were used with hydrogen counterion and additionally with trimethylammonium, triethylammonium, and tributylammonium counterions. All membranes were selective to water, but the transport mode and selectivity properties of membranes were dependent on both the character of the ion-exchange group and the ionic form of the membrane. The results obtained suggest that pervaporation of water–pyridine mixtures could be used with standard distillation in the large-scale dehydration process of pyridine.

1. INTRODUCTION

The pervaporation technique, in which the liquid feed mixture is maintained in contact with one side of a nonporous membrane and the permeate is continuously removed from the other side as a vapor (Fig. 1), is one of the new methods to attain separation of azeotropic mixtures, structural isomers, or even to displace the equilibrium of chemical reactions (*1*–*5*).

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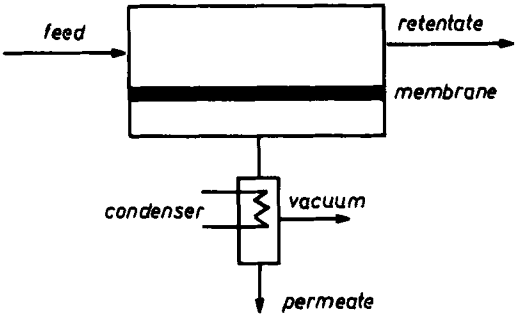

FIG. 1. The schema of pervaporation operation.

Dense nonionic polymeric films, either hydrophilic or hydrophobic, are used nowadays as membranes in pervaporation. Recently, ionomer membranes have also been used for the pervaporation of water–organic mixtures. Ion-exchange membranes are selective to water due to the strong affinity of the ionic sites to water molecules (*6–8*).

For water–organic mixtures which form about 50–50 wt% azeotropes (e.g., cyclohexylamine–water, hexylamine–water, pyridine–water), pervaporation followed by standard distillation seems to be an interesting method to break an azeotrope and recover the dehydrated organic solvent (*4*, *9*).

In this contribution, results on pervaporation of the water–pyridine system are reported. Different nonporous ion-exchange and neutral membranes were used as the selective barrier.

The water–pyridine mixture is an azeotropic system that forms one liquid phase over the entire concentration range. The distillation azeotropic composition for this system is 41.3 wt% of water and a boiling point of 93°C (Fig. 2).

2. EXPERIMENTAL

2.1. Membranes

In order to determine the applicability of vacuum pervaporation for the separation of a water–pyridine mixture, we performed experiments using six different nonporous polymeric membranes as the selective barriers. The general characteristics of these membranes are presented in Table 1.

The ionic membranes, either with sulfonic or carboxylic groups, were used in the hydrogen form. Additionally, we examined the effect of different organic counterions (i.e., trimethylammonium, TMA; triethylam-

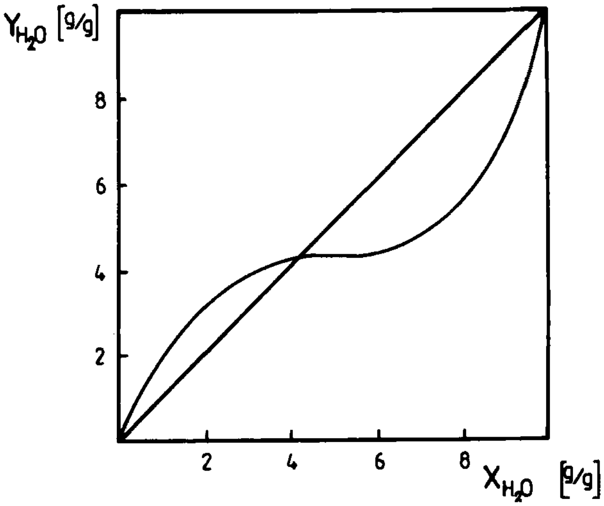

FIG. 2. Vapor–liquid equilibrium for water–pyridine system.

monium, TEA; and tributylammonium, TBA cations) on the membrane selectivity and fluxes.

The neutral polyvinyl alcohol membrane (GFT) was used in both the unmodified form and after modification with crosslinking agents.

TABLE 1
General Characteristics of Polymeric Membranes Used for Dehydration of Pyridine

Membrane	Polymeric backbone	Ionic sites	Thickness (μm)
PEAA	Polyethylene grafted with acrylic acid	—COO^-	30
PESS	Interpenetrating network of polyethylene and sulfonated polystyrene-*co*-divinylbenzene (*10*)	—SO_3	180
PETS	Polyethylene grafted with sulfonic acid	—SO_3	315
NAFION	Poly(tetrafluoroethylene-*co*-perfluoro-3,6-dioxa-4-methyl-7-octen-sulfonic acid)	—SO_3	170
RAIPORE	Poly(tetrafluoroethylene-*co*-styrene sulfonic acid)	—SO_3	50
GFT	Multilayer supported polyvinyl alcohol	—	3

2.2. Pervaporation System

The pervaporation experiments were performed by using the set-up described elsewhere (*11*). The system was operated at 40°C and at a pressure on the permeate side below 1 hPa.

Water–pyridine mixtures in the concentration range of 0 to 100 wt% of water were used as the feed. A permeate flux and a separation factor were determined for each feed concentration. Separation analysis was conducted on a gas chromatograph.

3. RESULTS AND DISCUSSION

3.1. Properties of Sulfonated Ion-Exchange Membranes

Figure 3 presents the separation diagram for the sulfonic ion-exchange membranes. All these membranes were selective to water, but the extents were different depending on the nature of the polymeric backbone. The permeate water content (W') for a given feed concentration decreases in the following order (Fig. 3): $W'_{\mathrm{PETS}} > W'_{\mathrm{RAIPORE}} \geq W'_{\mathrm{PESS}} > W'_{\mathrm{NAFION}}$.

The good selectivity of the pervaporative membrane used to break-out the 50–50 azeotropes should be accompanied by a relatively high flux of the permeate. The permeate flux is inversely proportional to the membrane thickness (*1*, *12*).

Table 2 compares the transport parameters of the mixture through sul-

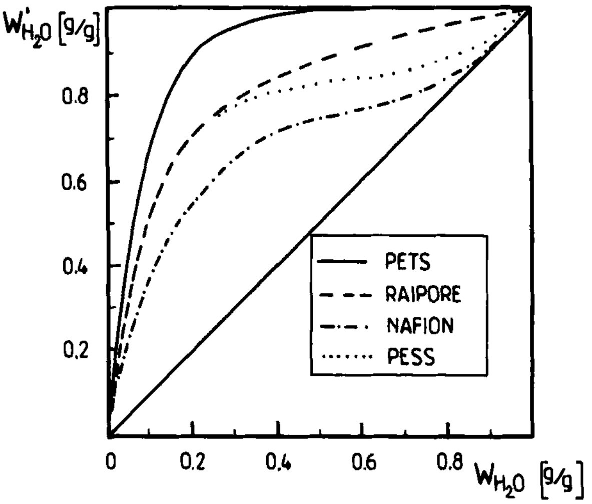

FIG. 3. Influence of the feed composition (W) on the permeate composition (W') of different sulfonic membranes. Pervaporation temperature: 40°C.

TABLE 2
Transport Parameters of Sulfonated Ion-Exchange Membranes at a Feed Composition of 41.3 wt% Water (azeotropic point). T = 40°C

Membrane	Permeate (wt% H_2O)	Flux ($kg \cdot m^{-2} \cdot h^{-1}$)		Normalized flux ($kg \cdot \mu m \cdot m^{-2} \cdot h^{-1}$)	
		Total	Water	Total	Water
PETS	98.0	0.52	0.51	164	160
RAIPORE	85.7	3.85	3.30	192	165
PESS	81.0	0.93	0.75	167	136
NAFION	72.2	0.68	0.49	116	84

fonated ion-exchange membranes at a feed composition of 41.3 wt% of water (the azeotropic point). Because the investigated membranes were of different thicknesses, the right-hand columns present the normalized fluxes, i.e., fluxes through a membrane with a thickness equal to 1 μm.

From these data it is seen that the best transport parameters were obtained with the RAIPORE 1010 membrane, where a very high flux is accompanied by relatively good selectivity.

The NAFION membrane has the lowest selectivity in pervaporation of water–pyridine mixtures. This can be explained by the higher affinity of the ether segments in the polymer backbone to the pyridine as compared to other membranes (*5*). Also, the flux of pyridine across the NAFION membrane is much higher at a low water content compared with RAIPORE and PESS membranes (Fig. 4). The variation of pyridine flux as a function of water content is quite different for NAFION and other sulfonic membranes. High and constant flux across the NAFION membrane up to a 20 wt% concentration of water in the feed suggests that pyridine is transported independent of the water. On the other hand, the increase in the fluxes for RAIPORE and PESS membranes indicates strong coupling during transport. Such a synergetic behavior of ion-exchange membranes was also observed for water–ethanol mixtures (*5*, *6*, *8*).

3.2. Properties of Sulfonated vs Carboxylated Membranes

The affinity of a given membrane for different solvents can be quantitatively expressed by the swelling (*13*).

Table 3 presents results of swelling for sulfonic and carboxylic membranes in water and pyridine. The degree of swelling in pure solvents reflects the equilibrium properties of a given membrane, and it can be used to a certain extent for a qualitative prediction of the transport properties (*7*).

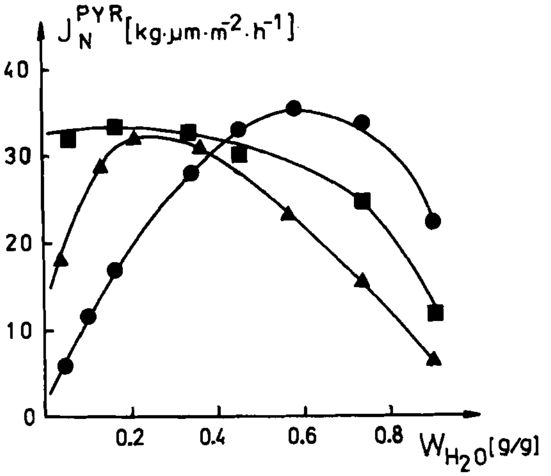

FIG. 4. Influence of the feed composition (W) on the pyridine flux (J) across sulfonic membranes. (●) PESS; (▲) RAIPORE; (■) NAFION.

It is seen that the carboxylic PEAA membrane swells in pyridine to a much greater extent than do the sulfonic membranes. Nevertheless, both sulfonic and carboxylic membranes show preferential sorption of water although to a different extent. Because the networks of PESS and PEAA membranes are similar (Table 1), such substantial differences must be attributed to the different ionic groups present in these membranes.

In order to compare the transport properties of carboxylic and sulfonic membranes, the PEAA (PE-COOH) and PETS (PE-SO_3H) membranes were chosen (Table 1). In the case of these two membranes, any differences in the membrane properties will be caused by the different characters of the ion-exchange sites.

TABLE 3
Swelling of Ion-Exchange Membranes in Water and Pyridine

		Swelling			
		Water		Pyridine	
Membrane	Solvent	g/g	mmol/g	g/g	mmol/g
PESS	—SO_3H	0.40	22.2	0.25	3.16
RAIPORE	—SO_3H	0.31	17.2	0.23	2.91
PEAA	—COOH	0.43	23.9	0.86	10.87

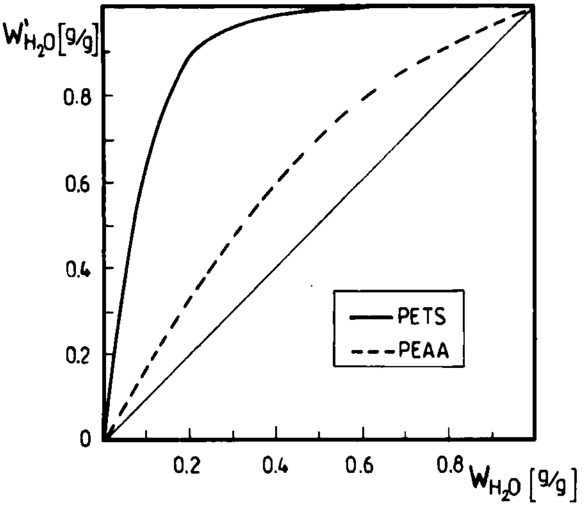

FIG. 5. Influence of the feed composition (W) on the permeate composition (W') of carboxylic (PEAA) and sulfonic (PETS) ion-exchange membranes.

The selectivity in pervaporation shows (Fig. 5) that although water molecules are transported preferentially for both of these membranes, the presence of the carboxylic groups in the ACOM membrane causes a significant drop in membrane selectivity.

Comparison of the permeate fluxes through PEAA and PETS membranes is shown in Fig. 6. The differences in the concentration depen-

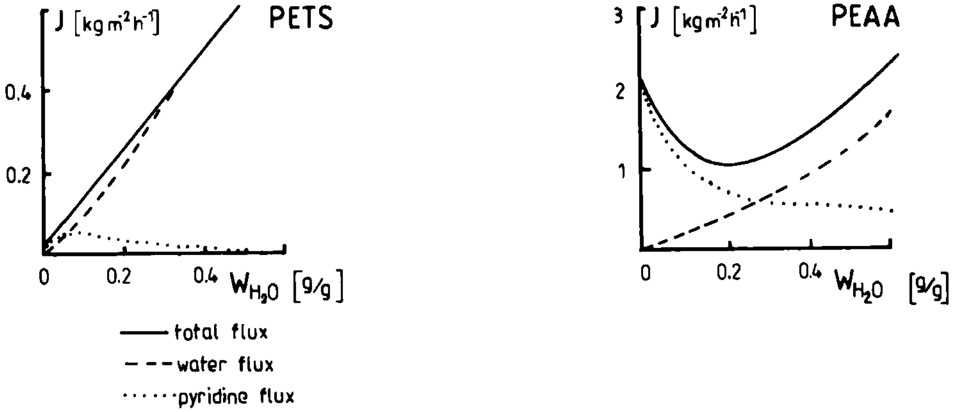

FIG. 6. Influence of the feed composition (W) on the flux (J) across carboxylic (PEAA) and sulfonic (PETS) ion-exchange membranes.

dence of pyridine flux suggests there are different transport modes for pyridine molecules in PEAA and PETS membranes. The high affinity of the carboxylic membrane to pyridine in the lower concentration range indicates the possibility of strong short-range interactions between the carboxylic groups and the pyridine molecules (*13, 14*). Such interactions result in two bands observed in the IR spectrum around 2500 and 1900 cm^{-1} due to proton transfer (*13*, *14*). Knowing this, we can conclude that pyridine molecules are transported in the carboxylic membranes not only by a so-

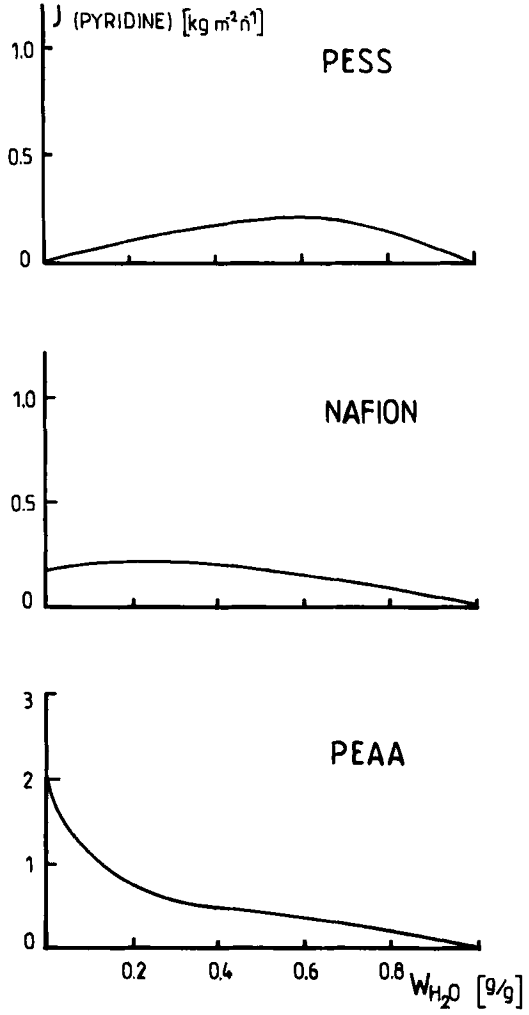

FIG. 7. Comparison of the concentration dependence of the pyridine flux (*J*) across different ion-exchange membranes.

lution-diffusion mechanism through the nonionic region of the membrane but also by a push-pull mechanism through the ionic sites (*15–18*).

Through comparison of the pyridine flux through different membranes, it can be stated that there are three different modes of transport of pyridine molecules through the membrane, depending both on the backbone structure and the nature of the ion-exchange grouping (*7*, *19*) (Fig. 7):

In sulfonated polyethylene and similar membranes, the flux of the pyridine passing is at the maximum because of coupling with the water flux.

In Nafion-type membranes, transport occurs in the hydrophobic regions and is constant up to 20 wt% of the feed, and then it decreases.

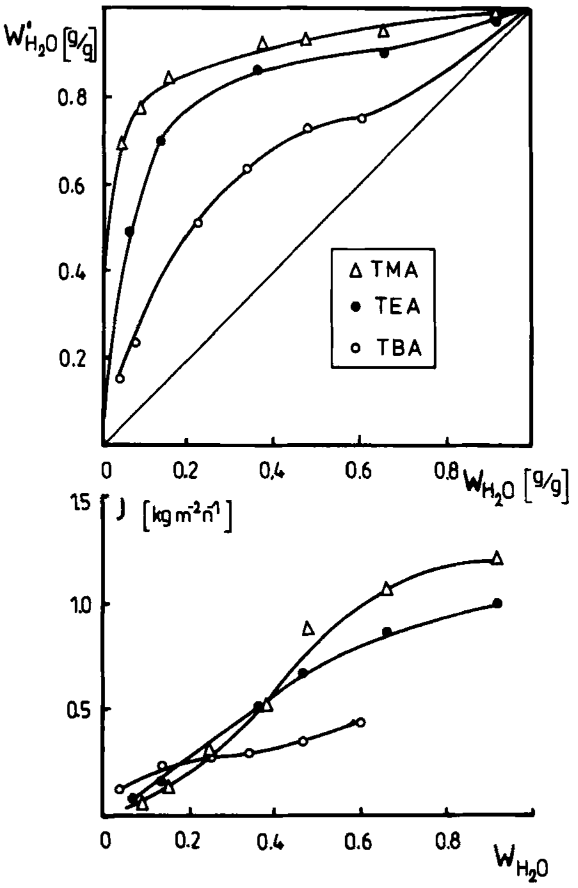

FIG. 8. Influence of the different organic counterions on the permeate composition (W') and permeate flux (J) in the PESS membrane. TMA = trimethylammonium ion; TEA = triethylammonium ion; TBA = tributylammonium ion.

In carboxylic ion-exchange membranes, transport occurs both by the push-pull mechanism and by sorption-diffusion through the amorphous region. The sharp decrease at low concentration is due to replacement of the pyridine molecules by the water molecules around the ionic sites.

3.3. The Influence of Organic Counterions on PV with PESS Membrane

Figure 8 shows the transport properties of the PESS membrane loaded with different organic counterions: TMA, TEA, and TBA. The increasing

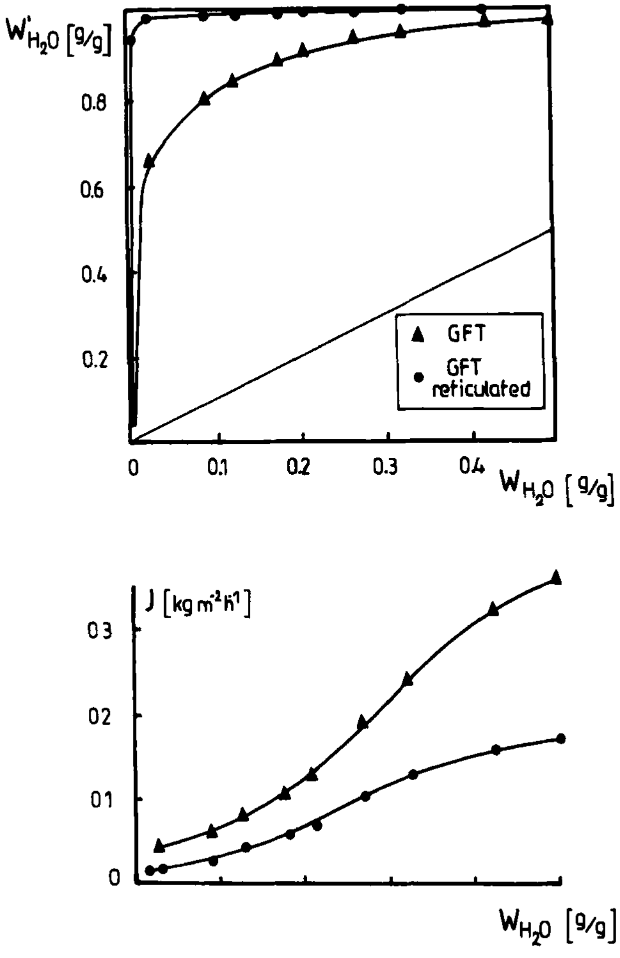

FIG. 9. Performance parameters (permeate composition and flux vs feed composition) of the neutral GFT membranes used in pervaporation of water–pyridine mixtures.

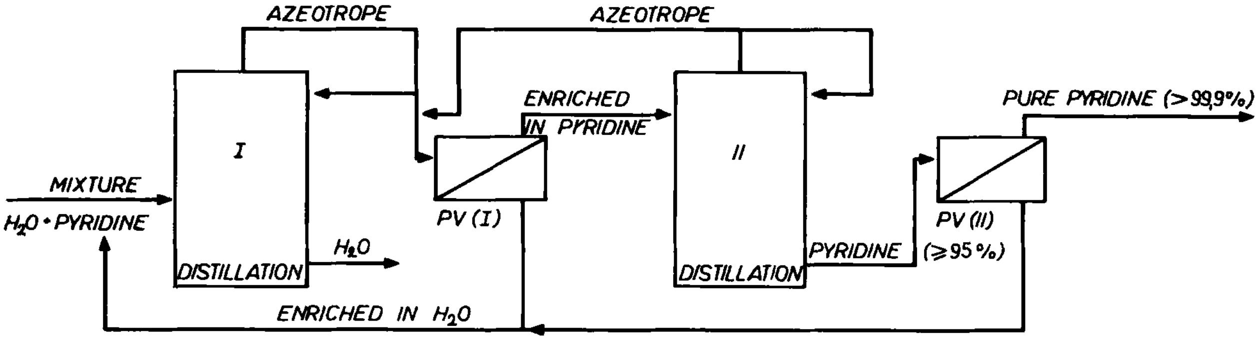

FIG. 10. The process schema of a combination of distillation and two stages of pervaporation. PV I: With high-flux membranes (e.g., RAIPORE). PV II: With high-selective membranes (e.g., GFT).

dimensions and hydrophobicities of the counterions result in both a drop in selectivity and in the total permeation rate. Only at low water content does the permeate flux increase, i.e., transport of pyridine also proceeds through the ionic sites.

3.4. Pervaporation of Pyridine with Neutral GFT Membrane

Figure 9 shows the results obtained with the neutral GFT membrane. This polyvinyl alcohol membrane supported on polyacrylonitrile is widely used nowadays for the industrial dehydration of ethanol.

The GFT membrane used for the pervaporation of the water–pyridine mixture was also selective to water, but the unmodified membrane was very unstable at higher feedwater concentrations because of progressive dissolving of the PVA layer. After crosslinking of this membrane, it is practically impermeable to pyridine (Fig. 9).

4. CONCLUSIONS

The results presented of the application of pervaporation to water–pyridine mixtures with ionic and neutral membranes prove the applicability of this technique to the dehydration of pyridine.

The combination of pervaporation with high-flux ionic membranes used to break the azeotrope, followed by standard distillation, and a final pervaporation using a GFT membrane may offer a time- and energy-saving technique for obtaining dehydrated pyridine on an industrial scale (Fig. 10).

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