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A. M. Urtiaga[a]; C. Casado[a]; C. Aragoza[b]; I. Ortiz[a]
[a] Departamento de Ingeniería Química, ETSIIT, Universidad de Cantabria, Santander, Spain [b] Departamento Ingeniería de Alimentos, Valencia, Universidad Simón Rodríguez, Estado Carabobo, Venezuela

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Dehydration of Industrial Ketonic Effluents by Pervaporation. Comparative Behavior of Ceramic and Polymeric Membranes

A. M. Urtiaga,[1] C. Casado,[1] C. Aragoza,[1,2] and I. Ortiz[1,*]

[1]Departamento de Ingeniería Química, ETSIIT, Universidad de Cantabria, Santander, Spain
[2]Universidad Simón Rodríguez, Departamento Ingeniería de Alimentos, Valencia, Estado Carabobo, Venezuela

ABSTRACT

Pervaporation dehydration of an industrial ketonic waste mixture was studied. The performance of two membranes were investigated: (1) a polymeric membrane based on cellulose sulfate polyelectrolytes (Symplex membrane, GKSS) and (2) an inorganic microporous silica membrane (Pervap SMS, Sulzer Chemtech). The main components of the industrial feed mixture were acetone and water, initial water content C_{H_2O} : 25–30 wt%. For both membranes, the total flux and the water flux decreased as the feed water concentration decreased. The effect of pervaporation temperature in the 40°C to 70°C range was investigated.

*Correspondence: I. Ortiz, Departamento de Ingeniería Química, ETSIIT, Universidad de Cantabria, Avda. de los Castros. s/n. 39005, Santander, Spain; Fax: 34 942 201591; E-mail: ortizi@unican.es.

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The compared results show that the feed can be efficiently dehydrated with the two membranes under study, although the dehydration process is more efficient using the polyelectrolyte membrane since it provides a much higher water flux. The corresponding retentate could be incinerated without additional fuel in both cases. However the ceramic silica membrane yields an aqueous permeate with homogenous organic content and better environmental characteristics than the polyelectrolyte membrane. Apparent activation energies for water permeation through the polyelectrolyte and the silica membranes were calculated.

Key Words: Pervaporation; Dehydration; Acetone; Ceramic membrane; Polymeric membrane.

INTRODUCTION

In the synthesis of p-phenylenediamines, the water formed during the reaction is accumulated and yields a mixture of the product (IPPD), water, acetone, and the hydrogenation catalyst. The acetone is partially recovered by distillation and the residual water–ketones mixture is sent to combustion, with the extra cost for additional required fuel. The content of water in the waste mixture is in the range 25 to 30 %wt.; 800 tons/year of this waste are obtained in one production unit.

In this work, the application of a membrane pervaporation process to the waste water–ketones mixture for further dehydration prior to combustion was studied. The objective was to obtain a concentrated-ketone retentate that might be incinerated without addition of extra fuel and an aqueous permeate acceptable for further treatment. Recent works mention pervaporation as an efficient technology for the treatment of waste streams, although pervaporation alone is considered unable to provide, at least economically, both a high-purity retentate and a high-purity permeate.[1]

Pervaporation is a membrane separation process in which the feed liquid mixture to be separated is placed in contact with one side of a dense selective membrane, producing an enriched vapor permeate on the other side of the membrane. The separation is governed by the physicochemical affinity between the membrane material and the permeating species and thus by sorption and solubility phenomena.[2] The transport through the membrane is affected by diffusion and the differences in diffusivities of the different components in the membrane are important for the separation efficiency.

Recent works mention pervaporation as an efficient technology for the treatment of waste streams. Moulin et al[3] proposed pervaporation for

the treatment of an aqueous effluent of the chemical industry containing organics and salts. As a result, an aqueous retentate containing the salts with adequate characteristics for biological treatment is obtained, while the organic permeate might be incinerated. Baus et al[4] presented a pilot plant study combining pervaporation and UV photolysis for the treatment of industrial waste water contaminated with organic substances. Lipnizki and Field[5] proposed a hybrid pervaporation–adsorption process to recover phenol from industrial waste streams. A polishing adsorption unit was necessary to obtain a water stream for direct discharge in accordance with environmental standards.

Some relevant studies on the pervaporative separation of water–ketones mixtures can be referenced.[6–12] Most of these references contribute to the characterization of polymeric pervaporation membranes in terms of flux and selectivity for acetone–water mixtures, as data given in Table 1. Reported flux and selectivity values are markedly influenced by temperature and feed composition. According to the data in Table 1, polyelectrolyte membranes[6,7] offer high fluxes, even at moderate temperatures and reasonably high selectivity values.

More recently, the use of ceramic pervaporation membranes based on silica materials is being introduced, with the aim of increasing the operation temperature of the pervaporation process.[13–22] Additionally ceramic pervaporation membranes offer good compatibility with aprotic solvents. Published research data on the performance of silica pervaporation membrane are given in Table 2. Most data referred to the dehydration of azeotropic alcohol–water mixtures. Only one reference[17] to the separation of an acetone–water mixture was found, showing moderate values of flux and selectivity.

In this work, the dehydration of an industrial water–ketones mixture was studied using two different types of pervaporation membranes with preferential flux for water: (1) a polymeric membrane based on polyelectrolytes and (2) an inorganic membrane based on microporous silica. The comparison between the performances of both membranes was made in terms of flux and selectivity. The influence of the operation parameters, temperature, and aqueous concentration of the feed mixture is discussed for each type of membrane.

EXPERIMENTAL

Industrial waste feed solutions obtained in the production of p-phenylenediamines were used in all the experiments. The initial water content was in the range 25 to 30 wt%. The main components of the feed were water and acetone, with minor concentrations of other organic components.

Table 1. Comparative performance of polymeric pervaporation for acetone dehydration.

Mixture	Membrane	Temperature (°C)	Water flux ($kg/m^2\,h$)	Total flux ($kg/m^2\,h$)	Selectivity $\alpha_{w/acetone}$	Reference
Acetone–water: 10 wt% water	Polyelectrolyte membrane (Symplex, GKSS)	25		0.5	2000	6
Acetone–water: 9 wt% water	Polyelectrolyte complex membrane	50		2.4	2518	7
Product mixture, acetone–MIBK–water: 6 wt% water	PVA-1000 (Sulzer)	80		0.2	76	8
	PVA-1001	80		0.8	376	
		90		1.1		
		100		1.8		
Acetone–water: 15–2 wt% water	PVA crosslinked membranes	30	1.3–0.1		16–150	9
Acetone–water: 25–5 mol% water	Sulphonate containing aromatic polyamides	60	0.6–0.1		1500–20,000	10
Acetone–water: 10 wt% water	Potassium alginate composite membranes	50		0.835	$>10^5$	11
Acetone–water: 20 wt% water	Sodium alginate dense membrane	50		2.1	$\propto$	12
Acetone–water: 20 wt% water	Polyelectrolyte membrane (Symplex, GKSS)	40		2.0	30	This study
		70		4.3	20	
Acetone–water: 10 wt% water	Polyelectrolyte membrane (Symplex, GKSS)	40		0.47	150	This study
		70		2.15	60	

Table 2. Comparative performance of silica pervaporation membranes for solvent dehydration.

Type of membrane	Mixture	Temperature (°C)	Water flux ($kg/m^2 h$)	Total flux ($kg/m^2 h$)	Selectivity α_w	Reference
Silica	IPA–water: 5 wt% water	70		0.3	500	13
Silica	IPA–water: 5 wt% water	70		1.0	100	14
	Butanol–water: 5 wt% water	75		3.0	250	
Silica ECN	IPA–water: 5 wt% water	70	2.1		600	15
Silica ECN	IPA–water: 5 wt% water	60	1.0		2500	16
Silica ECN	IPA–water: 4.5 wt% water	80	1.9		1150	17
	Acetone–water: 10 wt% water	50	0.75		33	
Silica Pervap SMS (Sulzer)	t-Butanol–water: 5 wt% water	60	1.5		142	18
		80	5.0		1260	
		100	8.0		562	
Silica Pervap SMS (Sulzer)	IPA–water: 8.2 wt% water	70	1.9		53	19
	IPA–water: 6.9 wt% water	90	7.9		94	
Silica Pervap SMS (Sulzer)	Industrial acetone–water mixture: 10 wt% water	40	0.3		28,000	This study
		70	0.52		9000	

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Pervaporation Membranes

The Symplex membrane was kindly supplied by GKSS (Geesthacht, Germany). It is a composite membrane formed by polyelectrolytes on a microporous poly(vinylidine fluoride) support.[6] Polyelectrolytes based on cellulosic materials are well known for their affinity to water. In the membrane manufacturing process, the polyelectrolyte complex is formed in situ from aqueous solutions of the polyanion (cellulose sulfate) and polycation [poly(dimethylallyl ammonium chloride)]. The active layer of the composite membrane has a thickness of about 2 μm.

The microporous silica membrane PERVAP SMS was purchased from Sulzer Chemtech (Germany). The SMS membrane is formed by three layers: (1) a microporous amorphous silica membrane layer (estimated pore size 0.4 nm) deposited in the outer surface of the tube; (2) an intermediate layer that accommodates the surface roughness and pore size; and (3) a macroporous α-alumina support tube (pore size 3 to 5 μm).

Pervaporation Units

Experiments were performed in two laboratory scale pervaporation units. A schematic representation of the pervaporation set-up is shown in Fig. 1. In the experiments performed with the polymeric Symplex membrane, the Sulzer Chemtech bench scale pervaporation unit was employed.[23,24] The maximum operation pressure of this unit is 3 bar. In the experiments performed using the SMS ceramic membrane, a specially designed pervaporation unit was used. The characteristics of the second unit permits work at a maximum operation pressure in the feed side of 10 bar and 150°C. In both units, 1 kg of the feed is introduced in a jacketed vessel with a capacity of 2 L. The experiments were run batch wise. A centrifugal pump was used to recirculate the feed from the feed tank through the pervaporation unit. The flow rate was monitored using a flowmeter equipped with a backpressure valve for the fine adjustment of the flow rate. The temperature of the feed was measured at the inlet and outlet ports of the pervaporation module using two thermocouples. The temperature of the feed was maintained constant at the feed tank by circulation of a heating fluid through the jacket.

The main difference between both experimental systems lies in the vacuum/condenser equipment. In the experiments performed with the Symplex membrane the permeate pressure was maintained under 15 mbar using a rotary vacuum pump (Telstar 2P-9, Spain). The vacuum was monitored using a digital vacuum gauge installed in the vacuum line connecting the pervaporation module and the condenser unit. Permeate was

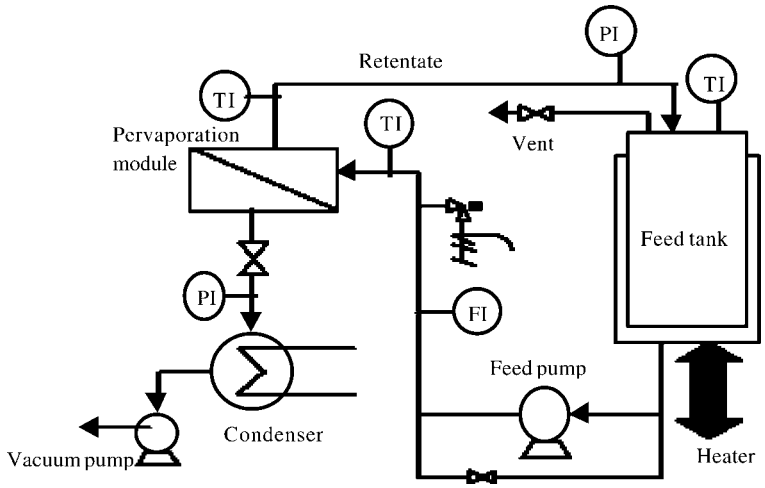

Figure 1. Schematic diagram of the experimental system.

collected in a cold trap (cooled with liquid nitrogen). Two cold traps were set in parallel, allowing the experiment to be carried out in a continuous mode. In the experiments performed with the SMS membrane, vacuum was obtained using a PC2008 Vario vacuum system (Vacuubrand, Germany), formed by a diaphragm pump fitted with a frequency converter, allowing automatic vacuum pressure control. The residual waste vapor was condensed using coolant water at a temperature of 7°C obtained from a cryogenic bath (Polyscience digital temperature controller, model 9510, USA). This vacuum system permitted maintenance of the permeate pressure below 8 mbar.

The Symplex flat membrane was inserted in a circular plate and frame pervaporation test cell, providing 0.0178 m^2 of membrane area. The feed flow rate through the membrane module was 5 L/min in the experiments using the Symplex membrane. Due to the geometry of the pervaporation cell,[25] the feed Reynolds number varied along the radial position in the membrane module from a maximum value at the center of the cell (feed inlet position) to a minimum value at the maximum radius (feed exit position). At the maximum radius, the values of the Reynolds as a function of temperature is in the range $2073\ (T = 40°C) < Re < 2925\ (T = 70°C)$.

The SMS tubular membrane consists of a 13-cm long coated ceramic tube and 0.0060 m^2 of membrane area inserted in a stainless steel tubular housing. The liquid feed flows via the annular passage on the outside of the ceramic tube. Permeating vapor is extracted by vacuum applied to the inside of

the ceramic tube. The flowrate through the module was 1.5 L/min in the experiments using the SMS membrane, providing a Reynolds number in the range 4682 (T = 40°C) < Re < 6605 (T = 70°C).

Analytical Techniques

The feed mixture and the permeate were sampled at regular intervals of time. The water concentration in the feed retentate was monitored by titration using a Mettler Toledo Karl Fisher titrator, model DL31 (Spain). The permeate weight and volume were measured. Permeation flux of water was determined by analyzing the feed samples. The chemical oxygen demand of the permeate was determined by the oxidation with chromosulfuric acid method, analog to DIN 38409H41/ISO 6060-1989.

RESULTS AND DISCUSSION

Polymeric Membrane

The effect of the feed temperature and feed composition on the dehydration of the ketonic mixture using the Symplex polyelectrolyte membrane was investigated. Figure 2 shows the evolution with time of the water content in the industrial ketonic mixture at four temperatures of the feed: 40, 50, 60, and 70°C. The experiments were run batch wise. The permeation of water through the pervaporation membrane makes the concentration of water

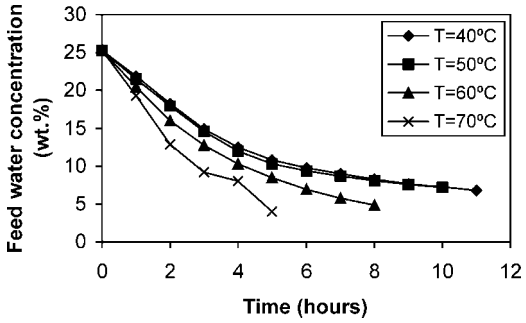

Figure 2. Symplex polyelectrolyte membrane. Evolution with time of the concentration of water in the feed recirculation tank.

in the recirculation tank diminish with time. In the experiment performed at 70°C with initial water concentration of 25.5 wt%, the final concentration of water in the organic mixture was reduced to a value of 0.4 wt%. A total amount of 250 g of permeate phase was collected. It is observed that the rate of water removal is enhanced with increasing values of the feed temperature.

The total flux (J) was calculated using Eq. (1):

$$J = \frac{m}{A\Delta t} \tag{1}$$

where J is the permeate flux in kg/m^2 h, m the mass of permeate in kg, A the membrane surface area in m^2, and Δt the permeation time in hours. Thus the flux data are obtained as average values in the time interval of sample collection. The partial flux of water J_w was calculated using the feed concentration data. Organic fluxes were calculated from a mass balance.

Figure 3 shows the total flux and the water flux through the pervaporation membrane as a function of the concentration of water in the feed at two experimental temperatures, 40°C and 70°C. For a fixed water concentration in the feed of 20 wt%, the total flux increased from 2.3 kg/m^2 h to 5.2 kg/m^2 h, for an increase in temperature from 40°C to 70°C. The water flux increased from 2 kg/m^2 h to 4.2 kg/m^2 h in the same temperature range.

The capacity of the pervaporation membrane to produce an enriched water permeate was monitored using the chemical oxygen demand (COD) of the permeate as a control parameter. Figure 4 shows the evolution of the COD of the permeate with the water concentration in the feed. The COD values of the permeate are very high, up to 165,000 mgO_2/L for the initial concentration

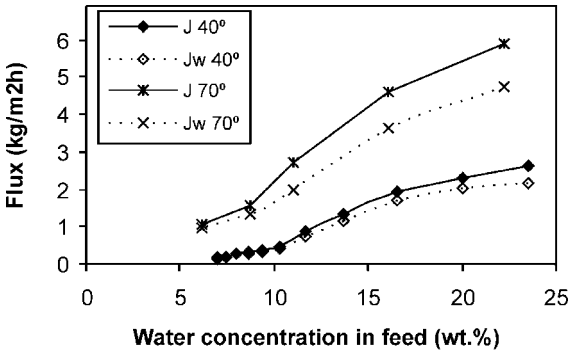

Figure 3. Symplex polyelectrolyte membrane. Total flux and water flux as a function of water concentration in the feed retentate. Influence of feed temperature.

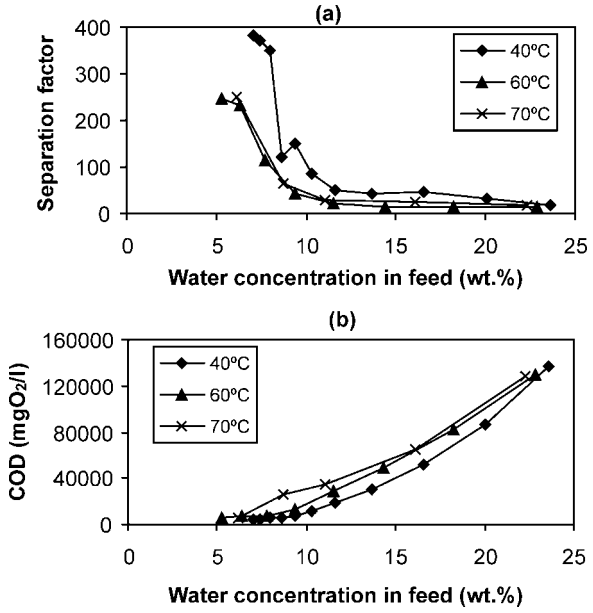

Figure 4. Symplex polyelectrolyte membrane. Quality of the permeate. (a) Separation factor; and (b) chemical oxygen demand of the permeate, as a function of the water concentration of the feed.

of water, 30 wt%, in the feed. As a point for reference, a binary acetone–water solution 99 wt% water–1 wt% acetone has an approximate COD value of 22,600 mgO_2/L. Regarding the influence of the temperature on the permeate quality, it is observed that for a constant feed concentration, the permeate COD is higher as the feed temperature is increased. For a fixed water concentration in the feed of 10 wt%, the permeate COD increased from 11,000 to 30,000 mgO_2/L, for an increase in temperature from 40°C to 70°C. However, the COD of the permeate tends to a uniform value around 5000 mgO_2/L, independent of feed temperature for feed water concentrations under 5 wt%.

The chemical oxygen demand of the permeate is closely related to the separation factor, α value, that is the most common way to indicate the selectivity of the pervaporation. α is defined in Eq. (2):

$$\alpha_w = \frac{y_w / y_{org}}{x_w / x_{org}} \tag{2}$$

where y_w the weight fraction of water in the permeate, y_{org} the weight fraction of organics in the permeate, x_w the weight fraction of water in the feed retentate, and x_{org} the weight fraction of organics in the feed retentate.

The dependency of the water separation factor, calculated as given by Eq. (2) with water concentration in the feed retentate, is also given in Fig. 4. The value of α is under 50 when the water concentration in the feed is above 10 wt%. Also, in the water concentration range 25 wt% to 10 wt%, a slow increase of α values with decreasing water concentrations is observed. A significant change of behavior is observed for feed water concentrations in the range 10 wt% to 5 wt%. In this interval, the value of the separation factor increased as the water concentration in the feed decreased, reaching values close to 400 at 40°C. Regarding the influence of feed temperature on the separation factor, slightly higher values of the separation factor are obtained at 40°C, while the α values obtained at 60°C and 70°C follow the same trend.

The experimental results show that the higher the water concentration in the feed, the higher the flux of organics. Burshe et al[9] reported water flux and selectivity values for the acetone–water mixture (range of water concentrations: 15 wt% to 2 wt%) using crosslinked PVA membranes and showed that with increasing water concentration in the feed, the selectivity decreased. The investigators assigned this observation to membrane plasticization. Water swells the amorphous regions of the polymer matrix. With increasing concentrations of water in the feed, the extent of swelling of the amorphous regions of the polymer increases. This leads to an increase in flexibility of polymer chains and hence permeation is less selective. Similar observations were reported recently by Huang et al[26] and Gallego-Lizon et al[18] in the pervaporation of water–alcohol mixtures using a modified e-PTFE membrane and a commercial PVA membrane, respectively.

Microporous Silica Membrane

The performance of the SMS membrane is shown in Figs. 5 and 6. Experiments were performed in the same concentration and temperature range as with the polyelectrolyte membrane. Figure 6 shows the total flux through the SMS membrane as a function of the concentration of water in the feed at three experimental temperatures, 40°C, 50°C, and 70°C. For a fixed water concentration in the feed of 20 wt%, the total flux increased from 0.5 kg/m^2 h to 1.1 kg/m^2 h, for an increase in temperature from 40°C to 70°C. The COD of the permeate is given in Fig. 6. COD values at a feed temperature of 40°C remain under 2000 mgO_2/L for all the experimental feed concentrations; at 50°C the maximum COD value is 3000 mgO_2/L. The experiment performed at

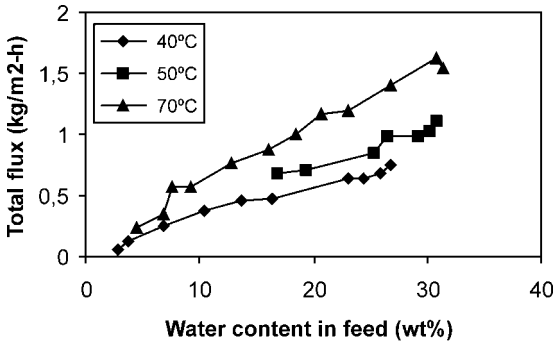

Figure 5. Silica SMS ceramic membrane. Total flux as a function of water concentration in the feed retentate. Influence of feed temperature.

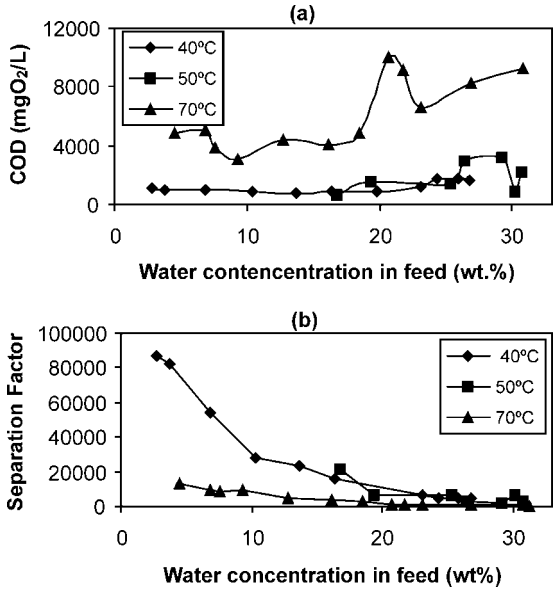

Figure 6. Silica SMS ceramic membrane. Quality of the permeate. (a) Separation factor; and (b) chemical oxygen demand of the permeate, as a function of the water concentration of the feed.

70°C generated higher values of the COD of the permeate, with a maximum of 10,000 mgO_2/L obtained for a feed water concentration of 30 wt%, which is stabilized in an average value of 5000 mgO_2/L for feed water concentrations under 20 wt%. These experimental data can be compared with the data reported by van Veen et al[17] using a silica membrane manufactured by ECN. The investigators reported a slightly higher water flux, 0.75 $kg/m^2 h$ at an operation temperature of 50°C and 10 wt% water in the feed, and a value of the separation factor α of 33. These values are low if compared with flux and selectivity reported for isopropyl alcohol–water mixtures, as shown in Table 2.

Comparison of Polyelectrolyte and Silica Membranes

The comparison was made in terms of the water flux and selectivity obtained with both membranes. The feed temperature of 70°C was used for comparison. As shown in Figs. 3 and 5, the largest flux values were obtained using the polyelectrolyte membranes. At a fixed feed water concentration of 20 wt%, the water flux with the polyelectrolyte membrane is 4.2 $kg/m^2 h$, while the flux with the SMS silica membrane is 1.1 $kg/m^2 h$. Thus, in the high water concentration range, the polyelectrolyte membrane offers a value of the water flux 3.7 times the water flux obtained with the silica membrane.

The selectivity of the separation at the high concentration range is higher when using the silica membrane. Figure 7 shows the percentage of water in the permeate as a function of the water concentration in the feed, for the polyelectrolyte and the silica membranes. This type of data offer a clearer meaning than the separation factor data when dealing with wastewaters. It is shown that the silica membrane yields water concentrations in the permeate higher than 99.5 wt%, in all the operation conditions under study. As a result, the permeate is convenient for further biological treatment.[3] The discussion about the selectivity performance of the polyelectrolyte membrane can be divided in two concentration regions. For water concentrations in the feed below 9 wt%, the separation efficiency of the polyelectrolyte membrane is similar to the silica membrane. In this range, the water content of the permeate is also higher than 99.5 wt% at any temperature in the range of 40 to 70°C. However at higher than 9 wt% water feed concentrations, the permeate water content decreases down to about 93 wt%, showing an approximately linear dependency with feed concentration.

The compared results show that the feed can be efficiently dehydrated with the two membranes under study, although the dehydration process is more efficient using the polyelectrolyte membranes since it provides a much

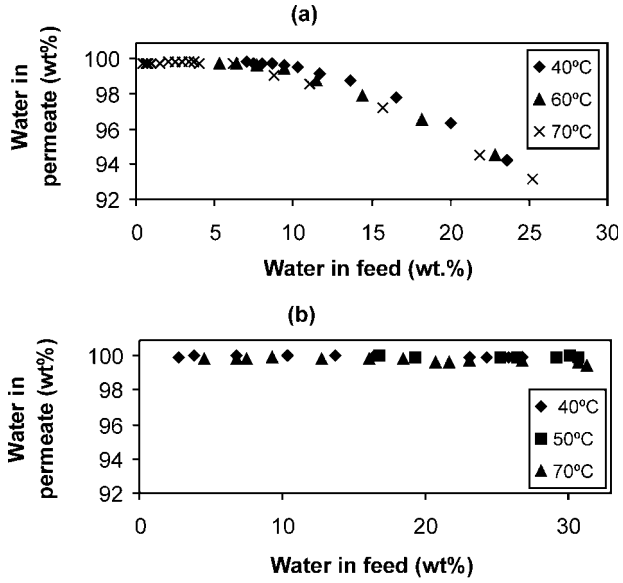

Figure 7. Water percentage in the permeate as a function of the water concentration in the feed. (a) Symplex polyelectrolyte membrane; and (b) silica SMS membrane.

higher water flux. The corresponding retentate could be incinerated without additional fuel in both cases. However, the ceramic silica membrane yields an aqueous permeate with homogenous organic content and better environmental characteristics than the polyelectrolyte membrane.

As described by Feng and Huang[27] the experimental data of the temperature dependence of the permeation flux generally exhibits an Arrhenius type dependency:

$$J_w = J_{0,w} \exp\left(-\frac{E_{J,w}}{RT}\right) \tag{3}$$

where $E_{J,w}$ is considered to be the activation energy for water permeation. $E_{J,w}$ is a useful parameter to characterize temperature dependence of water flux. A thorough discussion on the significance of $E_{J,w}$ is given by Feng and Huang.[28] Figure 8 illustrates the water permeation flux with respect to temperature at a feed concentration of 20 wt% water. The values of parameter $E_{J,w}$ for the polyelectrolyte and silica membranes were calculated to be 21.7 and 20.3 kJ mol^{-1}, respectively. An extensive group of E_J data was collected by Feng and Huang,[28] finding that the numerical values of this parameter are

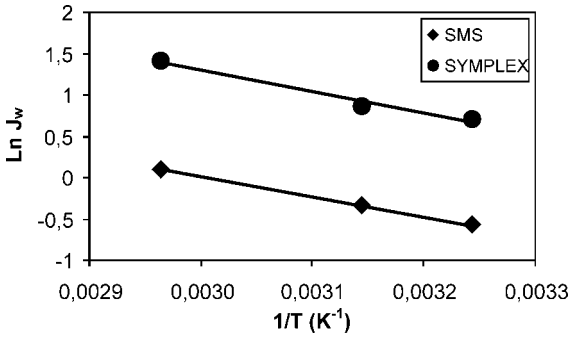

Figure 8. Effect of operation temperature on water permeation flux. Feed concentration, 20 wt% water.

in the range of 4 to 92 kJ mol^{-1}. It can be concluded that for the system under study, i.e., pervaporation of industrial water–ketones mixtures, the temperature does not influence the differences observed in the values of pervaporation fluxes obtained with the two membranes under study. Differences in flux rely more on the specific interactions of solute and membrane.

CONCLUSION

Pervaporation dehydration of an industrial ketonic waste mixture was studied. The main components of the industrial feed mixture are acetone and water, initial content C_{H_2O}:25 wt% to 30 wt%. The performance of two membranes was investigated; a polymeric membrane based on cellulose sulfate polyelectrolytes (Symplex membrane, provided by GKSS) and an inorganic microporous silica membrane (Pervap SMS, Sulzer Chemtech). At 70°C and 20 wt% water concentration, larger fluxes were obtained using the polyelectrolyte membrane (4.2 kg/m^2 h) than the silica membrane (1.1 kg/m^2 h). For both membranes, fluxes decreased as the feed water concentration decreased. The effect of pervaporation temperature was investigated in the range 40 to 70°C. Increased temperatures resulted in larger fluxes. For a fixed water concentration value in the feed of 20 wt%, the water flux through the polyelectrolyte membrane increased from 2 kg/m^2 h to 4.2 kg/m^2 h.

The silica membrane permitted water concentrations in the permeate higher than 99.5 wt% in all the operation conditions under study. The behavior

of the polyelectrolyte membrane was similar for water concentrations in the feed below 9 wt%, but at higher than 9 wt%, water feed concentrations the water concentration in the permeate decreases down to about 93 wt%, when the feed water content is 30 wt%.

The compared results shows that the industrial ketonic feed can be efficiently dehydrated with the two membranes under study, although the dehydration process is more efficient using the polyelectrolyte membrane since it provides a much higher water flux. The corresponding retentate could be incinerated without additional fuel in both cases. However, the ceramic silica membrane provides an aqueous permeate with better environmental characteristics than the polyelectrolyte membrane.

NOMENCLATURE

A	membrane surface area, m^2
E	activation energy, $kJ\,mol^{-1}$
J	flux, $kg/m^2\,h$
m	mass of permeate, kg
R	ideal gas law constant, $kJ\,mol^{-1}\,K^{-1}$
T	temperature, K
t	time
x	weight in the feed
y	weight in the permeate

Greek Letters

α	separation factor

Subscripts

org	organic
w	water

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