8.1. LISTADO DE MEMBRANAS PREPARADAS EN EL INSTITUT EUROPÉEN DES MEMBRANES (MONTPELLIER, FRANCIA)

muestra n°	fecha depósito	Zr%	método de preparación del sol	color del sol	tiempo de contacto (min)	tiempo cambio sentido (min)	Nº depósitos (-)	peso del soporte (g)	peso tras depósito (g)	peso tras tratamiento térmico (g)	ganancia %peso	Observaciones
t1	10/03/03	0	con reflujo - 80°C	amarillo	3,0	6,0	1	3,2015	3,2773	3,2619	1,85	secado al aire
t2	10/03/03	0	con reflujo - 80°C		3,5	3,0	2	3,3171	3,4664	3,4352	3,44	secado al aire
t3	11/03/03	0	con reflujo - 80°C		3,0	3,0	1	3,3132	3,3952	3,3775	1,90	secado al aire
4	13/03/03	10	con reflujo - 80°C	verde amarillento	3,0	3,0	1	3,3331	3,4365	3,4162	2,43	secado al aire
5	13/03/03	10	con reflujo - 80°C		3,1	3,0	2	3,3074	3,5757	3,4613	4,45	secado al aire
6	14/03/03	10	without reflux - 25°C		2,7	3,3	1	3,3017	3,4073	3,38	2,32	secado al aire
7	14/03/03	10	without reflux - 25°C		3,0	3,0	1	3,1958	3,3045	3,2767	2,47	secado al aire
8	17/03/03	10	without reflux - 25°C		3,0	3,7	1	3,4039	3,5021	3,4809	2,21	secado al aire
9	17/03/03	50	without reflux - 25°C	verde amarillento	3,2	3,0	1	3,1117	3,2245	3,1814	2,19	secado al aire
10	17/03/03	50	con reflujo - 80°C		3,1	3,0	1	3,2243	3,3746	3,3142	2,71	secado al aire
11	19/03/03	25	without reflux - 25°C	beige	2,0	2,0	1	3,115	3,2051	3,1812	2,08	secado al aire
12	19/03/03	25	without reflux - 25°C		3,8	3,0	1	3,271	3,3845	3,3366	1,97	secado en humedad controlada (98%)
11b	21/03/03	25	without reflux - 25°C	beige	2,0	2,0	1	3,4228	3,4937	3,4916	1,97	secado al aire
12b	21/03/03	25	without reflux - 25°C		3,8	3,0	1	3,3243	3,5154	3,3994	2,21	secado en humedad controlada (98%)

muestra n°	fecha depósito	Zr%	método de preparación del sol	color del sol	tiempo de contacto (min)	tiempo cambio sentido (min)	Nº depósitos (-)	peso del soporte (g)	peso tras depósito (g)	peso tras tratamiento térmico (g)	ganancia %peso	Observaciones
13	20/03/03	0	con reflujo - 80°C	incoloro	3,1	3,1	1	3,2751	3,3570	3,3227	1,43	secado al aire
14	20/03/03	0	sin reflujo - 80°C		3,0	3,0	1	3,2946	3,3492	3,3263	0,95	secado al aire
15	31/03/03	0	con reflujo - 80°C	incoloro	5,0	3,0	1	3,365	3,4448	3,4242	1,73	secado al aire / soporte envuelto
16	31/03/03	0	con reflujo - 80°C	incoloro	4,0	4,5	1	16,475	16,618	16,585	0,66	secado al aire / L = 15cm (*)
17	03/04/03	5	sin reflujo - 25°C	beige	6,0	3,0	1	3,3068	3,4023	3,3846	2,30	secado al aire
18	03/04/03	5	sin reflujo - 25°C		3,0	3,3	1	3,3982	3,5672	3,4758	2,23	secado en humedad controlada (98%)
19	03/04/03	5	sin reflujo - 25°C		4,4	6,7	1	3,3281	3,4159	3,3993	2,09	soporte envuelto
20	03/04/03	10	sin reflujo - 25°C	verde claro	3,0	3,0	1	3,2013	3,3637	3,2758	2,27	secado en humedad controlada (98%)
21	03/04/03	10	sin reflujo - 25°C		3,0	3,1	1	3,3976	3,4911	3,4718	2,14	soporte envuelto
22	08/04/03	15	sin reflujo - 25°C	verde muy claro	3,8	3,1	1	3,153	3,2542	3,2287	2,34	secado al aire
23	08/04/03	15	sin reflujo - 25°C		3,1	3,0	1	3,2653	3,4216	3,3439	2,35	secado en humedad controlada (98%)
24	08/04/03	15	sin reflujo - 25°C		5,4	3,0	1	3,3019	3,4023	3,3731	2,11	soporte envuelto
25	08/04/03	0	con reflujo - 80°C	incoloro	3,3	3,0	1	16,825	17,205	16,954	0,76	soporte envuelto / L = 15cm
26	10/04/03	0	con reflujo - 80°C	incoloro	3,0	3,0	1	3,1768	3,3461	3,2359	1,83	con surfactante TX35
27	14/04/03	10	sin reflujo - 25°C	beige	3,3	3,2	1	3,2447	3,3833	3,3137	2,08	secado en humedad (98%) / envuelto
28	14/04/03	10	sin reflujo - 25°C		3,2	-	1	16,561	17,233	16,949	2,29	secado en humedad (98%) / L=15cm

muestra n°	fecha depósito	Zr%	método de preparación del sol	color del sol	tiempo de contacto (min)	tiempo cambio sentido (min)	Nº depósitos (-)	peso del soporte (g)	peso tras depósito (g)	peso tras tratamiento térmico (g)	ganancia %peso	Observaciones
29	15/04/03	0	sin reflujo - 80ºC	verde muy, muy claro	3,3	3,0	1	3,2281	3,3043	3,2877	1,81	secado al aire / soporte envuelto
30	15/04/03	0	sin reflujo - 80ºC		3,2	3,2	1	3,2655	3,3675	3,3228	1,72	secado en humedad (98%) / envuelto
31	16/04/03	10	sin reflujo - 25°C	verde muy claro	3,1	3,0	2	3,2446	3,3654	-	3,59	secado al aire
32	16/04/03	10	sin reflujo - 25°C		3,0	-	1	8,1057	8,2802	-	2,11	secado en humedad (98%) / L=7,5cm
33	18/04/03	10	sin reflujo - 25°C	verde muy claro	1,0	1,0	1	3,234	3,3681	3,2891	1,68	secado al aire / con surfactante TX35 (**)
34	18/04/03	10	sin reflujo - 25°C		1,0	1,0	1	3,1471	3,2452	3,1863	1,23	secado en aire frío / TX35 0,3
35	18/04/03	10	sin reflujo - 25°C		1,0	1,0	1	3,2683	3,5017	3,3249	1,70	secado en aire frío y húmedo (98%) / con TX35 0,3
36	18/04/03	10	sin reflujo - 25°C	beige	1,0	1,0	1	3,2621	3,3444	3,3219	1,80	secado al aire
37	18/04/03	10	sin reflujo - 25°C		1,0	1,0	1	3,0956	3,1963	3,1688	2,31	secado al aire
38	18/04/03	10	sin reflujo - 25°C		1,000	1,0	1	3,178	3,3601	3,2597	2,51	secado en aire frío y húmedo (98%)
40	22/04/03	10	sin reflujo - 25°C	beige	1,0	1,0	1	3,3693	3,5335	3,4448	2,19	secado al aire / con TX15 0,3
41	22/04/03	10	sin reflujo - 25°C	beige	1,0	1,0	1	3,1984	3,3172	3,2703	2,20	secado al aire / con TX15 0,1
42	23/04/03	0	con reflujo - 80°C	verde claro	1,0	1,0	1	3,2801	3,3578	3,3371	1,71	secado en aire frío (4ºC)
43	23/04/03	0	con reflujo - 80°C	verde claro	1,0	1,4	1	4,3843	4,4899			secado en aire frío (4ºC)
44	25/04/03	10	sin reflujo - 25°C	beige	1,0	1,0	1	3,283	3,4187	3,3634	2,39	secado en aire frío (4ºC) / TX35 0,1
45	25/04/03	10	sin reflujo - 25°C		1,0	1,0	1	3,3603	3,5888	3,4468	2,51	secado en aire frío y húmedo (98%) / TX35 0,1

muestra n°	fecha depósito	Zr%	método de preparación del sol	color del sol	tiempo de contacto (min)	tiempo cambio sentido (min)	Nº depósitos (-)	peso del soporte (g)	peso tras depósito (g)	peso tras tratamiento térmico (g)	ganancia %peso	Observaciones
46	28/04/03	10	sin reflujo - 25°C	verde claro	1,0	1,0	1	8,2342	8,3634			secado en aire frío (4ºC) / TX15 0,1 / L=7,5cm
47	28/04/03	10	sin reflujo - 25°C	beige	1,0	1,1	1	8,0663	8,2076			secado en aire frío (4ºC) / TX35 0,1 / L=7,5cm
48	28/04/03	10	sin reflujo - 25°C	amarillo	1,0	1,4	1	8,1652	8,3473	8,3058	1,69	secado en aire frío (4ºC) / L=7,5cm
49	29/04/03	20	sin reflujo - 25°C	beige	1,0	1,0	1	8,0999	8,2444			secado en aire frío (4ºC) / L=7,5cm
50	29/04/03	20	sin reflujo - 25°C	beige	1,1	1,1	1	8,17	8,3621			secado en aire frío (4ºC) / TX15 0,1 / L=7,5cm
51	29/04/03	20	sin reflujo - 25°C	beige	1,0	1,2	1	8,3915	8,6143			secado en aire frío (4ºC) / TX35 0,1 / L=7,5cm
52	07/05/03	0	sin reflujo - 80°C	incoloro	1,0	1,2	1	3,2135	3,3006	3,2864	2,22	secado en aire frío (4ºC) / effect of 2nd coating
53	07/05/03	10	sin reflujo - 22°C	beige	1,0	1,0	1	3,2741	3,3517	3,3396	1,96	secado en aire frío (4ºC) / effect of 2nd coating
M1(a)	09/05/03	0	sin reflujo - 80°C	incoloro	1,033	1,367	1	17,481				secado en aire frío (4ºC)/ tubo esmaltado / L = 15cm
M1 (b)	09/05/03	0			1,050	1,083	1	17,067				secado en aire frío (4ºC) / tubo esmaltado / L = 15 cm
54	14/05/03	5	sin reflujo - 25°C	amarillo	1,050	1,150	1	16,6825	17,125	17,04	2,10	secado en aire frío (4ºC) / L=15cm
55	14/05/03	0	sin reflujo - 80°C	incoloro	1,000	1,083	1	3,3886	3,4705	3,451	1,81	secado en aire frío (4ºC) / nuevo TEOS
M2(a)	19/05/03	5	sin reflujo - 25°C	amarillo	1,033	1,167	1	-	17,1112	(***)		secado en aire frío (4ºC) / tubo esmaltado / L=15cm
M2(b)	19/05/03	5	ídem	ídem	1,050	1,067	1	-	17,1247	(***)		secado en aire frío (4ºC) / tubo esmaltado / L=15cm
M3 (a)	20/05/03	10	sin reflujo - 25°C	amarillo verdoso	1,033	1,133	1	-	17,3094	17,2897	-0,11	secado en aire frío (4ºC) / tubo esmaltado / L=15cm
M3 (b)	20/05/03	10	Idem	idem	1,300	1,000	1	-	17,0076	16,9826	-0,15	secado en aire frío (4ºC) / tubo esmaltado / L=15cm

muestra n°	fecha depósito	Zr%	método de preparación del sol	color del sol	tiempo de contacto (min)	tiempo cambio sentido (min)	Nº depósitos (-)	peso del soporte (g)	peso tras depósito (g)	peso tras tratamiento térmico (g)	ganancia %peso	Observaciones
56	21/05/03	0	con reflujo - 80°C	incoloro	1,033	1,150	1	3,1453	3,2142			secado en aire frío (4ºC) / nuevo TEOS
M4 (a)	22/05/03	10	sin reflujo - 25°C	amarillo	1,100	1,100	1	16,8807	-	(***)		secado en aire frío (4ºC) / tubo esmaltado / L=15cm TX15 0,3
M4 (b)	22/05/03	10	Idem	Idem	1,100	1,233	1	16,981	-	(***)		secado en aire frío (4ºC) / tubo esmaltado / L=15cm TX15 0,3
M5(a)	22/05/03	20	sin reflujo - 25°C	verde muy claro	1,217	1,067	1	17,6078	17,6626	17,6324	0,14	secado en aire frío / tubo esmaltado / L=15cm
M5(b)	22/05/03	20	Idem	Idem	1,067	1,017	1	16,8758	17,009	16,9554	0,47	secado en aire frío / tubo esmaltado / L=15cm
57	26/05/03	5	sin reflujo - 25°C	amarillo verdoso muy claro	1,067	1,200	1	16,8637				secado en aire frío / tubo esmaltado / L=15cm / **reciclado**
58(a)	26/05/03	10	sin reflujo - 25°C	amarillo	1,067	1,617	1	17,0623				secado en aire frío / tubo esmaltado / L=15cm / **reciclado**
58(b)	26/05/03	10	Idem	Idem	1,250	1,000	1	16,9697				secado en aire frío / tubo esmaltado / L=15cm / **reciclado**
59(a)	26/05/03	15	sin reflujo - 25°C	beige	1,083	1,050	1	17,5131				secado en aire frío / tubo esmaltado / L=15cm / **reciclado**
59(b)	26/05/03	15	Idem	idem	1,050	1,000	1	17,0499				secado en aire frío / tubo esmaltado / L=15cm / **reciclado**
60(a)	26/05/03	0	con reflujo - 80°C	incoloro	1,067	1,617	1	16,9716				secado en aire frío / tubo esmaltado / L=15cm
60(b)	26/05/03	0	Idem	idem	1,067	1,333	1	17,3154				secado en aire frío / tubo esmaltado / L=15cm

(*) A menos que se indique lo contrario, todas las muestras recogidas en la tabla han sido depositadas en tubos de soporte de 3 cm de longitud,
(**) De esta muestra en adelante, todos los recubrimientos se han realizado según el procedimiento de "inundación desde abajo".
(***) Completamente agrietada, el reciclado con HF se juzga necesario.

8.2. SELECCIÓN DEL MÉTODO DE ESTIMACIÓN DE COEFICIENTES DE ACTIVIDAD

En este Anexo se presenta el procedimiento seguido para seleccionar el método de estimación de propiedades termodinámicas más adecuado al sistema agua/acetona, y luego ampliado a los sistemas agua/IPA y agua/THF.

Los cuatro factores que se han de considerar al elegir un método de estimación de propiedades son (Carlson, 1996):

i. la naturaleza de las propiedades de interés (son compuestos polares no electrolitos)
ii. la composición de la mezcla (se trata de mezclas binarias acuosas-orgánicas con mayoría de compuesto orgánico)
iii. el rango de presión y temperatura y,
iv. la disponibilidad de los parámetros.

En base a estos criterios, se seleccionaron tres métodos termodinámicos basados en el concepto de composición local (Perry y Green, 1997):

- Ecuación de Wilson
- Ecuación NRTL (*Non-Random-Two-Liquid*)
- Método UNIFAC (UNIQUAC, *Universal Quasi-Chemical, Functional group Activity Coefficients*)

La ecuación de Wilson contiene sólo dos parámetros para un sistema binario (A_{12} y A_{21}) que se escribe:

$$\frac{G^E}{RT} = -x_1 \ln(x_1 + x_2 A_{12}) - x_2 \ln(x_2 + x_1 A_{21}) \tag{8.1}$$

$$\ln \gamma_1 = -\ln(x_1 + x_2 A_{12}) - x_2 \left(\frac{A_{12}}{x_1 + x_2 A_{12}} - \frac{A_{21}}{x_2 + x_1 A_{21}} \right) \tag{8.2}$$

$$ln\,\gamma_2 = -ln(x_2 + x_1 A_{21}) - x_1\left(\frac{A_{12}}{x_1 + x_2 A_{12}} - \frac{A_{21}}{x_2 + x_1 A_{21}}\right) \tag{8.3}$$

Tanto A_{12} como A_{21} son números positivos, y para el agua en acetona toman los valores: A_{12} = 107,38 y A_{21} = 469,55.

La ecuación NRTL contiene tres parámetros para un sistema binario, y se escribe así:

$$\frac{G^E}{x_1 x_2 RT} = \frac{G_{21}\tau_{21}}{x_1 + x_2 G_{21}} + \frac{G_{12}\tau_{12}}{x_2 + x_1 G_{12}} \tag{8.4}$$

$$ln\,\gamma_1 = x_2^2\left[\tau_{21}\left(\frac{G_{21}}{x_1 + x_2 G_{21}}\right)^2 + \frac{G_{12}}{(x_2 + x_1 G_{12})^2}\right] \tag{8.5}$$

$$ln\,\gamma_2 = x_1^2\left[\tau_{12}\left(\frac{G_{12}}{x_2 + x_1 G_{12}}\right)^2 + \frac{G_{21}}{(x_1 + x_2 G_{21})^2}\right] \tag{8.6}$$

Aquí $G_{12} = exp(-\alpha\,\tau_{12})$ y $G_{21} = exp(-\alpha\,\tau_{21})$

y $\tau_{12} = \frac{b_{12}}{RT}$; $\tau_{21} = \frac{b_{21}}{RT}$

donde α, b_{12} y b_{21} son parámetros específicos para una pareja particular de substancias, e independientes de la composición y la temperatura. Para el agua en acetona toman los valores: α = 0,2994, b_{12} = -253,88 y b_{21} = 845,21.

El método UNIFAC está basado en la ecuación UNIQUAC, para facilitar el cálculo de coeficientes de actividad a partir de las contribuciones de los distintos grupos que conforman las moléculas de una disolución. El coeficiente de actividad es la suma de un término combinatorio y uno residual, según las expresiones siguientes:

$$ln\,\gamma_i = ln\,\gamma_i^C + ln\,\gamma_i^R \tag{8.8}$$

$$ln\,\gamma_i^C = 1 - J_i + ln\,J_i - 5q_i\left(1 - \frac{J_i}{L_i} + ln\frac{J_i}{L_i}\right) \tag{8.9}$$

$$ln\,\gamma_i^R = q_i\left(1 - ln\,s_i - \sum_j \theta_i \frac{\tau_{ij}}{s_j}\right) \tag{8.10}$$

donde

$$\theta_i \equiv \frac{x_i q_i}{\sum_j x_j q_j} \tag{8.11}$$

$$\tau_{ij} = exp\frac{-\left(u_{ji} - u_{ii}\right)}{RT} \tag{8.12}$$

$$J_i = \frac{r_i}{\sum_j r_j x_j} \tag{8.13}$$

$$L_i = \frac{q_i}{\sum_j q_j x_j} \tag{8.14}$$

$$s_i = \sum_l \theta_l \tau_{li} \tag{8.15}$$

De nuevo, el subíndice *i* identifica a la substancia, y *j* y *l* son índices mudos. Los valores de los parámetros r_i, q_i y $(u_{ij} - u_{ii})$ vienen recogidos en Perry y Green (1997) para el agua y la acetona.

Las simulaciones de las curvas de equilibrio líquido-vapor para el sistema agua/acetona utilizando estos métodos termodinámicos han sido llevadas a cabo

mediante la herramienta de *software* Aspen Plus, Estas curvas de equilibrio se representan en la Figura 8.1.

Se calcularon las desviaciones de los valores de temperatura y fracción másica de vapor de agua obtenidos en las simulaciones, respecto de los datos experimentales. La Tabla 8.1 recoge la media geométrica de estas desviaciones.

Tabla 8.1, Desviaciones (media geométrica) de los datos de equilibrio calculados respecto de los datos experimentales, para el sistema agua/acetona,

	Wilson - exp	NRTL - exp	UNIFAC - exp
Temperatura, *T*	2,73	2,96	1,85
fracción másica del vapor, *y*	1,33	1,68	0,64

Esta tabla demuestra que el método termodinámico que menos se aleja de los resultados experimentales es UNIFAC, por eso es este método el que se utiliza en este trabajo para calcular coeficientes de actividad de las mezclas de alimentación con que se ha trabajado.

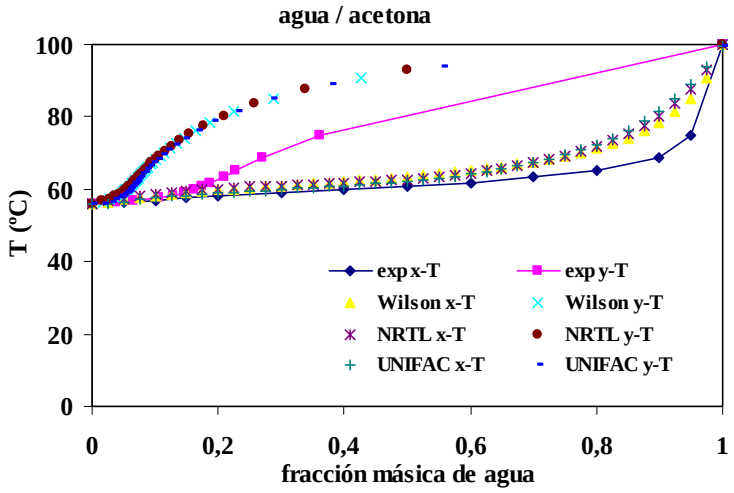

Figura 8.1. Estimación de curvas de equilibrio para el sistema agua/acetona a presión atmosférica. Los datos experimentales de Perry y Green (1997) se incluyen para la comparación.

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

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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.

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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	∞	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	

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

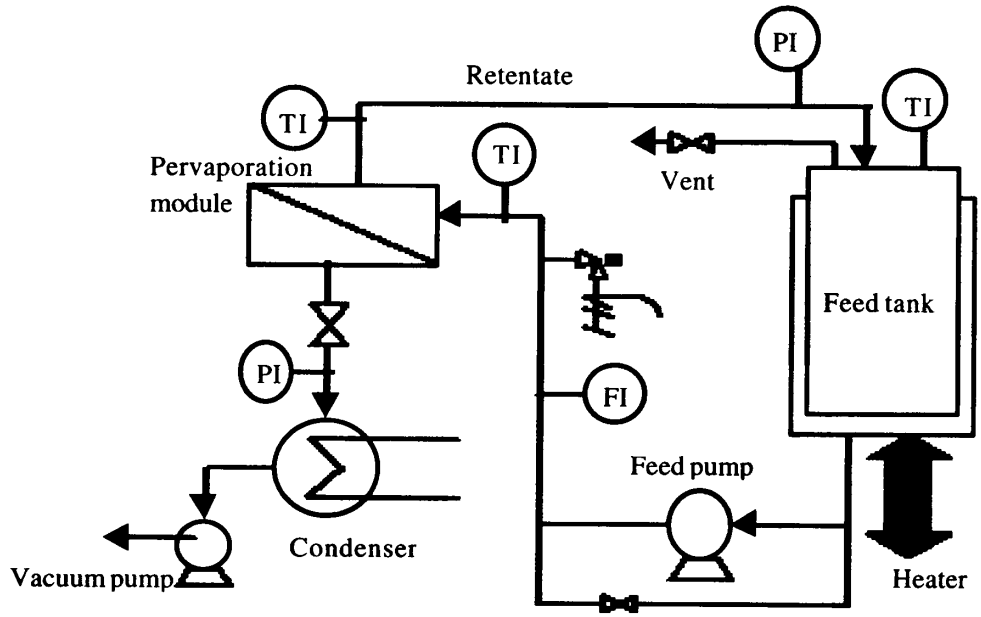

Figure 1. Schematic diagram of the experimental system.

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

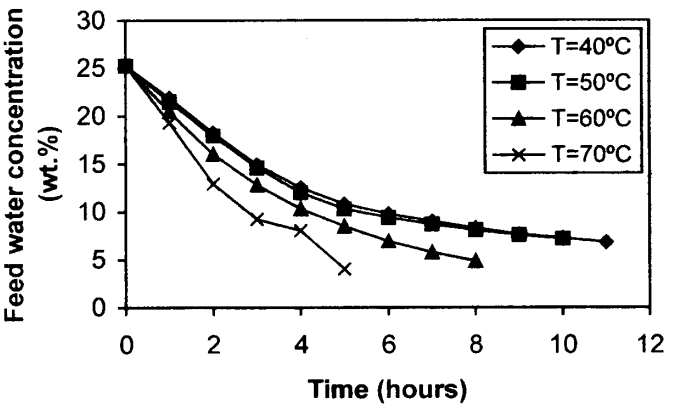

Figure 2. Symplex polyelectrolyte membrane. Evolution with time of the concentration of water in the feed recirculation tank.

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

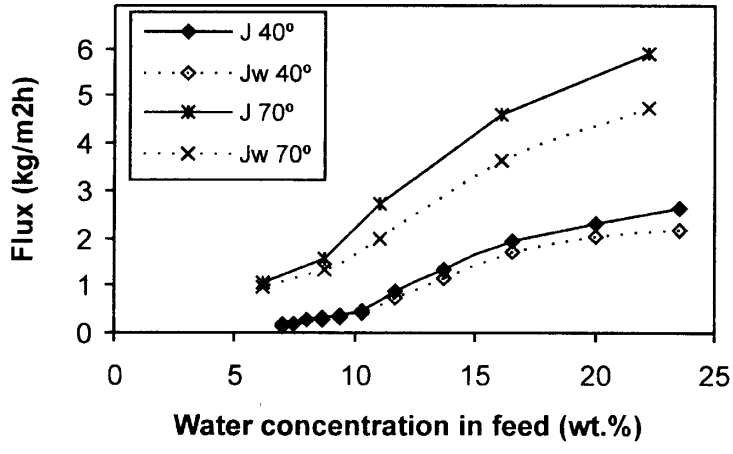

Figure 3. Symplex polyelectrolyte membrane. Total flux and water flux as a function of water concentration in the feed retentate. Influence of feed temperature.

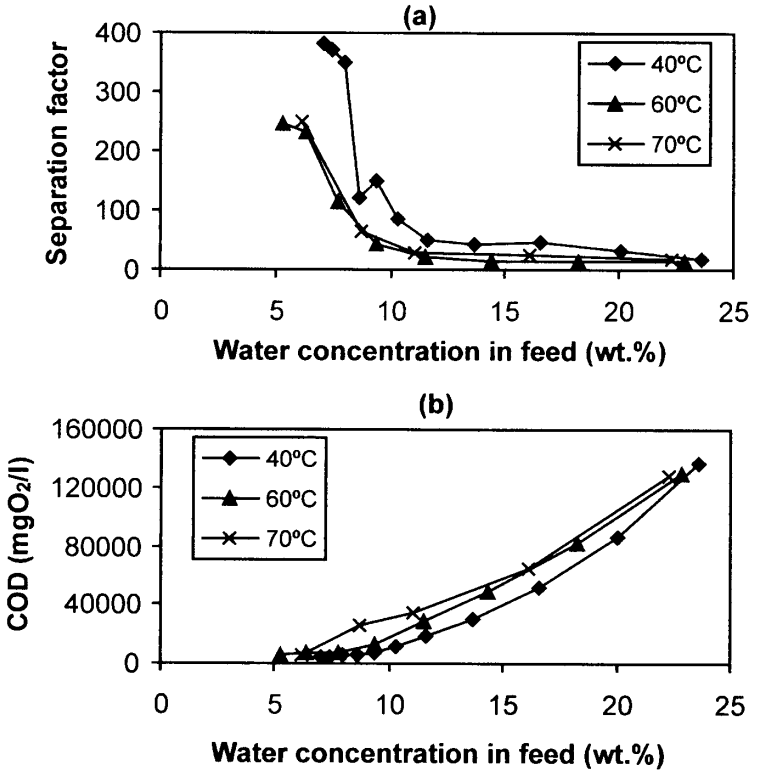

Figure 4. Symplex polyelectrolyte membrane. Quality of the permeate. (a) Separation factor; and (b) chemical oxygen demand of the permeate, as a function of the water concentration of the feed.

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

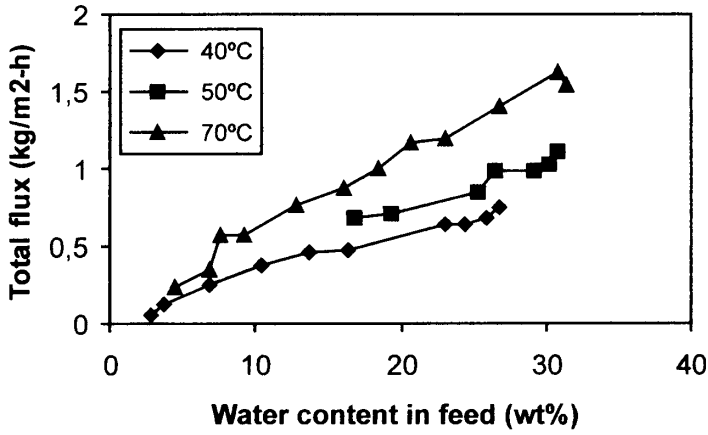

Figure 5. Silica SMS ceramic membrane. Total flux as a function of water concentration in the feed retentate. Influence of feed temperature.

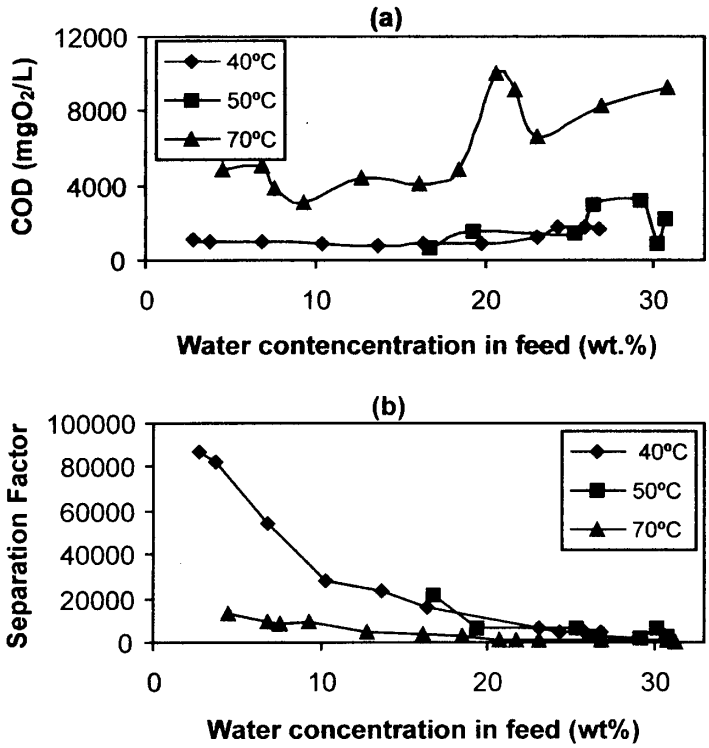

Figure 6. Silica SMS ceramic membrane. Quality of the permeate. (a) Separation factor; and (b) chemical oxygen demand of the permeate, as a function of the water concentration of the feed.

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

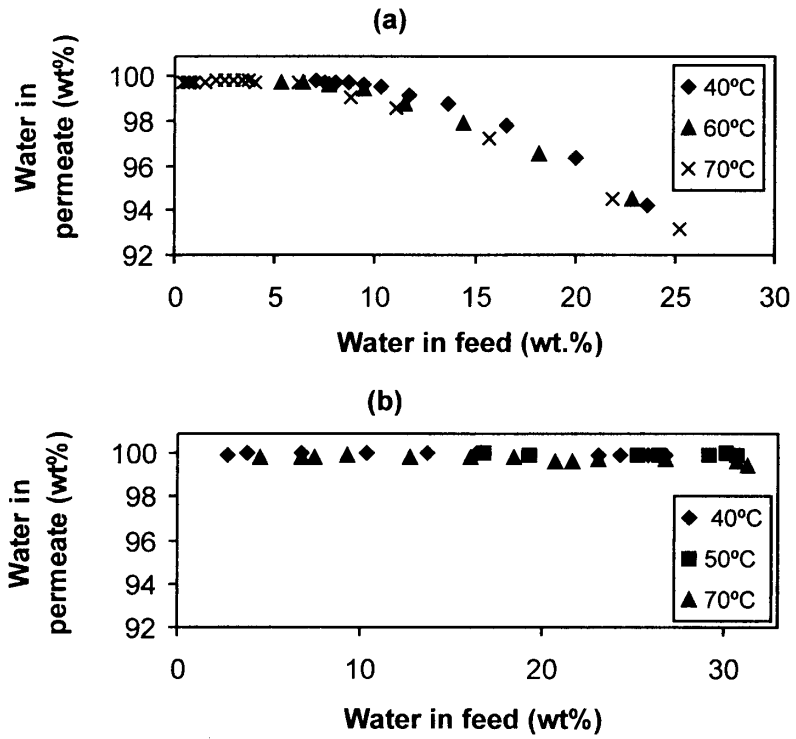

Figure 7. Water percentage in the permeate as a function of the water concentration in the feed. (a) Symplex polyelectrolyte membrane; and (b) silica SMS membrane.

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

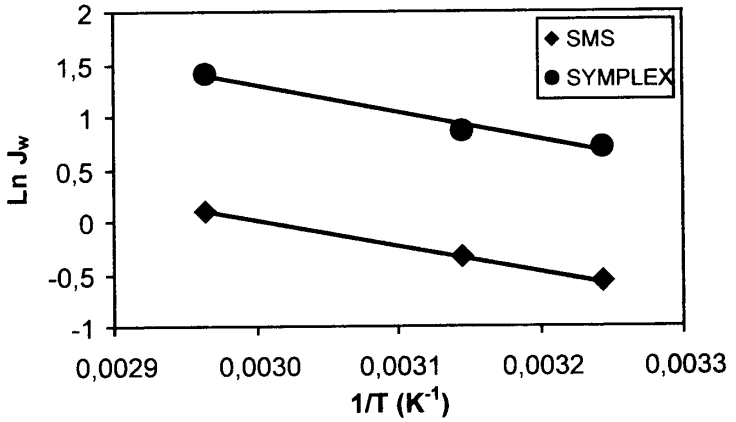

Figure 8. Effect of operation temperature on water permeation flux. Feed concentration, 20 wt% water.

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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Pervaporative dehydration of industrial solvents using a zeolite NaA commercial membrane☆

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Abstract

This work reports an experimental study on the pervaporative dehydration of two industrial solvents using a commercial zeolite NaA-type ceramic membrane (SMART Chemical Company Ltd., UK). The mixtures studied are tetrahydrofuran (THF) with an initial water content of 7.9 wt.% and acetone with an initial water content of 3.25 wt.%. Batch experiments were carried out until final water content was lower than 0.1 wt.% in THF mixtures and lower than 0.2 wt.% in acetone mixtures. The influence of feed composition and feed temperature on the pervaporation fluxes and selectivities has been investigated. In the THF dehydration for a water concentration in the retentate of 7 wt.%, the water flux increased from 0.43 to 0.98 kg m^{-2} h^{-1} for a temperature increase from 45 to 55 °C. In the acetone dehydration for a water concentration in the retentate of 3 wt.%, the water fluxes increased from 0.13 to 0.314 kg m^{-2} h^{-1} for a temperature increase from 40 to 48 °C. The separation factor for the THF–water separation was as high as 20 000, although the separation factor was found to be dependent on the feed water concentration. The water flux through the ceramic membrane shows a linear dependency with the driving force, which is the partial equilibrium vapor pressure of water in the retentate minus the partial pressure in the permeate, $p_w^* - p_w^p$. From the regression of the experimental data, preliminary values of water permeability were obtained that varied in the range 5.5×10^{-3} kg/(m^2/(h/mbar)) $\leq K_w \leq 7.4 \times 10^{-3}$ kg/(m^2/(h/mbar)) in the experimental range of operation temperatures.

Keywords: Zeolite membranes; Pervaporation; Tetrahydrofuran; Acetone; Dehydration

1. Introduction

Pervaporation is a membrane separation technology where a liquid feed mixture contacts the feed side of a selective membrane and the other side is typically under vacuum to provide vapor permeate [1]. Pervaporation has been widely studied as means of dehydrating solvents, whose recovery in the industry is frequently sought but difficult when an azeotrope is involved. In the case

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of tetrahydrofuran (THF), the mixture 95 wt.% THF/water forms an azeotrope at atmospheric pressure. In the case of acetone–water, the vapor and liquid equilibrium compositions are very close for water contents of 3.5 wt.%.

A number of studies have been published reporting the successful dehydration of industrial solvents using polymeric membranes [2–4]. However, the application of polymeric pervaporation membranes to dehydration is limited by the insufficiency of their thermal, mechanical and chemical stability [5]. This fact has led to the latest developments in inorganic membranes syntheses and applications, reviewed by Cot et al. [6] recently. For example, Kondo et al. [5] prepared zeolite NaA membranes on the surfaces of porous tubular supports of mullite, alumina and/or cristobalite using the hydrothermal synthesis and examined their dehydration performance. For a 5 wt.% water/95 wt.% ethanol mixture, a flux of 2.35 kg m^{-2} h^{-1} and a separation factor greater than 5000 was obtained. Morigami et al. [7] developed this membrane to the first large-scale pervaporation plant in Japan, reporting the production of 530 l h^{-1} of different alcoholic solvents with less than 0.2 wt.% of water from an initial 90 wt.% solvent at 120 °C. Gao et al. [8] prepared and used composite hydrophilic membranes, consisting of potassium A (KA), sodium A (NaA), calcium A (CaA) and sodium X (NaX) zeolites and PVA at the polymer matrix to investigate the separation characteristics of different solvent–water mixtures. Among these, acetone showed better results than that of ethanol–water system did. Similarly, Shah et al. [9] studied the pervaporation of different alcohol–water mixtures through zeolite NaA membranes and compared it with other systems like acetone–water, finding a very similar behavior. They give a description of the transport mechanism through the zeolite membrane. The enhancement of the yield of the esterification reaction of lactic acid with ethanol to give ethyl acetate using zeolite A vapor permeation membrane has also been demonstrated [10].

The membrane used in this study was a commercial NaA zeolite type prepared by hydrothermal synthesis and applied to dehydration of two solvent mixtures with an industrial origin: THF/water and acetone/water. The influence of feed composition and feed temperature on the fluxes and selectivities are presented and discussed.

2. Experimental

2.1. Membranes and materials

The hydrophilic membranes used for this research are commercial, composite zeolite NaA membranes, manufactured by SMART Chemical Company Ltd., UK. The membranes are basically made of an active NaA layer, deposited on the inner face of a ceramic porous support with cylindrical geometry. The membrane module possesses the following characteristics: effective area: 0.05 m^2; selective layer membrane thickness: 5–10 μm; kinetic diameter: 0.42 nm; pH range recommended: 6–8; maximum temperature: 150 °C; maximum pressure: 10 bar; and sensitivity to divalent metallic ions $>1\%$. The use of this commercial membrane for the dehydration of water/*t*-butanol mixtures has been recently published by Gallego-Lizón et al. [11].

Two industrial solvent mixtures were tested. Solvent 1: THF/water with an initial 7.9 wt.% water content and solvent 2: acetone/water with an initial 3.25 wt.% water content. The THF boiling point is 65 °C and at atmospheric pressure it forms an azeotrope with water at 63.4 °C, where the organic content is 95.5 wt.%. The acetone boiling point is 56 °C.

2.2. Apparatus and procedures

The pervaporation experiments were carried out in a laboratory-scale unit supplied by Sulzer Chemtech (Germany), previously used by the authors in other pervaporation studies [12,13], where the zeolite membrane tubular module was mounted. A schematic layout of the experimental set-up is shown in Fig. 1. The zeolite cell has the form of a double pipe heat exchanger, where the zeolite membrane is the inner pipe and the outer shell is made up of stainless steel. The feed was placed in the feed tank (volume of 2 l), heated and recirculated using a single-stage rotary vane pump.

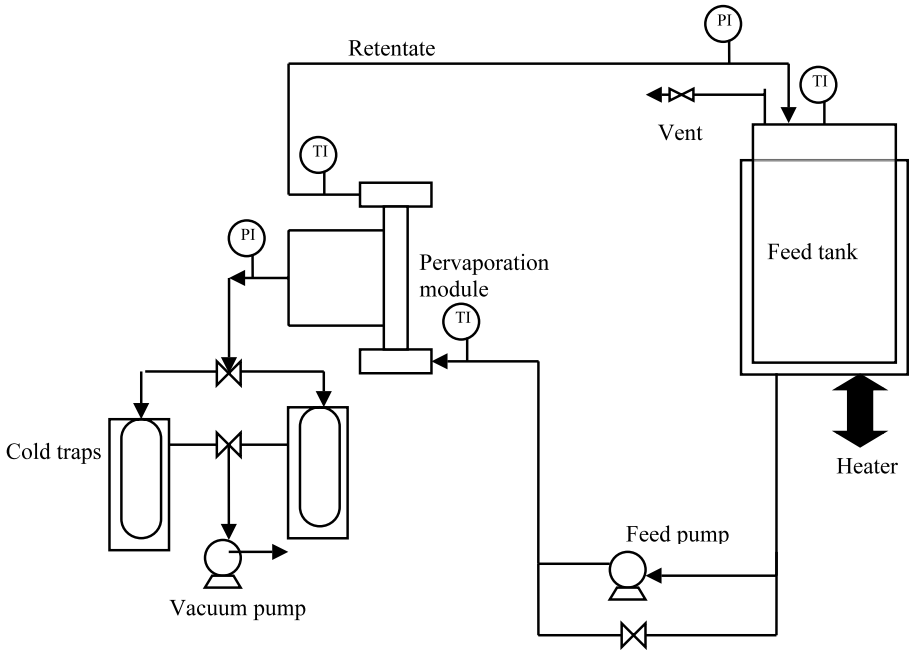

Fig. 1. A schematic layout of the laboratory pervaporation unit.

The temperature was selected to range between 40 and 55 °C, and vacuum on the permeate side was maintained below 10 mbar. The vacuum was monitored using a digital rough vacuum gauge. The temperature in the cell was measured by two thermocouples placed at the entrance and exit of the chamber.

Retentate and permeate samples were collected over time. Two cold traps were set in parallel allowing the collection of the permeate without rupture of vacuum. Water concentration in the retentate was monitored by titration using a Mettler Karl Fischer titrator. The permeate weight and volume were measured.

3. Results and discussion

Initial experiments were performed with the aim of investigating the viability of the pervaporation process to achieve a high degree of dryness. Fig. 2 shows the evolution of the water concentration in the feed tank with time for the two solvents under investigation. The water content in THF was reduced down to 0.1 wt.%. The final water content in the acetone solvent was 0.2 wt.%. The water evolution in duplicate experiments was very simi-

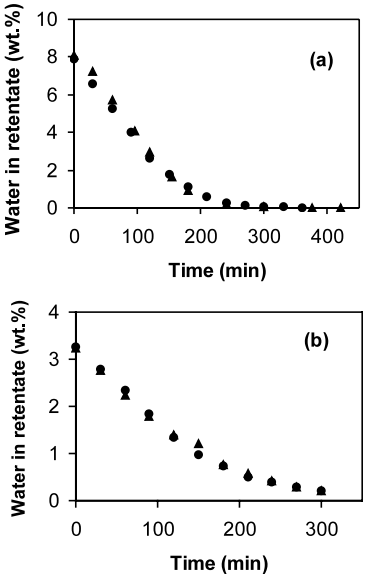

Fig. 2. Water concentration in the retentate vs. time for the dehydration of: (a) THF/water, feed temperature 55 °C and (b) acetone/water, feed temperature 48 °C.

lar, as observed in Fig. 2. These values of dryness attain the industrial standards and make possible the recycling of the solvent to the production processes.

The study of the effect of feed temperature on water pervaporation flux was investigated in the range of interest: THF: 45–55 °C; and acetone: 40–48 °C. The water flux and separation factors as a function of the water concentration in the retentate obtained in the dehydration of THF are shown in Fig. 3. As expected, the water flux increased with increasing feed temperatures. For a fixed water concentration in the retentate of 7 wt.%, water fluxes increased by 2.3 times for a temperature increase from 45 to 55 °C. Specially relevant are the high values of the separation factor obtained in the dehydration of THF. The water separation factor, α, is defined as follows:

$$\alpha = \frac{y_w / x_w^r}{y_{sol} / x_{sol}^r}, \quad (1)$$

where y_w, x_w^r, y_{sol} and x_{sol}^r are the fractions of the water and solvent in the permeate and retentate, respectively. At 45 °C the water separation factor was found to remain approximately constant at an average value of 1500 for water concentration in the retentate in the range 7.9–4 wt.%, followed by a sharp increase to a maximum value of 20 000 for a water concentration of 0.8 wt.%. A similar behavior was obtained at 55 °C, although an important decrease in the value of α was observed at water concentrations in the retentate below 0.6 wt.%.

Fig. 4 shows flux results obtained in the dehydration of acetone as a function of the water concentration in the retentate at two operation temperatures, 40 and 48 °C. For a fixed water concentration in the retentate of 3 wt.%, fluxes increased from 0.13 to 0.314 kg m^{-2} h^{-1} for a temperature increase from 40 to 48 °C. The values of the separation factor for acetone–water mixtures remain below 100 when working at 40 °C. Larger α values were obtained at 48 °C, ranging between 50 and 1000 as a function of the water concentration in the feed in the range 3–0.25 wt.%.

Flux and selectivity data corresponding to pervaporation of THF–water and acetone–water mixtures obtained from the literature using different inorganic membranes are shown in Table 1. Flux and selectivity values are significantly influenced by temperature and feed composition. In the THF–water separation, the membrane prepared by Li et al. [15] shows higher fluxes at similar feed

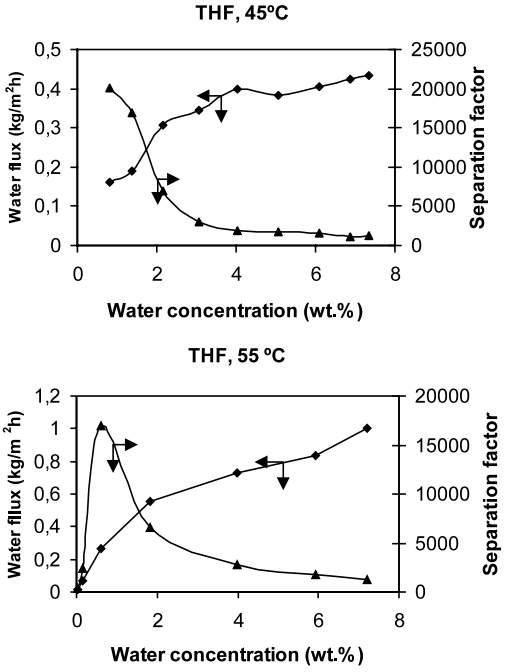

Fig. 3. Water flux and separation factor vs. water concentration in the retentate for the dehydration of THF.

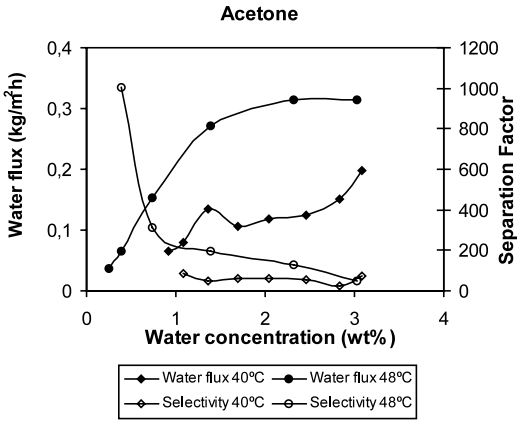

Fig. 4. Water flux and separation factor vs. water concentration in the retentate for the dehydration of acetone.

Table 1
Comparison of pervaporation results using inorganic membranes for THF–water and acetone–water mixtures in the literature

Membrane	Solvent	T (°C)	Water (wt.%)	Flux (kg m^{-2} h^{-1})	α (separation factor)	Reference
Zeolite NaA	Acetone	50	5	0.83	6800	[14]
Zeolite NaA	Acetone	50	10	0.91	5600	[7]
Zeolite-type Y	THF	30	6.7	0.5	45	[15]
		60	5	2.1	360	
		60	6.7	2.4	200	
Silica	Acetone	50	10	0.75	33	[16]
Zeolite NaA	Acetone	40	3	0.13	50	This study
		48	3	0.314	50	
Zeolite NaA	THF	45	7	0.43	1240	This study
		55	7	0.98	1240	

concentration and temperature, although the separation factors obtained in this study are higher.

The quality of the permeate was determined by analyzing its organic content. Fig. 5 shows the chemical oxygen demand (COD) of the permeate obtained in the acetone dehydration. The high COD values indicate high organic content in the collected permeate. Thus acetone is dehydrated down to the required level of dryness, but the aqueous permeate contains high quantities of the organic solvent. The results are completely different in the THF dehydration. The aqueous permeate contained less than 1 wt.% of THF at both 45 and 55 °C. Only when the water concentration in the feed is below 0.15 wt.%, the permeate is enriched in THF. Thus the solvent is dehydrated and at the same time, the permeate is mainly water with a low THF content.

The partial equilibrium vapor pressure of water in the retentate minus the partial pressure in the permeate, $p_w^* - p_w^p$, is a measure of the driving force for the water transport [17]:

$$J_w = K_w(p_w^* - p_w^p), \quad (2)$$

where K_w is the permeability of water through the zeolite membrane and $p_w^* = \gamma_w x_w P_w^0$. The activity coefficient of water in the acetone–water feed mixture, γ_w, was calculated using the Wilson equation. In Fig. 6, the water flux is plotted as a function of the driving force for water for all the experimental data including the variation of the water concentration in retentate and temperature. It can be seen that the water flux through the membrane varies linearly with the partial pressure

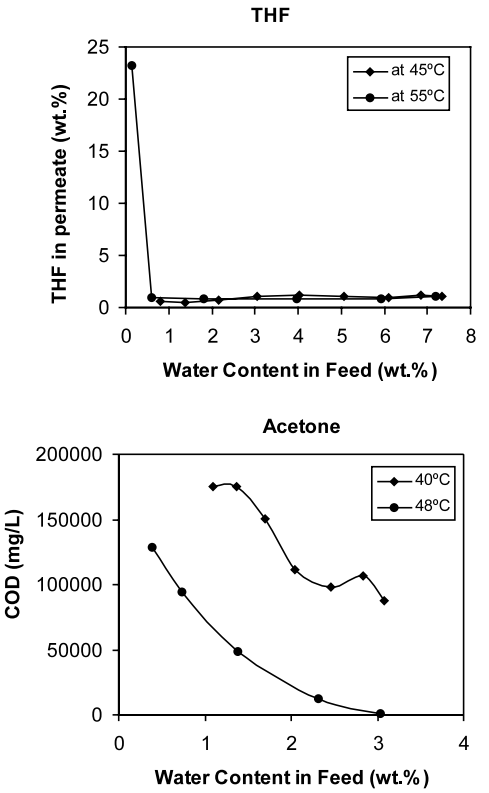

Fig. 5. Quality of the permeate as a function of the water feed concentration: (a) THF content in the permeate and (b) chemical oxygen demand of the permeate, acetone–water separation.

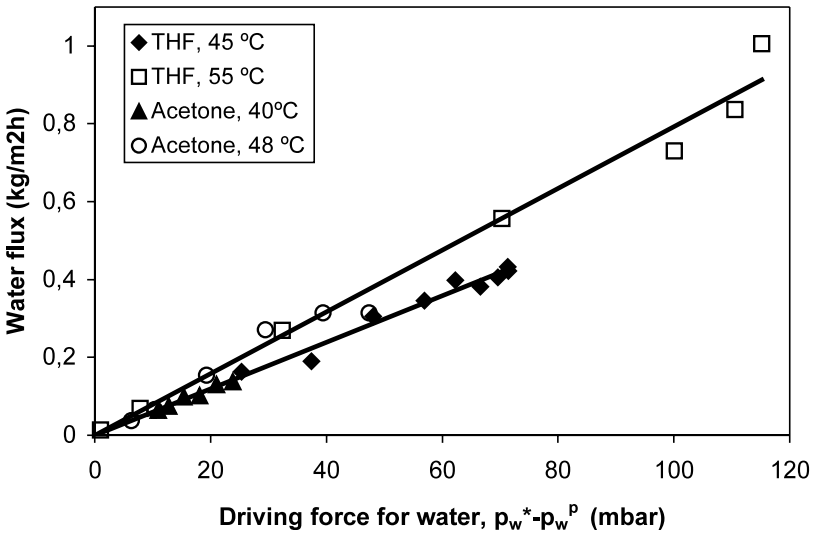

Fig. 6. Water flux for THF and acetone dehydration vs. the driving force for water flux $p_w^* - p_w^p$ with variations of water concentration and temperature.

driving force. Individual regression lines are given in Table 2. It appears that the water flux is not only dependent on the driving force but also on changes of experimental process conditions, temperature and type of organic solvent. For the water/THF results, the value of K_w increases from 5.5×10^{-3} to 7.2×10^{-3} kg/(m^2/(h/mbar)) for a temperature increase from 45 to 55 °C. A similar behavior is observed for the water/acetone mixture.

4. Conclusions

This work reports an experimental study on the pervaporative dehydration of THF/water and acetone/water mixtures using a commercial zeolite NaA-type membrane. The water content in THF was reduced from an initial value of 7.9 to a final value of 0.1 wt.%. The water content in acetone was reduced from an initial value of 3.25 wt.% to a final value of 0.2 wt.%. The influence of feed composition and feed temperature on the water fluxes and pervaporation selectivities was investigated. Water fluxes decreased with water concentration in the feed. The effect of temperature on the water flux was investigated in the range 40–55 °C. Increased temperatures resulted in larger values of water fluxes for both solvent mixtures. High selectivities were obtained in the THF dehydration. The water flux through the ceramic membrane shows a linear dependency with the driving force, i.e. the partial equilibrium vapor pressure of water in the retentate minus the partial pressure in the permeate, $p_w^* - p_w^p$. From regression of the experimental data, preliminary values of water permeability were obtained that varied in the range 5.5×10^{-3} kg/(m^2/(h/mbar)) $\leq K_w \leq$ 7.4×10^{-3} (m^2/(h/mbar)). Further work will deal with the modeling of the system and obtention of the representative parameters for flux prediction.

Table 2
Values of the permeability of water K_w through the zeolite NaA pervaporation membrane

Solvent	T (°C)	K_w (kg/(m^2/(h/mbar)))
Acetone	40	5.7×10^{-3}
Acetone	48	7.4×10^{-3}
THF	45	5.5×10^{-3}
THF	55	7.2×10^{-3}

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Funcionamiento de una membrana de zeolita 4-A comercial en la deshidratación de disolventes industriales mediante pervaporación

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En este trabajo se estudia el comportamiento de una membrana comercial de pervaporación con una capa activa de zeolita NaA (Smart Chem., Reino Unido) aplicada a la separación de dos mezclas de origen industrial: tetrahidrofurano/agua con un contenido inicial de agua de 7,9% en peso y acetona/agua con un contenido inicial de agua de 3,25% en peso. Se ha caracterizado el flujo de agua y la selectividad de la separación, estudiándose la influencia de la composición y de la temperatura, en el rango 40 ºC - 65 ºC sobre ambos factores. Asimismo, se ha estudiado la estabilidad de la membrana en ciclos consecutivos de operación.

***Palabras clave**: membrana zeolita NaA, pervaporación, tetrahidrofurano, acetona, deshidratación, estabilidad.*

Behavior of a zeolite 4-A commercial membrane in the dehydration of industrial solvents by pervaporation

The performance of a commercial zeolite NaA pervaporation membrane supplied by Smart Chem., U.K.) was studied with respect to the dehydration of industrial mixtures of tetrahydrofurane/water (C_{H2O}≤7.9 wt.%) and acetone/water (C_{H2O}≤3.25 wt.%). The influence of water concentration and temperature in the range 40 ºC - 65 ºC on fluxes and selectivities was described. The stability of the membrane in consecutive operation cycles is also reported.

***Keywords:** Zeolite membrane, pervaporation, tetrahydrofuran, acetone, dehydration, stability*

1. INTRODUCCIÓN

La aplicación de materiales cerámicos en tecnologías de separación está siendo impulsada por el desarrollo de nuevas membranas y nuevos procesos. En el caso de la pervaporación los avances más recientes se encuentran en el desarrollo de dos tipos de membranas cerámicas: i) membranas de zeolitas (1,2) y ii) membranas de sílice amorfa (3,4), con un tamaño de poro en la capa selectiva en el rango de 0,4 nm a 0,5 nm. Este tipo de membranas se adapta al problema de separación planteado como la deshidratación de disolventes orgánicos de uso frecuente en la síntesis de productos químicos y farmacéuticos, especialmente en los disolventes que forman azeótropos con agua, una característica que dificulta e incluso hace económicamente inviable la separación de las mezclas mediante las habituales operaciones de destilación. Otras ventajas de las membranas cerámicas respecto a las poliméricas son su elevada estabilidad térmica y mecánica. La aparición en fechas recientes de membranas cerámicas comerciales permite prever el desarrollo de esta tecnología.

En el proceso de pervaporación aplicado a la separación de una mezcla líquida totalmente miscible de agua en un disolvente orgánico, el agua se adsorbe preferentemente en la membrana hidrófila y difunde a través de los poros, para evaporarse en la otra cara de la membrana, que se mantiene en condiciones de baja presión.

En este trabajo se presentan los resultados obtenidos en el estudio del comportamiento de una membrana comercial con una capa activa de zeolita NaA aplicada a la separación de dos mezclas de origen industrial: tetrahidrofurano/agua y acetona/agua. Los problemas asociados a la separación de estas mezclas mediante la operación habitual de destilación son que la mezcla THF/agua con un 95% en peso de THF forma un azeótropo a presión atmosférica. En el caso de la mezcla acetona/agua las composiciones de las fases líquida y vapor en equilibrio son muy similares para contenidos de agua inferiores a 3,5% en peso (5).

El funcionamiento de la membrana se ha caracterizado en términos de flujo de los componentes individuales de la mezcla y de la selectividad de la separación, estudiándose la influencia de la composición y de la temperatura sobre ambos factores. Asimismo, se ha estudiado la estabilidad de la membrana en ciclos consecutivos de operación.

2. METODOLOGÍA EXPERIMENTAL

2.1 Membranas y materiales

Las membranas hidrófilas utilizadas para esta investigación son membranas comerciales compuestas con una capa activa de zeolita NaA, fabricadas por Smart Chemical Co. Ltd. (Reino Unido). Las membranas básicamente están hechas de una capa activa de zeolita NaA, depositada sobre la cara interna de un soporte cerámico poroso con geometría cilíndrica. El módulo de membranas posee las siguientes características: (1) área efectiva: 0,05 m^2, (2) espesor de la capa de membrana selectiva: 5-10 μm, (3) diámetro de poros: 0,42 nm, (4) rango de pH recomendado: 6-8, (5) máxima temperatura de operación: 150ºC, (6) presión máxima: 10 bar, (7) sensibilidad de iones metálicos divalentes > 1%. El uso de esta membrana comercial para la deshidratación de mezclas *t*-butanol/agua ha sido publicado recientemente por Gallego-Lizón et al. (6).

Se trabajó en la separación de dos mezclas industriales: Mezcla 1: tetrahidrofurano/agua con un contenido inicial de agua de 7,9% en peso; Mezcla 2: acetona/agua con un contenido inicial de agua de 3,25% en peso.

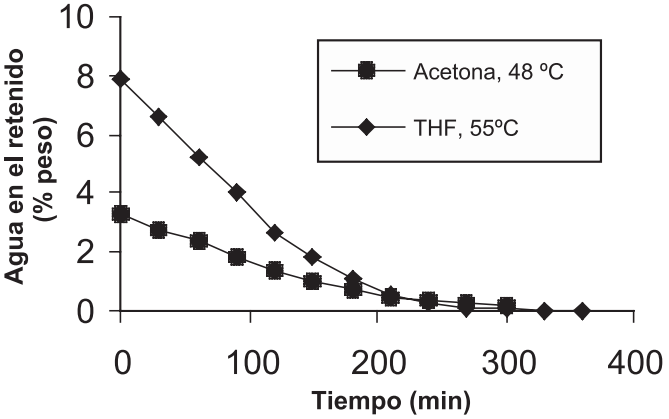

Figura 1. Variación de la concentración de agua en el tanque de alimentación frente a tiempo de experimentación

2.2 Equipos y procedimientos

Los experimentos de pervaporación se llevaron a cabo en una instalación a escala de laboratorio, utilizada por los autores en otros estudios (7-9), donde fue montado el módulo tubular de membranas zeolíticas. La mezcla líquida de alimentación (vol. = 2 l) se colocó en un tanque termostatizado a la temperatura de proceso y se hizo recircular a través de la instalación por medio de una bomba centrífuga. El vacío en la zona de permeado se mantuvo por debajo de 20 mbar. Se extrajeron muestras de retenido y de permeado a intervalos regulares de tiempo. Los vapores de permeado fueron condensados por medio de dos trampas frías colocadas en paralelo y enfriadas con nitrógeno líquido. La concentración de agua en el retenido fue determinada por titulación utilizando el método de Karl Fischer. La concentración de THF en el permeado se determinó mediante medida del índice de refracción.

3. RESULTADOS Y DISCUSIÓN

La figura 1 muestra la evolución con el tiempo de la concentración de agua en THF, ensayo realizado a 55 ºC y en acetona, ensayo realizado a 48 ºC. La concentración de agua en THF se rebaja desde el 7,9 % inicial hasta valores por debajo del 0,1 % en peso. En el caso de la acetona, desde el 3,25 % inicial al 0,2 % final. Se concluye que la tecnología permite deshidratar el THF y la acetona hasta un grado de sequedad suficiente para la recirculación del disolvente al proceso industrial.

La figura 2 muestra la dependencia del flujo con la concentración de agua en el retenido, en función de la temperatura de operación. Se observa que un incremento de la temperatura hace que aumente el flujo de agua a través de la membrana. Para un 7% de agua en THF el flujo aumenta desde 0,6 kg/m^2-h obtenido a 45 ºC a 1,5 kg/m^2-h obtenido a 65 ºC. Estos valores de flujo de agua son superiores a los reportados en la bibliografía (10) con membranas zeolitas tipo A, de 0,49 kg/m^2-h para mezclas 95%THF/5%agua a 60 ºC. Para un 3% de agua en acetona el flujo de agua tiene un valor de 0.13 kg/m^{2}h a 40ºC y de 0.314 kg/m^{2}h a 48ºC. Este valor es inferior al reportado en la bibliografía (2), de 0,83 kg/m^2-h, para una mezcla 95%acetona/5%agua a 50 ºC.

Los resultados que se muestran a continuación cuestionan la estabilidad de la membrana en las condiciones de proceso. La figura 3 muestra los resultados obtenidos en 9 ciclos consecutivos de deshidratación de THF realizados a 55 ºC; por razones de claridad, en la figura 3(b) solo se muestran 4 ciclos representativos de las tendencias.

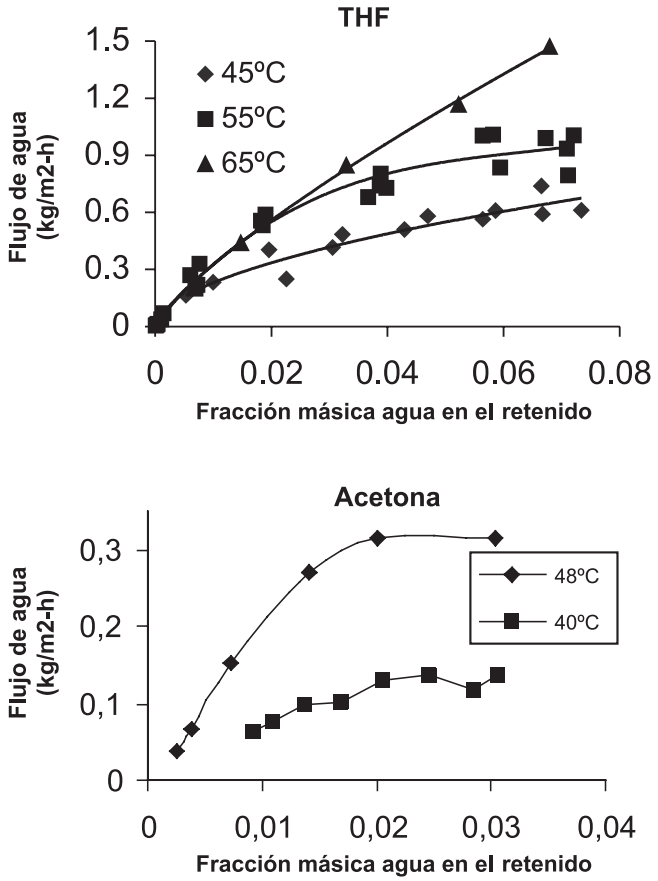

Figura 2. Flujo de agua en función de la fracción másica de agua en el retenido. Influencia de la temperatura. (a) mezcla THF/agua. (b) mezcla acetona/agua

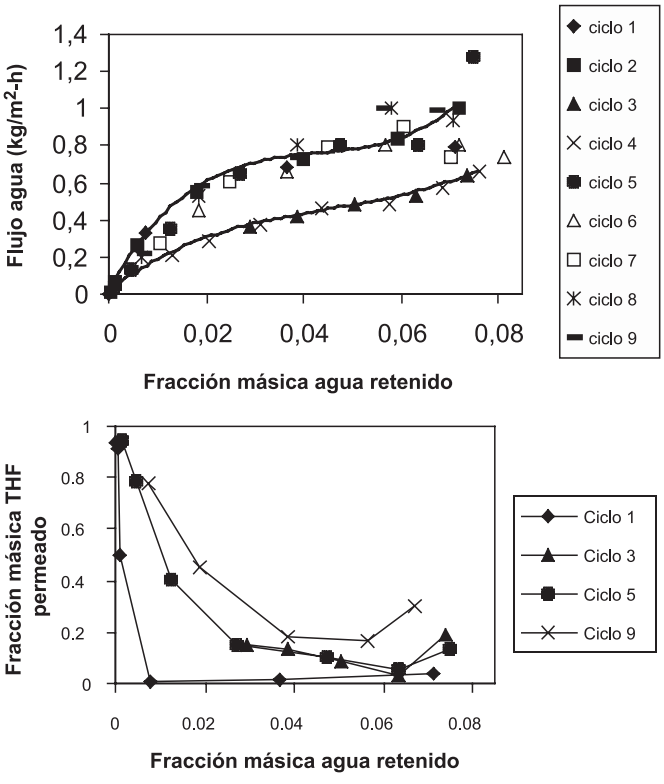

Figura 3. Flujo de agua y selectividad para la mezcla THF/agua, a 55 ºC, en nueve ciclos de operación.

En cada nuevo ciclo se repone la mezcla de alimentación con una concentración inicial de agua de 7,9 % en peso. A partir de los transcursos concentración-tiempo, se obtiene el flujo de agua, representado en la figura 3(a). La selectividad expresada como fracción de THF en el permeado, se representa en la figura 3(b). Los ciclos 1 y 2 ofrecen resultados repetitivos en cuanto a flujo de agua y la selectividad de la separación. En los ciclos 1 y 2 la concentración de THF en el permeado es inferior al 1 % en peso. Únicamente cuando la concentración de agua en el retenido es inferior a 0,05 %, el permeado se enriquece en THF.

Sin embargo en los ciclos 3 y 4 se observa la disminución del flujo de agua y de la selectividad. En esta situación se aplicó un procedimiento de limpieza que consistió en la realización de un ciclo de lavado y permeación con agua. Tras el procedimiento, en el ciclo 5 y consecutivos el flujo de agua volvió a los valores de los ciclos 1 y 2, tal como se observa en la figura 3(a). Sin embargo no ocurre lo mismo con la selectividad de la membrana, ya que se observa un aumento de la concentración de THF en el permeado, superando el 10% en la mayoría de las muestras. Estos resultados parecen indicar que la membrana puede haber modificado su estructura porosa debido al contacto con el agua. Las membranas utilizadas, comercializadas por Smart Chemicals, no vienen acompañadas de un procedimiento de limpieza y mantenimiento. Únicamente se conocen su extrema sensibilidad a pH inferior a 6, parámetro que no fue controlado en las operaciones de limpieza llevadas a cabo. En la literatura se encuentran referencias a ensayos de pervaporación con agua con membranas de tipo zeolita NaA (2,11) que sin embargo no hacen referencia a comportamientos inestables. El comportamiento inestable frente al agua de membranas cerámicas de pervaporación con un alto contenido en sílice ha sido referenciado por Asaeda et al. (12).

En la figura 4 se observa que el flujo de agua depende del gradiente de presión parcial de agua entre las dos caras de la membrana de pervaporación, el cual se suele considerar como la fuerza impulsora del transporte de agua a través de la membrana. En el caso de la mezcla THF/agua los datos obtenidos a 45ºC y 55 ºC pueden adaptarse a una relación lineal, que sin embargo no parece poder aplicarse a los datos obtenidos a 65 ºC. Para la mezcla acetona/agua la dependencia del flujo de agua con el gradiente de presión parciales similar que para el sistema THF/agua. En la bibliografía se recogen ambos tipos de dependencia del flujo con el gradiente de presión parcial, como la proporcionalidad entre ambos observada en la deshidratación de alcoholes con membranas zeolita tipo A y con membranas de sílice amorfa (3,11) o la dependencia de tipo exponencial (11,12).

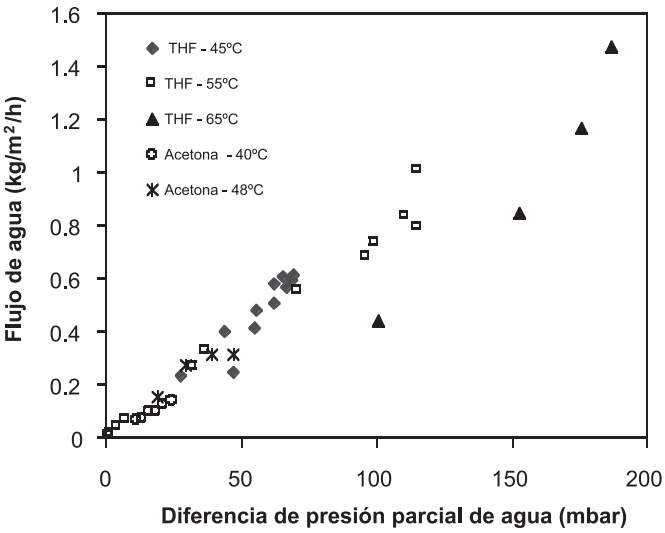

Figura 4. Dependencia del flujo de agua con el gradiente de presión parcial de agua

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Pervaporative dehydration of organic mixtures using a commercial silica membrane Determination of kinetic parameters

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Abstract

In this work, the performance of a pervaporation commercial silica membrane referenced as PVP (supplied by Pervatech BV, The Netherlands), has been studied. The solvent mixtures used in the experiments were: (i) a synthetic water–isopropanol mixture with 15–20 wt.% inital water content and (ii) an industrial mixture containing about 25 wt.% water–75 wt.% acetone, coming from a reaction process devoted to the manufacture of rubber antioxidants. In both systems the flux of water through the membrane was obtained at different water concentrations in the feed, as dehydration proceeded. The effect of temperature was studied in the range 40–90 °C. It was found that for the range of conditions investigated, water fluxes through the PVP membrane were larger than those previously reported through the Pervap SMS commercial membrane (supplied by Sulzer Chemtech). Water flux data were fitted to a semi-empirical correlation that expresses water flux as an exponential function of the water activity in the feed mixture, $\mathrm{Ln}(J_{w,mass}) = (\mathrm{Ln}\, J_{00,w} - E_{act}/RT) + \zeta a_w^f$. The values of the characteristic mass transfer parameters corresponding to the Pervatech PVP membrane, ζ, E_{act} and $\mathrm{Ln}\, J_{00,w}$, were obtained, as required for design purposes.

Keywords: Pervaporation; Silica membrane; Modelling water flux; Isopropanol; Acetone

1. Introduction

Pervaporation is a membrane separation process where the liquid mixture to be separated (feed) is placed in contact with one side of a membrane and the permeated product (permeate) is removed as a low-pressure vapour from the other side [1]. The separation is based on the selective solution and diffusion, i.e., the physical-chemical interactions between the membrane material and the permeating molecules. Therefore, on one hand, pervaporation is commonly considered to complement distillation for the separation of azeotropic and close-boiling mixtures, because of its high separation efficiency, together with potential savings in energy cost [2].

On the other hand, the use of pervaporation as a separation technique in multi-purpose equipment seems very attractive. The broad applicability of the membrane, e.g. in the dehydration of various solvents, is the main criteria to be used. Currently several commercial pervaporation units based on inorganic membranes are used at industrial level able to dehydrate routinely a variety of solvents, as reported by Martin [3], using an amorphous silica membrane and Kita [4] and Morigami et al. [5] using a zeolite NaA membrane.

Extensive research has been done in the field of membranes for the pervaporation process, focused on finding the optimised membrane material having selective interaction with a certain component in the feed mixture to maximise the performance in terms of separation factor, flux and stability [6].

Polymeric membranes have shown some limitations regarding their thermal and chemical stability [7-9], giving place to the interest on development of more stable multipurpose membranes. In particular, porous inorganic membranes (e.g. ceramic membranes) exhibit high permeabilities

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Nomenclature

a_w	water activity (mole fraction)
A	effective membrane area (m^2)
c_w	mass concentration of water (kg/m^3)
C_w	concentration of water in the feed (wt.%)
$C_{w,0}$	initial concentration of water in the feed (wt.%)
D	diffusion coefficient in the membrane (m^2/s)
D_0	intrinsic diffusion coefficient (m^2/s)
D_T	thermodynamic diffusion coefficient (m^2/s)
E_{act}	apparent activation energy (cal/mol)
J	flux through the membrane (kg/m^2h)
J_0	parameter of the model in Eq. (3) (kg/m^2h)
m	mass of permeate (kg)
R	ideal gas constant
t	time
T	operating temperature (K)
V_w	velocity of species water (m/s)
W	mass fraction

Greek letters

δ	selective layer thickness (m)
μ	chemical potential (J/mol)
ρ	mass density (kg/m^3)
τ	exponential parameter of diffusivity in the membrane
ζ	model parameter in Eq. (2)

Superscripts

f	feed solution
m	membrane phase
p	permeate

Subscripts

w	water

relative to dense membranes and high thermal stability relative to organic membranes [10,11]. In general, inorganic membranes allow working at elevated temperatures, which can be of the utmost importance, for example, in order to enhance the yield of an esterification reaction by coupling a pervaporation unit. [12]. Inorganic membranes, with the active pervaporation layer made of amorphous silica and having narrow pore size distribution have become commercially available [13,14].

In this work, the performance of a commercial microporous silica membrane referenced as Pervatech PVP, regarding its ability to dehydrate different solvents is characterised in terms of the pervaporation flux. This has been done for the separation of a prepared water/isopropyl alcohol mixture and an industrial water/acetone mixture. In both systems the effect of varying the concentration of water in the feed and the operation temperature has been studied. Also, a methodology for the determination of the mass transfer parameters that predict the water flux across the Pervatech PVP silica membrane is presented, that is needed for design purposes.

2. Theory

The performance of a pervaporation membrane is usually characterized in terms of the flux and selectivity. These features are commonly given as a function of temperature, downstream pressure and concentration of the permeating component in the feed mixture. In this work, it will be shown the relationship of the flux with the driving force for transport, i.e., the chemical potential gradient, which can be expressed in terms of the activity of the permeating compound in the liquid feed mixture and of the operation temperature.

Thus, in the case of dehydration of solvents, the flux of water through the pervaporation membrane can be written as

$$J_{w,mass} = v_w c_w^m = -D_{T,w}(c_w^m) c_w^m \left(\frac{d \operatorname{Ln} a_w^m}{dz} \right) \quad (1)$$

according to the description of flux in terms of friction [15], being the chemical potential gradient the driving force, and considering negligible variation of temperature and pressure within the pervaporation separation process. This expression has been developed by the authors in a previous work [16] in order to demonstrate its applicability to predict the flux through both polymeric and inorganic hydrophilic pervaporation membranes, for a wide range of solvent mixtures.

Assuming zero downstream pressure, equilibrium at the membrane surface, an exponential concentration dependence of diffusion coefficient [15,17] and, above all, a linear sorption isotherm of the penetrant, i.e. water in the cases analysed within this work, into the membrane surface, integration of Eq. (1) becomes,

$$\operatorname{Ln}(J_{w,mass}) = \operatorname{Ln}(J_{0,w}(T)) + \zeta a_w^f \quad (2)$$

with

$$J_{0,w}(T) = \frac{\rho^m D_{w,0}}{\delta \tau} \quad (3)$$

where $J_{0,w}(T)$ follows the Arrhenius law as

$$\operatorname{Ln} J_{0,w}(T) = \operatorname{Ln} J_{00,w} - \frac{E_{act}}{RT} \quad (4)$$

In Eqs. (2)–(4) the mass transfer parameters that must be determined empirically are ζ, $J_{00,w}$ and E_{act}. The first one, ζ, is related to the adsorption of the permeating species onto the membrane since it contains the influence of the adsorption equilibrium parameter. Secondly, $J_{0,w}$ depends proportionally on the density and the intrinsic diffusion coefficient of the permeating species in the feed solution, being inversely

proportional to the membrane thickness (δ) and the coefficient τ, as expressed in Eq. (3). It is expected that $J_{0,w}$ follows an Arrhenius-type dependence on the operation temperature, Eq. (4). Finally, E_{act} is the apparent activation energy for mass transport and it contains the major temperature dependence of the pervaporation flux, while the ordinate in the origin, Ln $J_{00,w}$, gathers the effect of system properties like membrane thickness.

3. Experimental

The solvent mixtures used in the experiments were: (i) a water–isopropanol mixture with 15–25 wt.% initial water content, prepared in the laboratory in order to characterise the membrane; and (ii) an industrial mixture containing about 25 wt.% water, 75 wt.% acetone, and traces of reaction products, coming from a process in a chemical industry devoted to the manufacture of rubber antioxidants.

A tubular membrane with a pervaporation layer made of amorphous silica coated on the inside of an γ-alumina support tube, referenced as Pervatech PVP, commercialised by Pervatech BV (The Netherlands), was used in the experiments. The ceramic tube had an inside diameter of 7 mm, an outside diameter of 10 mm. The effective membrane length was 235 mm, as the membrane tube was enamelled on both ends. The effective membrane area was 0.0051 m^2. The mean pore size and the selective layer thickness were 0.3–0.4 and 10–20 nm, respectively (data reported by supplier).

Experiments using another commercial silica membrane, referenced as Pervap SMS, have been included for comparison. This membrane was purchased from Sulzer Chemtech GmbH (Germany). It was formed by a microporous amorphous silica membrane layer (estimated pore size 0.42 nm) deposited on an α-alumina support tube. The selective PV layer has a nominative thickness of 200 nm.

The laboratory set-up (Fig. 1) where experiments were run consisted of a 2-l tank where the feed mixture was introduced and circulated by a centrifugal pump through the membrane module and back to the tank. Feed flow was kept at a relatively high rate of about 1.5 l/min (Reynolds number between 3500 and 8000) to minimize concentration polarization in the membrane module and to maximize mixing of the solution in the tank. The mixture in the tank was thermostated by a heating fluid, which was flowed from a thermostatic bath. The temperature was monitored at the entrance and exit of the pervaporation module. The flow rate was measured between the centrifugal pump and the entrance of the module. Vacuum pressure at the permeate side of the membrane was held below 8 mbar during all experiments, thus permitting to assume that the partial pressures of the components in the permeate were negligible if compared to the partial pressures in equilibrium with the liquid feed. The condensed permeate was collected at the exit of the diaphragm vacuum pump. More details on the experimental set-up can be found in previous works [18,19].

Retentate and permeate samples were collected simultaneously. Water content in the retentate was measured using a Karl–Fischer titrator (Mettler Toledo DL31). Isopropanol content in permeate was measured by means of the refraction index. Acetone content in permeate was calculated from the Chemical Oxygen Demand measurements of the collected samples.

4. Results and discussion

The dehydration of the mixture formed by water and isopropanol is shown in Fig. 2(a). The concentration of water in the feed decreased over the experimental time, as the experiments were carried out in batch mode. Data are given in dimensionless form, relative to the initial concentration of water in the feed, that had a value of approximately 25 wt.%. Experiments were performed at three values of the feed temperature: 50, 70 and 90 °C. It is observed that increasing the temperature of the feed resulted in an enhance of the water separation rate.

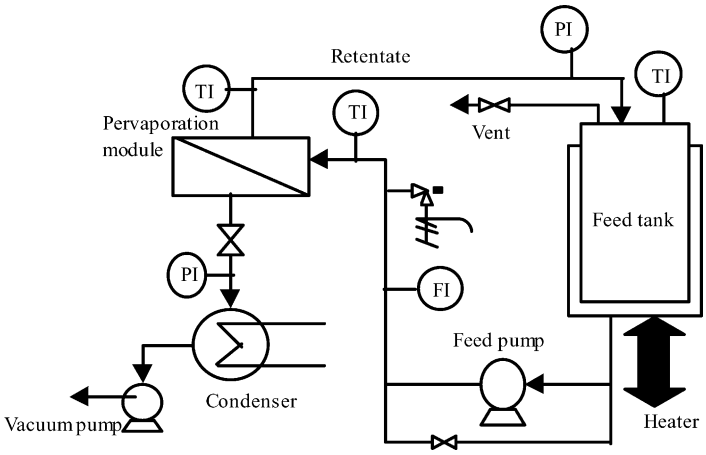

Fig. 1. Schematic layout of the pervaporation unit.

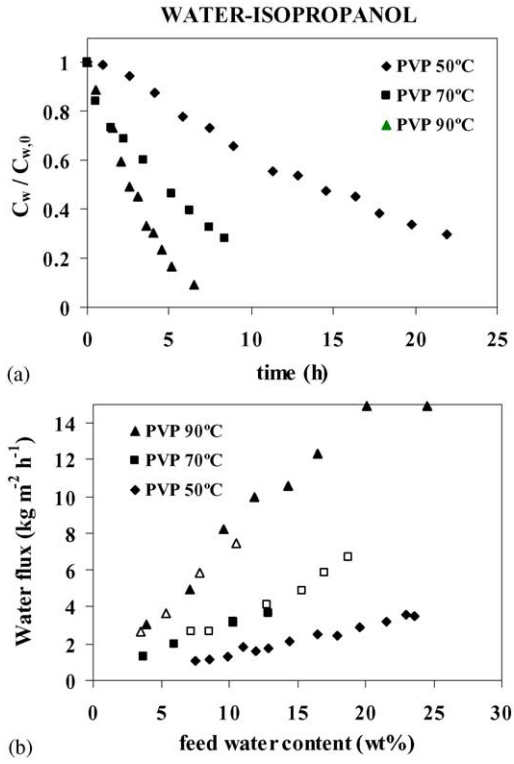

Fig. 2. Dehydration of the water–isopropanol mixture through the Pervatech PVP silica membrane, (a) reduced weight fraction water in the feed vs. time and (b) water flux vs. water content in the feed, (▲) PVP 90 °C; (■) PVP 70 °C; (♦) PVP 50 °C. The void symbols represent the duplicate experiments.

The water flux through the membrane was calculated by the expression

$$J_w = W_w^p J = W_w^p \frac{m}{\Delta t A} \quad (5)$$

where m is the permeate weight that goes through the effective membrane area, A, and is collected over the Δt period of sample time; W_w^p is the water content in the permeate, mass fraction.

Fig. 2(b) shows the evolution of the water flux corresponding to the water/isopropanol dehydration experiments, against the water content in the feed calculated as the averaged concentration between samples. Duplicates for experiments run at 70 and 90 °C are presented in Fig. 2; it was confirmed that the behaviour of the membrane in these conditions was reproducible. Therefore, from now on, all calculations performed in this work used all data obtained in all reproducible runs at the same working conditions.

For a water concentration in the retentate of 10 wt.%, the water flux through the membrane reached the values of 1.3, 3.2 and 8.2 kg/m^2 h at the working temperatures of 50, 70 and 90 °C, respectively. These values are also included in Table 1, which gathers a summary of data collected from the literature on pervaporation silica membranes used to dehydrate isopropanol. The data obtained in this work are slightly higher to the data referred by other authors, using proprietary silica membranes. However, direct comparison should be avoided since experimental flux data could be influenced by the hydrodynamic conditions determined by the different membrane module configurations used in each case.

In order to validate the applicability of Eq. (2) Fig. 3(a) was plotted. This figure shows the water flux through the membrane as a function of the water activity in the feed liquid mixture. Water activities were calculated according to a group contribution method (UNIFAC). An exponential relationship is observed, so the application of Eq. (2) is plausible for the experiments performed using the PVP membrane.

A plot of Ln water flux versus water activity in the liquid mixture is shown in Fig. 3(b) for the three operation temperatures 50, 70 and 90 °C. The linear relationship between the Ln water flux and the water activity in the feed mixture is thus confirmed. Seen that the lines obtained are almost parallel, the value of the slope ζ clearly appears as temperature-independent, while the parameter $J_{w,0}$, obtained from the ordinate in figure, is temperature dependant. Fig. 4 validates the Arrhenius type temperature dependence of parameter $J_{w,0}(T)$, according to Eq. (4), and allowed us to calculate the activation energy for the pervaporation flux of water from a water/isopropanol mixture through this silica Pervatech PVP membrane, as well as the ordinate in the origin Ln J_{00}. Therefore, the corresponding regression parameters

Table 1
Review of pervaporation water flux of various silica membranes in the systems water–isopropanol and water–acetone

Membrane	Solvent	Water content (wt.%)	T (°C)	Water flux (kg m^{-2} h^{-1})	Reference
SiO_2 over alumina	Acetone	10	50	0.75	[22]
SiO_2 over alumina, Pervap SMS	Acetone	10	40	0.38	This study
			70	0.52	
SiO_2 over alumina, Pervatech PVP	Acetone	10	40	0.44	This study
			70	2.72	
SiO_2 over alumina	IPA	4.5	80	1.86	[22]
SiO_2 over alumina	IPA	5	70	1.6	[21]
SiO_2 over alumina	IPA	5	70	1.0	[23]
SiO_2 over alumina, Pervap SMS	IPA	10	70	2.8	[20]
SiO_2 over alumina, Pervatech PVP	IPA	5	70	2	This study
		10	70	3.2	

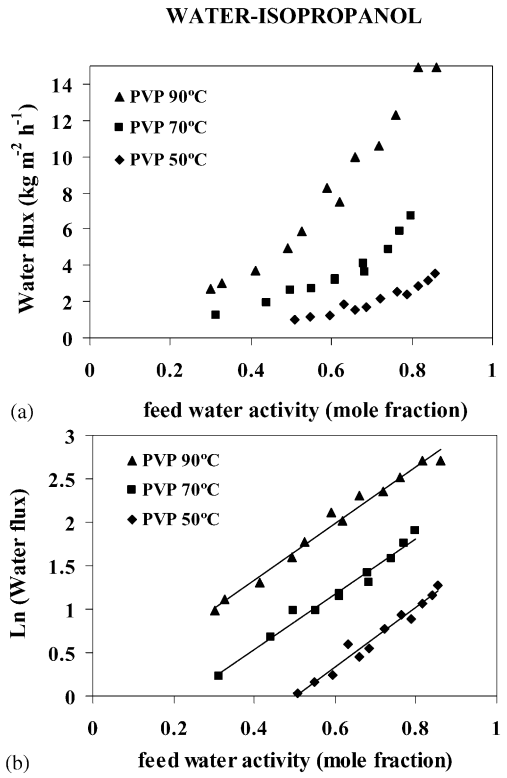

Fig. 3. Dehydration of the water–isopropanol mixture through the Pervatech PVP silica membrane (a) evolution of water flux vs. water activity in the feed and (b) Ln water flux vs. water activity, (▲) PVP 90 °C; (■) PVP 70 °C; (♦) PVP 50 °C.

of Eqs. (2) and (4) are $\zeta = 3.29$, $E_{act} = 10{,}453$ cal/mol and $J_{00} = 1.89 \times 10^6$ kg/m^2 h.

The performance of the Pervatech PVP membrane for the separation of the industrial water–acetone mixture was also studied. Fig. 5(a) represents the evolution of the water concentration in the feed over time, at two working temperatures, 40 and 70 °C. As expected, the kinetics of water separation increased as temperature increased. Fig. 5(b) shows the water flux in this case against the water concentration in the retentate. For a value of water content in the feed of

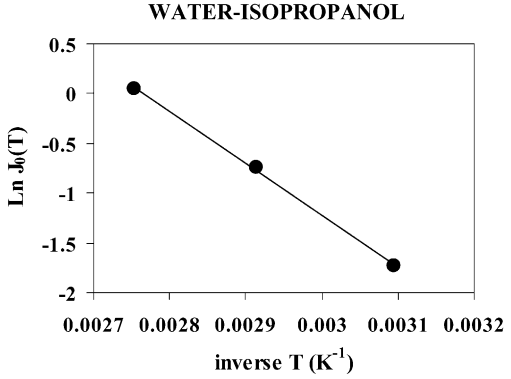

Fig. 4. Dehydration of the water–isopropanol mixture through the Pervatech PVP silica membrane. Arrhenius-type temperature dependence of the J_0 parameter according to Eq. (4).

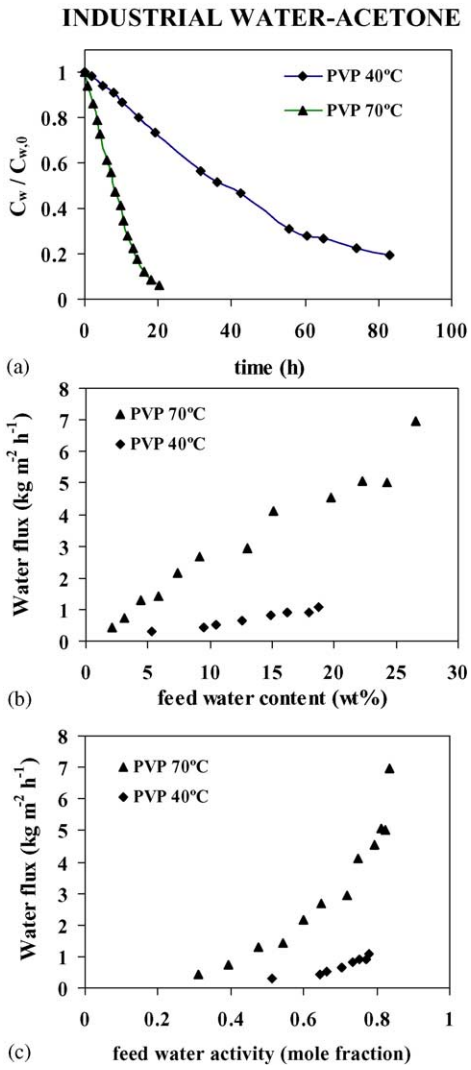

Fig. 5. Dehydration of the industrial water–acetone mixture through the Pervatech PVP membrane (a) reduced weight fraction water in the feed over time, (b) water flux vs. water content in the feed and (c) water flux vs. water activity in the bulk liquid solution. (▲) PVP 70 °C; (♦) PVP 40 °C; (■) PVP 50 °C.

10 wt.%, the pervaporation flux through the membrane took the values of 0.44 and 2.7 kg/m^2 h, at 40 and 70 °C, respectively. On Fig. 5(c) the exponential dependency of water flux with water activity in the feed, as within the experiments run for the synthetic water–isopropanol mixture are observed. Thus, the same assumptions seem to be valid for the industrial water–acetone mixture.

Fig. 6 shows some pervaporation results, already reported by Ortiz et al. [16] for the dehydration of the industrial water–acetone mixture through the Pervap SMS membrane, commercialized by Sulzer. The water fluxes across the Pervap SMS membrane are substantially lower compared to the Pervatech PVP membrane. For a value of water content in the feed of 10 wt.%, the pervaporation flux through the Pervap SMS membrane took the values of 0.38 and 0.56 kg/m^2 h, at 40 and 70 °C, respectively. In general, the water flux

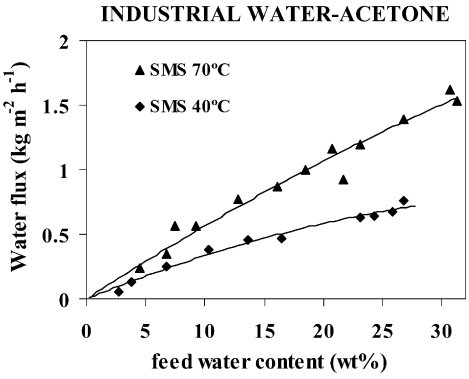

Fig. 6. Evolution of the water flux through the Pervap SMS membrane vs. water content in the feed.

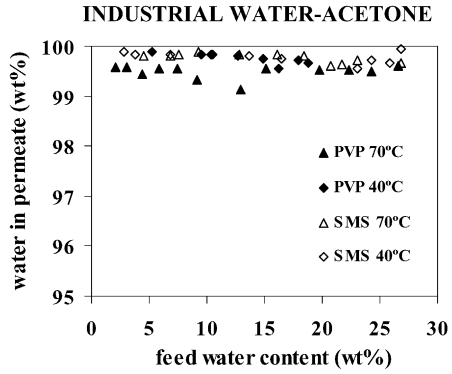

Fig. 8. Permeate water content vs. feed water content for water–acetone dehydration through the Pervatech PVP and Pervap SMS membranes.

decreases with increasing values of the membrane thickness. A reason for the higher water flux through the Pervatech PVP membrane used in this study may be the thinner selective layer, given that the former is 10 times thinner than the Pervap SMS membrane, as obtained by data given by manufacturers.

Fig. 7 shows the representation of Ln Water flux as a function of feed water activity for the dehydration of the industrial water–acetone mixture using both commercial silica membranes, Pervatech PVP and Pervap SMS, at two different operating temperatures (40 and 70 °C). All four lines are parallel, two of them superimposed, with an average value of the slope ζ = 4.85 indicating that the parameter ζ has a similar value when dehydrating the same organic solvent, in this case, water–acetone mixtures, even when using silica membranes produced by different manufacturers, and with different nominal thickness. On the contrary, the parameter ζ obtained for the PVP–water–isopropanol system is lower ζ = 3.29, which means that the organic component may modify the adsorption of water onto the membrane surface.

Finally, in order to give an idea of the permeate quality of the membranes investigated here, Fig. 8 is presented. In this figure, the water content in the permeate is plotted as a function of the water content in the feed, for the dehydration of the industrial water–acetone mixture using both the Pervatech PVP and the Pervap SMS membranes. Both membranes showed a remarkable high selectivity, providing a permeate with water concentration higher than 99.5 wt.% in most of the experimental conditions under study. Also, the water content of the permeate seems to be nearly independent of the feed composition, regardless the data scattering, that was attributed to the experimental error.

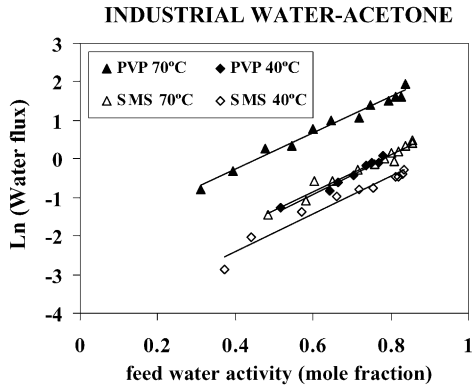

Fig. 7. Ln (water flux) vs. water activity in the feed for the industrial water–acetone mixture through the Pervatech PVP and the Pervap SMS membranes.

5. Conclusions

The performance of an inorganic commercial pervaporation membrane referenced as Pervatech PVP was experimentally tested for the dehydration of two solvent mixtures: water–isopropanol and a ketonic mixture from industrial origin containing traces of other products. Fluxes decreased as the feed water concentration decreased. The effect of temperature was studied in the range 40–90 °C. Increasing temperatures resulted in higher fluxes. A similar trend was remarked for both systems in the linear dependence of water flux on the water activity in the feed.

To predict the membrane performance, the permeate flux across the membrane should be known, based on the transport mechanism through the membrane and the diffusion and sorption properties. Thus, experimental data have been adjusted to a previously referenced correlation, $J_w = J_{w00} \exp(-E_{aw}/RT) \exp(\zeta a_w^f)$ and the values of the mass transfer parameters that characterize separation of water/IPA mixtures using the PVP membrane have been determined, ζ = 3.29, E_{act} = 10453 cal/mol and $J_{00} = 1.89 \times 10^6$ kg/m^2 h.

With respect to the dehydration of industrial acetone mixtures, the water flux provided by the PVP membrane are larger than that of the Pervap SMS membrane reported in a previous work. Nevertheless, the value of the parameter ζ = 4.85 is the same for the two membranes, indicating that the parameter ζ is related to the adsorption of the permeating species onto the membrane.

Acknowledgements

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