Effect of Swelling on Mass Transfer Performance in Membrane Extraction

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ABSTRACT: The membrane extraction experiments were performed with tributyl phosphate/acetic acid (HAc)/water, *n*-butanol/HAc/water and 20% Alamine (in kerosene); HAc; and water as working systems. HAc was transferred from the aqueous phase to the organic phase. The effect of flat membranes swelling on mass transfer was studied. The membranes were microporous polysulfone and microporous polytetrafluoroethylene. The overall mass transfer coefficients based on the water phase were calculated and compared between nonswollen and swollen membranes. The experimental results show that the physical structure of the flat membranes used in our experiments was changed if soaked by organic solvents; however, change in thickness was not found. The overall mass transfer coefficients clearly were decreased after the flat membranes were swollen. The most likely reason is that the mass transfer resistance was increased because of the change of the membrane structure. The results also show that it is better to choose a hydrophilic membrane to reach high mass transfer performance when the equilibrium constant is very low. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 1555–1561, 1999

Key words: membrane extraction; swelling; mass transfer

INTRODUCTION

In recent years there has been significant interest in studying the nondispersion membrane extraction process, especially using microporous hollow fiber membranes.[1–6] Membrane extraction using microporous polymer as a barrier between the aqueous and organic phases has been used successfully for the removal and concentration of different compounds, e.g., metals, anions, and organic compounds. In conventional solvent extraction, the two liquids are mixed intimately, then separated by coalescence into two phases. In the mixing process, there are some problems of backmixing and foam generation which reduce the mass transfer rate and subsequently prevent complete phase separation which causes solvent loss. Membrane extraction processes present several advantages in comparison with the traditional mixer-settlers. They are simple and their energy consumption is low. In membrane extraction modules, both phases get into contact without mixing, avoiding the dispersion of the organic phase into the aqueous stream or vice versa and thus eliminating emulsion formation and phase entrainment. Therefore, the organic losses are very small if the pressure control is done properly. There is no need for a difference in phase densities, and no problems due to loading and flooding. If hollow fiber membranes are used, a high surface-to-volume ratio in a very compact bundle can be reached. It is important to note that the membrane material used in this process does not function as a species-selective barrier, but rather prevents dispersion of one phase into another phase.

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Table I Physical Properties of Working Systems

	TBP/HAc/H_2O		n-Butanol/ HAc/H_2O		20% Alamine (in kerosene)/ HAc/H_2O	
	Solvent	Feed	Solvent	Feed	Solvent	Feed
Viscosity, μ (pa · s)	0.0332	0.0098	0.0301	0.0098	0.0223	0.0098
Density, ρ (kg/m^3)	972.7	1020.0	813.4	1020.0	801.8	1020.0
Equilibrium constant, m	2.905		1.341		0.0883	

TBP, tributyl phosphate; HAc, acetic acid.

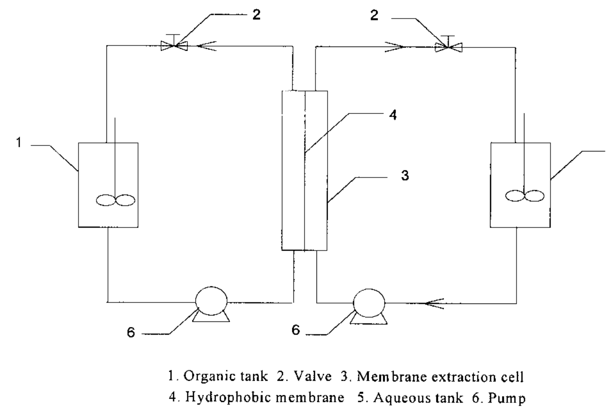

Figure 1 The experimental setup.

In a sense, the membrane extractor behaves as a high efficiency packing with a high surface area for mass transfer without sacrifice in throughput capacity. Although these innovative processes have so many advantages, some disadvantages still exist. The obvious disadvantages of the membrane extraction device are the much slower nature of its mass transfer processes and the instability of membranes under the action of organic solvent. The mass transfer performance is strongly affected by characteristics of swelling and wetting of membranes, because the membranes will be swollen by organic solvents, then the physical structure of membranes will be changed. Therefore, it is a very important to study the effect of swelling on mass transfer in membrane extraction.

Prasad et al.[7–9] have shown that hydrophobic membranes provide a higher mass transfer coefficient K than hydrophilic membranes if $m > 1$; conversely, hydrophilic membranes yield a higher K when $m < 1$. In their article, they stated that besides a higher K, there are other important factors in the membrane extraction processes such as: Chemical/pH stability of membrane and pore size of membrane. Xu et al.[10] studied the swelling of some different hollow fiber membranes in several organic solvents at different temperatures. They found the length of almost all the used hollow fibers was changed. Zhand et al.[11] reported that the mass transfer coefficients in hollow fiber modules were decreased after the membranes were swollen.

In this work, some flat membranes from different materials were used to study the swelling characteristics by different solvents, because a flat membrane is very simple and it is much easier to measure its structure changes. The mass transfer performance in a membrane extraction module was compared between the two conditions of the membranes: swollen or nonswollen.

EXPERIMENTAL

Experimental Material

Tributyl phosphate (TBP)/acetic acid/water, n-butanol/acetic acid/water, and water/acetic acid/20% Alamine (in kerosene) were used as working sys-

Table II Physical Properties of Membranes

	PSU	PTFE BSF-II-020	PTFE BSF-II-050	PTFE	PP	PE	PVC
Style	Microporous	Microporous	Microporous	Dense	Dense	Dense	Dense
Thickness (μm)	130	80	100	100,50,35	50	100	200
Pore size (μm)	0.4	0.2	1.0				
Porosity (%)	45	55	60				

PSU, polysulfone; PTFE, polytetrafluoroethylene; PP, polypropylene; PE, polyethylene; PVC, polyvinyl chloride.

Table III Swelling Ratios of Dense Membranes

	PTFE	PTFE	PTFE	PP	PE	PVC
Thickness (μm)	100	50	35	50	100	200
TBP	8.6×10^{-4}	2.28×10^{-3}	3.08×10^{-3}	1.73×10^{-2}	[a]	Dissolved
n-Butanol	3.58×10^{-4}	4.63×10^{-4}	6.02×10^{-4}	7.07×10^{-3}	[a]	[a]
20% Alamine (in kerosene)	4.12×10^{-4}	5.86×10^{-4}	6.14×10^{-4}	1.16×10^{-3}	[a]	[a]

PTFE, polytetrafluoroethylene; PP, polypropylene; PE, polyethylene; PVC, polyvinyl chloride; TBP, tributyl phosphate.
[a] The weight of the swollen membrane is less than that of the original dry membrane.

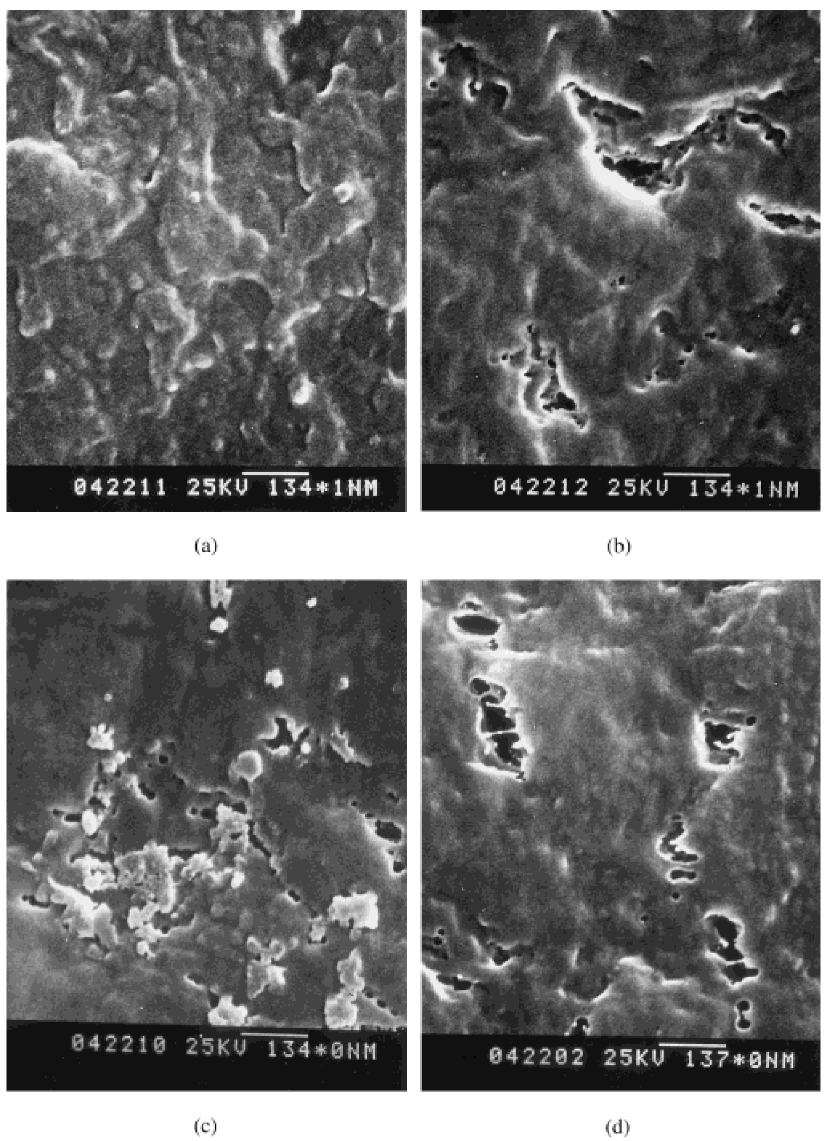

Figure 2 SEM pictures of PTFE membrane; magnification 10,000×. (a) Nonswollen membrane; (b) swollen by TBP; (c) swollen by n-butanol; and (d) swollen by 20% Alamine (in kerosene).

Table IV Swelling Ratios of Microporous Membranes

	TBP	n-Butanol	20% Alamine (in Kerosene)
PSU	25.79	1.41	26.81
PTFE, BSF-II-020	21.1	1.64	15.91
PTFE, BSF-II-050	83.27	1.01	47.39

TBP, tributyl phosphate; PSU, polysulfone.

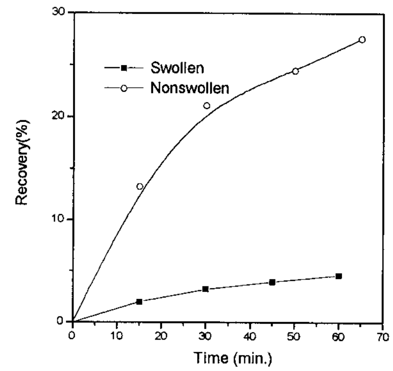

Figure 3 Recovery of HAc vs time.

tems. Acetic acid was extracted from the water phase into the organic phase. All the products purchased from Beijing Chemical Plant (Beijing, China) were chemical grade. Deionized water was made by us. Dense and microporous flat membranes made of polysulfone (PSU), polytetrafluoroethylene (PTFE), polypropylene, polyethylene, and polyvinyl chloride, were kindly provided by Beijing Plastic Institute (Beijing, China). The physical properties of the working systems and these membranes are listed in Table I and Table II, respectively.

Experimental Procedure

Swelling ratios and porosity of the membranes were measured by weight method, namely, weighted dry membranes were immersed in various solvents at room temperature for 48 h to allow the swelling to reach equilibrium. After swelling membranes were rapidly removed from the solvents and the solvents wiped on the surface of the membranes carefully with tissue paper, the membranes were weighted as quickly as possible. The swelling ratio, S, is defined by

$$S = \frac{W_s - W_d}{W_d} \times 100\% \qquad (1)$$

where W_d and W_s indicate the weight of the dry and the swollen membranes, respectively.

The experimental setup and the flat membrane test cell are given in Figure 1. The effective area of the cell is 100 cm^2. Extraction runs were done by placing the flat membrane in the cell. The two phases were fed concurrently through the cell. The pressure differential between the two sides of the membrane is maintained to 1 mH_2O. Mass transfer performance of the membrane extraction was characterized by calculating the overall mass transfer coefficient based on the aqueous phase.

RESULTS AND DISCUSSION

Swelling Characteristics

The swelling ratios of different dense membranes in three solvents are listed in Table III. It can be seen that the swelling ratios are very low. The swelling ratios of all the membranes in TBP solvent are larger than that in the other two solvents. Polyethylene and polyvinyl chloride are not suitable material for extraction membranes. For

Table V Changes of Porosity of Membranes after Swollen (%)

	PSU		PTFE, BSF-II-020		PTFE, BSF-II-050	
Porosity	Non-swollen	Swollen	Non-swollen	Swollen	Non-swollen	Swollen
TBP		10		11		9
n-Butanol	45	45	55	55	60	60
20% Alamine (in kerosene)		10		12		13

PSU, polysulfone; PTFE, polytetrafluoroethylene.

Table VI Changes of Thickness of Membranes after Swollen (%)

	PSU		PTFE, BSF-II-020		PTFE, BSF-II-050	
Thickness μm	Non-swollen	Swollen	Non-swollen	Swollen	Non-swollen	Swollen
TBP		132		83		98
n-Butanol	130	124	80	83	100	105
20% Alamine (in kerosene)		135		81		102

See Table I.

checking the action of these solvents on membranes, we have taken the SEM pictures of the surface of the nonswollen and swollen membranes. Figure 2 shows that organic solvents are corrosive compounds for extraction membranes.

The swelling ratios of microporous membranes were studied also, and the results are listed in Table IV. It can be seen that the swelling ratios in TBP are also the largest in the three solvents. For the same material, the PTFE, BSF-II-050 membrane has higher a swellings ratio than the PTFE, BSF-II-020 membrane. This is because the porosity and the pore size of BSF-II-050 are larger, so it can provide more contact area with solvents. Under the action of solvents, the path of the pore may be changed; therefore, the swelling ratios are much larger.

The changes of porosity and thickness of the membranes are shown in Tables V and VI, respectively. The porosity of the three kinds of membranes was changed seriously after being swollen by TBP or 20% Alamine (in kerosene), but there were no changes caused by n-butanol. It also was observed in our experiment that all the membranes became much harder and too fragile after the membranes were swollen; what may change the physical structure of the membranes are changed, e.g., pore plugging or passage distortion. Table VI shows that no changes in membrane thickness were observed after the membranes were swollen.

Mass Transfer Characteristics

TBP/Acetic Acid/H_2O System

The recovery of acetic acid (HAc) vs time is plotted in Figure 3 for a PSU membrane. For the other two membranes, similar curves were obtained. From this Figure, it can be seen that the recovery is increased with time, but the slope of the curves is decreased, which shows that the mass transfer becomes slow because the difference of concentration between the two sides of the membrane becomes smaller with the time changed. Figure 3 also shows that the great changes of mass transfer characteristic were caused by swelling. After the membrane is swollen, the mass transfer rate becomes much slower at the same experimental conditions. To compare the mass transfer performance, the calculated overall mass transfer coefficients for the three kinds of membranes are listed in Table VII.

Table VII clearly shows that the mass transfer coefficients were decreased seriously after the membranes were swollen. The changes were more serious in the PSU membrane than in the other two membranes. This was because the porosity was decreased after the membranes were swollen.

Table VII Overall Mass Transfer Coefficients in TBP/HAc/Water System ($\times 10^{-8}$ m/s)

	1		2		3	
Experimental No.	Non-swollen	Swollen	Non-swollen	Swollen	Non-swollen	Swollen
PSU	10.51	5.14	9.41	3.90	9.9	4.2
PTFE BSF-II-020	1.38	0.94	1.40	0.84	1.25	0.92
PTFE BSF-II-050	2.60	1.95	2.77	2.01	2.48	1.87

TBP, tributyl phosphate; HAc, acetic acid; PSU, polysulfone; PTFE, polytetrafluoroethylene.

Table VIII Overall Mass Transfer Coefficients in n-Butanol/HAc/Water System ($\times 10^{-8}$ m/s)

	1		2		3	
Experimental No.	Non-swollen	Swollen	Non-swollen	Swollen	Non-swollen	Swollen
PSU	9.64	3.61	10.63	3.63	10.12	3.43
PTFE BSF-II-020	2.81	0.61	2.98	0.64	2.65	0.58
PTFE BSF-II-050	1.78	0.57	1.95	0.65	1.68	0.52

See Table VII.

Because of the changes of the porosity and pore size, the membrane resistances were increased. Because the swelling ratios of the PSU membrane were the biggest, so the swelling caused PSU membrane changes more seriously than the other two membranes. For the same membrane material, PTFE membrane, PTFE BSF-II-020 was changed more greatly than PTFE BSF-II-05. The most likely reason is that the number of micropores in PTFE BSF-II-020 is higher than in PTFE BSF-II-050, so the physical structure of PTFE BSF-II-020 could be changed more seriously under the action of solvent.

n-Butanol/HAc/H_2O System

The overall mass transfer coefficients with *n*-butanol as solvent are listed in Table VIII. From the Table, it can be clearly seen that the overall mass transfer coefficients were also decreased after the membranes were swollen. In Table V, we have seen that the porosity of the membranes was not changed under the action of n-butanol; as such, why are the mass transfer coefficients decreased? It may be explained that the pore size and passage for mass transfer are changed under the solvent action. These changes cause the membrane resistance to be increased.

Twenty Percent Alamine (in Kerosene)/HAc/H_2O System

The mass transfer performance with 20% Alamine (in kerosene) as solvent was also studied and the results are listed in Table IX. Here, it should be noted that the mass transfer coefficients are much less than in the other two working systems; this is because the equilibrium constant is very small. Therefore, for the 20% Alamine (in kerosene)–HAc–water system, it is not reasonable to choose hydrophilic membranes.

Table IX Overall Mass Transfer Coefficients in 20% Alamine/HAc/Water System ($\times 10^{-9}$)

	PSU	PTFE BSF-II-020	PTFE BSF-II-050
Nonswollen	7.128	5.275	8.942
Swollen	5.488	3.331	1.491

See Table VII.

CONCLUSION

The porosity of the flat membranes used in our experiments was changed if soaked by organic solvents, and the membranes became much harder and too fragile; however, the thickness change was not found. The overall mass transfer coefficients were clearly decreased after the flat membranes were swollen. The most likely reason is that the mass transfer resistance is increased due to the change of the membrane structure. Accordingly, it may be concluded that the membrane physical structure is changed under the action of organic solvents, such as porosity, pore size, and passage. Therefore, the choice of an appropriate membrane material for membrane extraction plays an important role. Our experimental results also show that it is better to choose hydrophilic membranes to reach high mass transfer performance when the equilibrium constant is very low.

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