Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

Influence of organic solvents on the performance of polymeric nanofiltration membranes

Bart Van der Bruggen[a]; Jeroen Geens[a]; Carlo Vandecasteele[a]
[a] Department of Chemical Engineering, University of Leuven, Heverlee, Belgium

To cite this Article Van der Bruggen, Bart , Geens, Jeroen and Vandecasteele, Carlo(2002) 'Influence of organic solvents on the performance of polymeric nanofiltration membranes', Separation Science and Technology, 37: 4, 783 — 797

To link to this Article: DOI: 10.1081/SS-120002217

URL: http://dx.doi.org/10.1081/SS-120002217

SEPARATION SCIENCE AND TECHNOLOGY, 37(4), 783–797 (2002)

INFLUENCE OF ORGANIC SOLVENTS ON THE PERFORMANCE OF POLYMERIC NANOFILTRATION MEMBRANES

Bart Van der Bruggen,* Jeroen Geens, and
Carlo Vandecasteele

Department of Chemical Engineering, University of
Leuven, W. de Croylaan 46, B-3001 Heverlee, Belgium

ABSTRACT

Separations in organic solvents are a new field of application for nanofiltration. Only a few polymeric nanofiltration membranes are commercially available for these separations, the major problem being the limited chemical stability in organic solvents. This article studies the influence of different organic solvents (methylene chloride, acetone, hexane, ethyl acetate, and ethanol), their performance on the four nanofiltration membranes (N30F, NF-PES-10, MPF 44, and MPF 50) specified to be compatible with the solvents used. The pure water flux (distilled water) of these membranes and the rejection of maltose were measured before and after 10 days of exposure to one of the above-mentioned solvents. The results show that not all of the membranes are compatible with the solvents used, and that the membrane performance shifts towards lower rejections for the hydrophilic membranes (N30F, NF-PES-10, and MPF 44) and

---

*Corresponding author. Fax: (32) 16-322991; E-mail: bart.vanderbruggen@cit.kuleuven.ac.be

towards higher pure water fluxes for the hydrophobic membrane (MPF 50). The water flux is not significantly affected for the hydrophilic membranes, and the effect on maltose rejection is small for the hydrophobic membrane.

The results are explained by a reorganization of the membrane structure due to the clustering of hydrophobic and hydrophilic zones within the active layer of the membranes. Scanning electron microscopy images for MPF 44 and MPF 50 confirm these findings.

Key Words: Chemical stability; Membrane filtration; Nanofiltration; Organic solvents

INTRODUCTION

During the last decade, a large number of applications of nanofiltration in aqueous solution was developed (1–6). Until recently, the use of nanofiltration was limited to this field, due to the lack of nanofiltration membranes with sufficient chemical stability in organic solvents. However, the extension of nanofiltration towards separations in organic solvents would certainly open new possibilities in many industries (7–10). The main problem is the development of new chemically stable nanofiltration membranes. Therefore, a lot of research focuses on new membrane materials that would meet these requirements. Two different approaches can be distinguished: further improvement of the chemical stability of polymeric membranes, and development of ceramic membranes. In view of the chemical stability, ceramic membranes would be obviously advantageous. Promising results with silica–zirconia membranes having pore diameters of 1–5 nm were reported by Tsuru et al. (11), but generally the pore size obtained for ceramic membranes remains too large for applications in the nanofiltration range.

On the other hand, the production of polymeric membranes compatible with a wide range of organic problems is also difficult. The usual method is to increase the degree of cross-linking of the polymeric top layer (12). Additionally, alternative membrane materials such as poly(organophosphazene) were tested (13), or more common materials such as poly(acrylonitrile) were improved (14). As a result, new membranes were obtained with a better, although far from perfect resistance to organic solvents. Recurrent problems are the dissolution, deformation, or swelling of the membrane. Therefore, industrial application of these membranes is not yet possible. For the time being, application on a larger scale is not yet possible. Fundamental research on membrane properties and the influence of organic solvents on membrane performance (flux and rejection) should help to overcome these restrictions.

This research investigates the influence of organic solvents on nanofiltration membranes specified to be solvent stable. Usually, the influence of organic solvents is studied by measuring the solvent flux and the rejection of molecules in organic solvents. In contrast, this research describes the change in water flux and of the rejection of organic molecules in aqueous solution after exposure of the membrane to a series of organic solvents for a number of solvent-stable membranes. The reason for this approach is that rejections and fluxes with nanofiltration membranes are better known in aqueous solution, so that this can be taken as a reference for the membrane performance. It will be shown that experimental results are always worse than what follows from the manufacturer's information, and that solvent stability for some membranes is questionable. Moreover, the structure of the solvent-stable membranes might change due to the clustering of hydrophobic and hydrophilic groups during immersion in an organic solvent.

METHODS AND MATERIALS

A commercial laboratory scale nanofiltration setup (Amafilter Test Rig PSS1TZ, Amafilter, Alkmaar, The Netherlands) was used for the nanofiltration experiments. The filtration in the module occurred in cross-flow with flat sheet membranes (diameter 0.09 m). The active surface of the membrane was 0.0044 m^2 with a channel length of 293 mm.

After a thorough selection based on information of the manufacturers and data from literature (15,16), four solvent-stable membranes were selected. The membranes used are N30F and NF-PES-10, obtained commercially from Celgard (Wiesbaden, Germany), and MPF 44 and MPF 50, obtained commercially from Koch Membrane Systems (Wilmington, MA). The N30F and NF-PES-10 are hydrophilic polyethersulfone membranes. The MPF 44 and MPF 50 consist of several layers, with a backing made of a polypropylene–polyethylene blend. The polymeric layer and the top polymeric layer are a proprietary polymer (synthesized by Koch). The information provided by the manufacturers is summarized in Table 1. All membranes were specified to be compatible with the solvents used in this study (methylene chloride, *n*-hexane, ethyl acetate, ethanol, and acetone).

Solvents were chosen in order to cover a wide range of different chemical structures: a halogenated hydrocarbon (methylene chloride), an aliphatic hydrocarbon (*n*-hexane), an ester (ethyl acetate), an alcohol (ethanol), and a ketone (acetone). This is useful to gain a qualitative insight in the interaction mechanisms between different solvents and membranes. All of the solvents used were of analytical grade. Some physical properties for the four solvents (and water) are given in Table 2 (17,18).

Table 1. Membrane Characteristics as Indicated by the Manufacturers

Membrane	N30F	NF-PES-10	MPF 44	MPF 50
Nature	Hydrophilic	Hydrophilic	Hydrophilic	Hydrophobic
Manufacturer	Celgard	Celgard	Koch	Koch
Water flux (L/m^2 hr)	40–70[a]	200–400[a]	40[b]	0[b]
Sugar rejection	70–90[a,c]	30–50[a,c]	98[b,d]	n.a.
Maximum temperature (°C)	95	95	40	40
pH range	0–14	0–14	2–10	4–10

[a] At 40 bar, 20°C.
[b] At 30 bar, 30°C.
[c] 4% lactose (MW 342).
[d] 5% sucrose (MW 342).
n.a. not available.

Maltose was determined using a spectrophotometric method based on a condensation reaction of its furfural derivates with phenol (19). The furfural derivates were obtained by heating the maltose solution in concentrated sulphuric acid. The accuracy obtained by this method was ca. 5%.

The equipment used for microscopical analysis [scanning electron microscopy (SEM)] of the membranes was a Philips Scanning Electron Microscope XL30 FEG (Philips, Eindhoven, The Netherlands).

EXPERIMENTAL

The water flux and maltose rejection (using distilled water containing 100 mg/L maltose) was measured for five new sheets of each membrane type. The conditions for nanofiltration were: transmembrane pressure, 20 bar; temperature, 25°C; cross-flow velocity, 2 m/sec. The permeate fraction and retentate fraction were recycled continuously to the feed tank, so that no concentration effects occurred. Samples were taken after a stabilization period of 15 min. The flux was then further measured as a function of time during 1 hr (for the hydrophilic membranes) to 4 hr (for the hydrophobic membrane), time needed to gather the samples. The maltose concentration in the permeate and retentate fraction was then determined; the rejection (%) was calculated as the concentration difference between both fractions divided by the concentration in the feed.

After the nanofiltration experiment, the membranes were examined microscopically by SEM. Because only dry samples can be analyzed with SEM, the membranes were dried in an exsiccator for 15 hr. The dry membranes were fixed on a conductive, adhesive carbon support. On the top layer of the

Table 2. Physical Properties for the Solvents Used in the Experiments (16) (Dipole Moments (17) in Carbon Tetrachloride, Except for Hexane (Liquid Hexane); i = Insoluble)

	Water (H_2O)	Methylene Chloride (CH_2Cl_2)	Hexane (C_6H_{14})	Ethyl Acetate ($C_4H_8O_2$)	Ethanol (C_2H_5OH)	Acetone (C_3H_6O)
Molecular weight	18.02	84.93	86.18	88.11	46.07	58.08
Density (g/mL)	0.9980	1.3260	0.6594	0.9006	0.7894	0.7900
Viscosity (mPa sec)	1.002	0.393	0.326	0.426	1.078	0.337
Surface tension (mN/m)	72.75	28.12	17.9	23.75	22.32	23.32
Water solubility (g/L)	—	20	i	81	∞	∞
Boiling point (°C)	100	39.8	68.7	77.06	78.32	56.1
Dielectrical constant	78.3	8.9	1.9	6.0	24.3	20.7
Dipole moment (Debye)	1.85	1.82	0.07	1.68	1.78	2.83

membrane, a conductive carbon coating was applied with a carbonwire coater. Then the samples were analyzed with an electron microscope.

Afterwards, each sheet of the four membrane types was exposed during 10 days to one of the following solvents: methylene chloride, hexane, ethyl acetate, ethanol, and acetone. This was done by immersing the membrane sheets in Petri dishes, filled with the respective solvents, and refilled daily so that the membranes never became dry due to solvent evaporation. An exposure time of 10 days was selected because no additional visual damage could be observed after this period in preliminary experiments with each of the solvents.

After the solvent exposure, the membranes were again examined visually and microscopically with SEM. Finally, the pure water flux and maltose rejections were measured again under the same conditions as described above.

All experiments were repeated twice with the same membranes, i.e., measurement of initial pure water fluxes and maltose rejections and final measurement of pure water fluxes and maltose rejections after solvent exposure.

RESULTS AND DISCUSSION

Initial water fluxes and water fluxes after exposure to one of the solvents are presented in Table 3. The initial fluxes (1) for a given membrane with each of the solvents are expected to be constant, since the membrane has not yet been in contact with the solvent at this point. However, variations up to 10% were found for each of the membranes (standard deviations were 1.9, 11.4, 1.5, and 1.2 L/m^2 hr for N30F, NF-PES-10, MPF 44, and MPF 50, respectively). These variations may be caused by differences in pore size distribution between samples of one membrane type. Because only small surface areas are used, the experiments are susceptible to such differences between membrane samples.

Table 3. Water Fluxes (L/m^2 hr) Obtained with N30F, NF-PES-10, MPF 44, and MPF 50, Before (1) and After (2) Exposure to Different Organic Solvents

	N30F		NF-PES-10		MPF 44		MPF 50	
	(1)	(2)	(1)	(2)	(1)	(2)	(1)	(2)
Methylene chloride	36.4	—	162.8	—	33.5	31.0	5.1	6.1
Hexane	38.3	32.1	162.7	92.8	32.7	—	4.3	10.3
Ethyl acetate	33.7	38.0	148.0	34.5	34.4	33.7	5.0	39.6
Ethanol	35.0	27.5	144.8	167.8	36.1	40.0	6.5	22.6
Acetone	37.5	—	172.2	—	36.1	34.6	7.3	11.8

Other factors such as membrane setting conditions are thought to play a minor role; all fluxes measured remained constant in time during 1–4 hr.

For MPF 50, a small water flux was found, although a zero flux was to be expected because of the hydrophobicity of the membrane (see also Table 1).

Some of the membranes were visually damaged after exposure, to the extent that nanofiltration experiments were unnecessary because the integrity of the mechanical structure of the membrane was affected. This was found for N30F and NF-PES-10 after exposure to methylene chloride and acetone, and for MPF 44 after exposure to hexane, which proves that they are not compatible with these solvents (in contradiction to the manufacturer's information). The MPF 50 was the only membrane where no mechanical damage was observed for any of the solvents.

From Table 3, it can be seen that the water fluxes for N30F and MPF 44 are approximately constant before and after exposure to the organic solvents. The MPF 50 shows a general increase of the water flux. For ethyl acetate, the water flux increases with a factor of 8, so that the final water flux is in the same range as for the hydrophilic N30F and MPF 44 membranes. Somewhat different results were obtained for NF-PES-10. For two of the three solvents that were compatible with this membrane, the water flux decreased drastically. The third solvent, ethanol, resulted in a slight increase of the water flux.

The results for the fluxes before and after solvent exposure were confirmed in all cases by repeating the experiments. The difference between both the experiments was below 5% for all solvents with N30F, NF-PES-10, and MPF-44. Somewhat larger differences were found with MPF-50: the differences before exposure to solvents were 8.0, 2.0, 3.7, 2.8, and 2.0% for methylene chloride, hexane, ethyl acetate, ethanol, and acetone, respectively, and 2.6, 5.7, 2.8, 1.5, and 7.0% after exposure. These larger differences can be explained by the more difficult measurement of the water flux for the hydrophobic MPF-50 membrane, and possibly by nonuniformity in membrane structure.

The maltose rejections before and after exposure to the organic solvents are presented in Table 4. Again, the rejections before exposure to the organic solvents should be the same, but significant differences were found that cannot be explained by analytical errors (standard deviations were 8.1, 5.2, 7.1, and 3.1% for N30F, NF-PES-10, MPF 44, and MPF 50, respectively). Thus these differences must be attributed to differences in pore size distributions within one membrane type.

The initial rejections are in all cases lower than the values indicated by the manufacturers, where these are available. The difference is especially remarkable for N30F (70–90% indicated value; 24–47% experimental) and for NF-PES-10 (30–50% indicated value; 11–24% experimental), but lower rejections were also found for MPF 44 (98% indicated value; 80–97% experimental). Thus, all of the membranes except MPF 44 have a rather open porous structure, and NF-PES-10

Table 4. Maltose (MW 342) Rejections Obtained with N30F, NF-PES-10, MPF 44, and MPF 50, Before (1) and After (2) Exposure to Different Organic Solvents

	N30F		NF-PES-10		MPF 44		MPF 50	
	(1)	(2)	(1)	(2)	(1)	(2)	(1)	(2)
Methylene chloride	37.5	—	22.1	—	96.4	27.0	30.4	64.2
Hexane	38.9	4.3	10.6	22.6	97.4	—	29.5	43.0
Ethyl acetate	39.0	4.5	15.8	17.1	80.0	78.0	36.9	43.7
Ethanol	46.9	28.7	17.4	19.3	90.9	78.0	34.9	33.9
Acetone	24.5	—	23.7	—	87.3	82.0	33.8	20.8

in particular might be characterized possibly as a tight ultrafiltration membrane. Differences between the manufacturer's specifications and experimental rejections were also reported by Whu et al. (20).

The hydrophilic membranes N30F and MPF 44 showed a general decrease of the maltose rejection after exposure to the solvents. For N30F, this effect was dramatic: for two out of the three solvents that were compatible with the membrane (hexane and ethyl acetate), the maltose rejection was reduced to below 5%. For ethanol, a decrease of 61% was obtained.

The MPF 44 showed a somewhat comparable effect: the maltose rejection was lower after exposure for all compatible solvents (although for ethyl acetate the effect is not significant). The effect was smaller than for N30F (except for methylene chloride), which might be due to a difference in membrane material.

The results for NF-PES-10 are different: in the cases where the membrane was not damaged, the maltose rejection was higher than before exposure to the solvents.

A repetition of the experiment confirmed the maltose rejections for the three hydrophilic membranes to be within 5%.

For the hydrophobic MPF 50 membrane, no general decrease in maltose rejection was found; rejections after exposure to organic solvents seem to be even higher than before (except for acetone, where rejection is lower; for ethanol, the rejection is comparable). However, the differences that were found by repeating the experiment were considerably higher than for the hydrophilic membranes. All differences were in the range between 5 and 15%.

Solvent-stable membranes may be defined as membranes that are not damaged or changed by any organic solvent in any way, which includes that their performance (fluxes and rejections) should remain a constant. The results show that this is not the case for any of the membranes used, although a gradation between the four membranes can be seen. Therefore, membranes that are not visually damaged by the solvents will be denoted as "semi" stable in the specific solvent. A semi solvent-stable membrane keeps its mechanical strength, but its performance has changed due to the impact of organic solvents.

For an interpretation of these results, a distinction should be made between the hydrophilic membranes (N30F, NF-PES-10, and MPF 44) and the hydrophobic MPF 50 membrane. The latter membrane shows a general increase of the water flux due to exposure to an organic solvent. The initial fluxes are very small due to the hydrophobic character of the membrane top layer; after exposure to organic solvents, the top layer apparently becomes more hydrophilic. This can be explained by a reorganization of the polymer chains in the membrane top layer, as suggested by Roudman and DiGiano (21) and in agreement with phenomena in polymer chemistry (22). Hydrophilic groups tend to form small "clusters" so that the membrane becomes locally hydrophilic. This should have only a minor effect on the pore size, because the fraction of hydrophilic groups is supposed to be very small. However, the effect is sufficiently pronounced to lead to a flux increase.

The effect of chain reorganization is more dramatic for the hydrophilic membranes because the fraction of hydrophilic groups is obviously larger. The clusters become larger so that in this case, chain reorganization might affect the pore sizes as well. The corresponding effect of clustering on the pores would indeed result in less, but larger pores. Thus, the influence on the total surface taken by the pores at the membrane surface is small. The hydrophilic character is also supposed to remain unchanged, due to the larger initial fraction of hydrophilic groups; reorganization would not affect the overall hydrophilicity. As a result, the water flux should be approximately the same before and after exposure to the different solvents, with small effects in either direction. This was found indeed for N30F and MPF 44, where the difference between both water fluxes was less than 10% (MPF 44) or 20% (N30F). Moreover, deviations were found in both directions, i.e., increase of the flux as well as decrease.

The surprising results for NF-PES-10 with hexane and ethyl acetate are possibly related to the large initial pore sizes of the membrane (rejections of 30–50% for a component with a molecular weight of 342), which makes flux increase due to clustering difficult.

No correlation between solvent properties (Table 2) and the effect on the water flux was found. This is not surprising, because the nanofiltration experiments themselves are carried out in an aqueous phase, not in a solvent phase. An additional problem is that the changes in water flux are a result of interactions between the solvent and the membrane material, and the latter is largely unknown.

Rejection of maltose is mainly a result of size exclusion, and depends on pore size and pore size distribution in the membrane top layer (23). thus a change in rejection properties due to the exposure to an organic solvent should be related to a change in pore size or pore size distribution.

Clustering of hydrophobic and hydrophilic groups obviously increases the pore size of the N30F membrane, so that maltose rejections were accordingly lower after exposure to an organic solvent. The effect is smaller for MPF 44, because the solvent apparently had less impact on the membrane. Methylene chloride is an exception: this solvent is obviously more aggressive to the membrane material than the other solvents used, given the relatively large influence on maltose rejection. The more solvent proof the membrane is, the less mobile the polymeric chains in the top layer will be, and thus, the less the membrane performance will be affected by organic solvents. In this view, N30F should be characterized as semi solvent stable, allowing chain mobility and clustering of hydrophobic/hydrophilic groups. More aggressive solvents such as methylene chloride have a stronger effect, resulting in a complete dissolution or decomposition of the membrane.

The slight increase in maltose rejection for NF-PES-10 is related to the larger pore size in comparison to the other membranes. By comparing Tables 3 and 4, it can be deduced that the decrease of the water flux was due to an obstruction of the pores in the top layer. Because this is only possible when the polymeric chains are mobile, NF-PES-10 should also be characterized as a semi solvent-stable membrane.

For MPF 50, the shift towards a more hydrophilic nature of the membrane caused higher water fluxes. The pores in the top layer may remain approximately unchanged if the fraction of hydrophilic components is small; if the chain reorganizations are more significant, the same effects as obtained with the hydrophilic membranes may occur. If the pore sizes would remain constant, then the same amount of maltose molecules is retained, but the amount of water permeating through the membrane increases, so that the concentration of maltose in the permeate decreases (the rejection of maltose increases). If the effects of pore size increase are more significant, a decrease of rejections should be found. Thus, the maltose rejections may increase or decrease. However, no definite conclusions can be drawn from the results on this point, given the relatively large uncertainties on the maltose rejections that were found (large differences between the two experimental measurements).

Interactions between organic solvents and a membrane may take place instantly or gradually; this paper assumes that a steady state is approximately obtained after 10 days. This is acceptable, because the membranes were described by the manufacturers as solvent stable, i.e., in a steady state from the very first moment before or after immersion in the organic solvents. The rate at which the interactions between solvents and membranes take place was not studied in this paper, but might also play a role in the loss of membrane performance.

The SEM images for the different membranes before and after exposure to the organic solvents confirm that there were changes in the morphology of the top layer. Figure 1 shows the MPF 44 membrane before and after exposure to

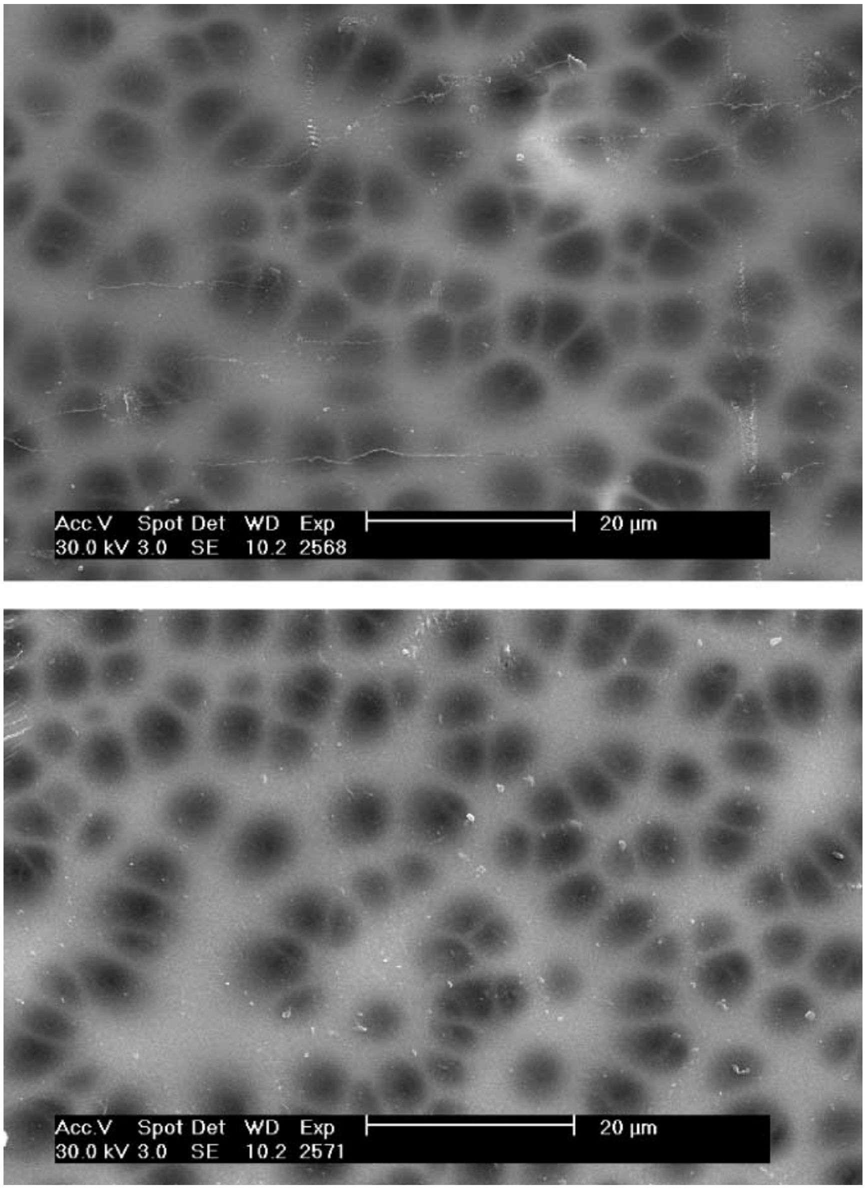

Figure 1. Scanning electron microscopy images of the MPF 44 membrane before (top) and after (bottom) exposure to methylene chloride.

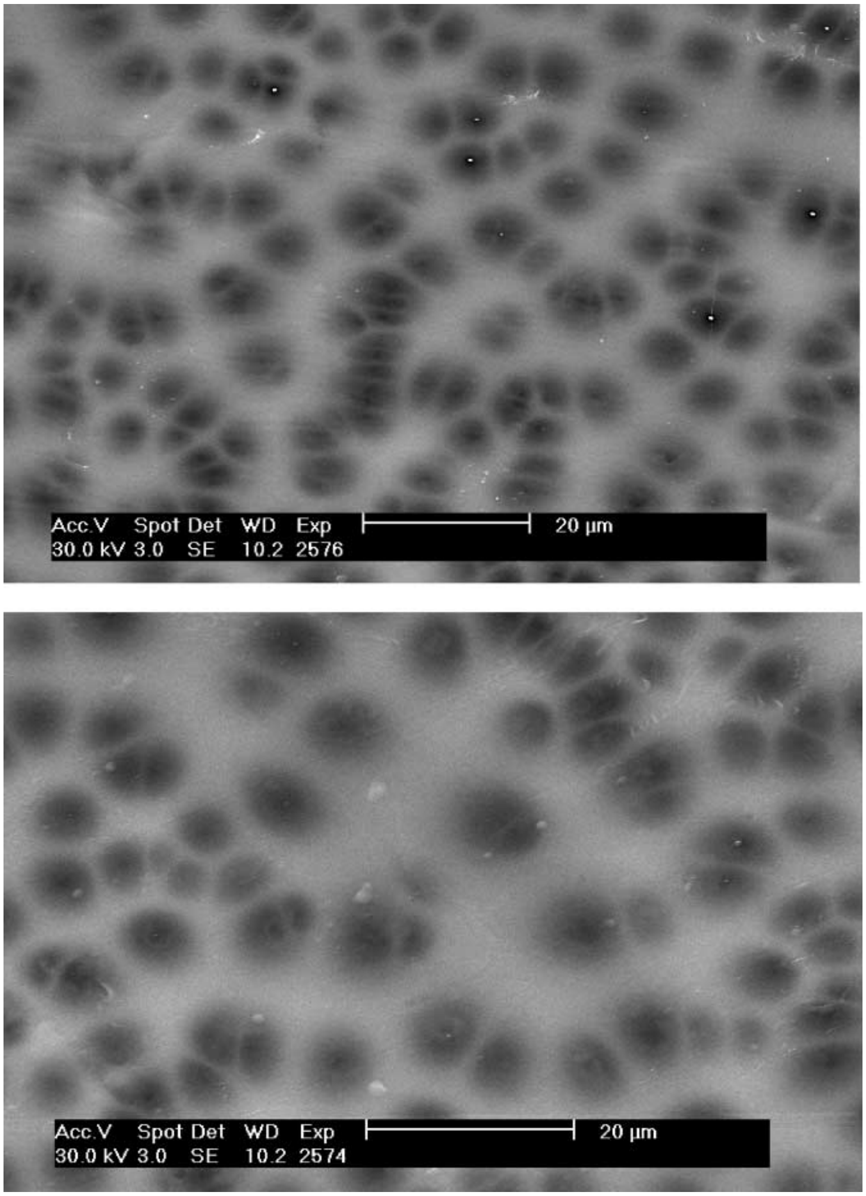

Figure 2. Scanning electron microscopy images of the MPF 50 membrane before (top) and after (bottom) exposure to ethyl acetate.

methylene chloride. The dark spots, with a diameter of several μm, are not the pores (which are expected to have a diameter of around 1 nm), but rather micro "valleys" at the membrane surface. After having been immersed in methylene chloride, these valleys are scarcer and the distance between the valleys is larger. This is only possible when the polymeric chains were mobile during the immersion in the solvent, and it can be expected that these changes also affect the (nanoscale) pores.

The same conclusions can be made for the hydrophobic MPF 50 membrane. Figure 2 shows the surface structure of MPF 50 before and after immersion in ethyl acetate. Valleys in the top layer are larger and scarcer after exposure to the solvent. Comparable results were obtained for other solvents.

CONCLUSIONS

Three out of four membranes in this research thought to be solvent stable showed visible defects after 10 days exposure to one or more organic solvents, and the characteristics of all four membranes changed notably after exposure to the solvents. This implies that the membranes should be denoted as semi solvent stable instead of solvent stable.

The interaction mechanisms between solvent and membrane proposed in this paper are different for hydrophilic and hydrophobic membranes. Hydrophilic membranes are thought to undergo a reorganization of the polymeric chains, resulting in larger pores and correspondingly lower rejections of dissolved components; water fluxes remain approximately unchanged. For hydrophobic membranes, the influence on the local character of the pores is thought to be more important: the pores become locally more hydrophilic, so that the water flux increases. Rejections may be smaller or equal when the chain reorganization is limited. Scanning electron microscopy images showed that these mechanisms are realistic. However, further verification with microscopic techniques such as transmission electronic microscopy (TEM) or atomic force microscopy (AFM) is needed, along with nanofiltration experiments in which the duration of the exposure is examined (kinetics of the interactions).

The performance of a nanofiltration membrane in an organic solvent instead of water is expected to be even more complicated. Changes in water fluxes are evidently related to hydrophilicity. When an organic solvent is transported through the membrane, the influence of changes in membrane structure should be different; hydrophilic groups play a very different role for organic solvents than they do for water. Experimental determination of the membrane performance in organic solvents should further clarify the mechanisms of interactions between membranes and organic solvents. However, understanding the impact of organic solvents on the performance of a membrane in aqueous solution will help to provide insight in the mechanisms involved during transport of organic solvents through the membrane.

REFERENCES

1. Raman, L.P.; Cheryan, M.; Rajagopalan, N. Consider Nanofiltration for Membrane Separations. Chem. Eng. Prog. **1994**, *68*, 68–74.
2. Ventresque, C.; Turner, G.; Bablon, G. Nanofiltration: from Prototype to Full Scale. J. Am. Wat. Works Assoc. **1997**, *89* (10), 65–76.
3. Williams, M.E.; Hestekin, J.A.; Smothers, C.N.; Bhattacharyya, D. Separation of Organic Pollutants by Reverse Osmosis and Nanofiltration Membranes: Mathematical Models and Experimental Verification. Ind. Eng. Chem. Res. **1999**, *38*, 3683–3695.
4. Van der Bruggen, B.; Daems, B.; Wilms, D.; Vandecasteele, C. Mechanisms of Retention and Flux Decline for the Nanofiltration of Dye Baths from the Textile Industry. Sep. Purif. Technol. **2001**, *22–23*, 519–528.
5. Van der Bruggen, B.; Schaep, J.; Maes, W.; Wilms, D.; Vandecasteele, C. Nanofiltration as a Treatment Method for the Removal of Pesticides from Ground Waters. Desalination **1998**, *117*, 139–147.
6. Agbekodo, K.M.; Legube, B.; Dard, S. Atrazine and Simazine Removal Mechanisms by Nanofiltration: Influence of Natural Organic Matter Concentration. Wat. Res. **1996**, *30* (11), 2535–2542.
7. Raman, L.P.; Cheryan, M.; Rajagopalan, N. Solvent Recovery and Partial De-acidification of Vegetable Oils by Membrane Technology. Fett-Lipid **1996**, *98* (1), 10–14.
8. Reddy, K.K.; Kawakatsu, T.; Snape, J.B.; Nakajima, M. Membrane Concentration and Separation of L-Aspartic Acid and L-Phenylalanine Derivates in Organic Solvents. Sep. Sci. Technol. **1996**, *31* (8), 1161–1178.
9. Whu, J.A.; Baltzis, B.C.; Sirkar, K.K. Modeling of Nanofiltration-Assisted Organic Synthesis. J. Membr. Sci. **1999**, *163*, 319–331.
10. Nwuha, V. Novel Studies on Membrane Extraction of Bioactive Components of Green Tea in Organic Solvents: Part I. J. Food Engng **2000**, *44* (4), 233–238.
11. Tsuru, T.; Sudou, T.; Kawahara, S.; Yoshioka, T.; Asaeda, M. Permeation of Liquids Through Inorganic Nanofiltration Membranes. J. Colloid Interface Sci. **2000**, *228* (2), 292–296.
12. Schmidt, M.; Mirza, S.; Schubert, R.; Rodicker, H.; Kattanek, S.; Malisz, J. Nanofiltration Membranes for Separation Problems in Organic Solutions. Chem. Ing. Technol. **1999**, *71* (3), 199–206.

13. Golemme, G.; Drioli, E. Polyphosphazene Membrane Separations—Review. J. Inorg. Organomet. Polym. **1996**, *6* (4), 341–365.
14. Musale, D.A.; Kumar, A. Solvent and pH Resistance of Surface Crosslinked Chitosan/Poly(Acrylonitrile) Composite Nanofiltration Membranes. J. Appl. Polym. Sci. **2000**, *77* (8), 1782–1793.
15. Machado, D.R.; Hasson, D.; Semiat, R. Effect of Solvent Properties on Permeate Flow Through Nanofiltration Membranes. Part I: Investigation of Parameters Affecting Solvent Flux. J. Membr. Sci. **1999**, *163*, 93–102.
16. Machado, D.R.; Hasson, D.; Semiat, R. Effect of Solvent Properties on Permeate Flow Through Nanofiltration Membranes. Part II: Transport Model. J. Membr. Sci. **2000**, *166*, 63–69.
17. Daubert, T.E.; Danner, R.P. *Physical and Thermodynamic Properties of Pure Chemicals—Data Compilation*; Hemisphere: Pennsylvania, PA, 1989.
18. McClellan, A.L. *Tables of Experimental Dipole Moments*; Chevron Research Company, Rahara Enterprises: El Cerrito, CA, 1989; Vol. 3.
19. Dubois, M.; Gilles, K.A.; Hamilton, K.; Rebers, P.A.; Smith, F. Colorimetric Method for Determination of Sugars and Related Substances. Anal. Chem. **1956**, *28* (3), 350.
20. Whu, J.A.; Baltzis, B.C.; Sirkar, K.K. Nanofiltration Studies of Larger Organic Microsolutes in Methanol Solutions. J. Membr. Sci. **2000**, *170*, 159–172.
21. Roudman, A.R.; DiGiano, F.A. Surface Energy of Experimental and Commercial Nanofiltration Membranes: Effects of Wetting and Natural Organic Matter Fouling. J. Membr. Sci. **2000**, *175*, 61–73.
22. Flory, P.J. Phase Equilibria in Polymer Systems—Swelling of Network Structures. In *Principles of Polymer Chemistry*; Cornell University Press: Ithaca, NY, 1953; 576–577.
23. Van der Bruggen, B.; Schaep, J.; Wilms, D.; Vandecasteele, C. Influence of Molecular Size, Polarity, and Charge on the Retention of Organic Molecules by Nanofiltration. J. Membr. Sci. **1999**, *156*, 29–41.

Received April 2000
Revised July 2001

Downloaded At: 10:36 25 January 2011

Request Permission or Order Reprints Instantly!

Interested in copying and sharing this article? In most cases, U.S. Copyright Law requires that you get permission from the article's rightsholder before using copyrighted content.

All information and materials found in this article, including but not limited to text, trademarks, patents, logos, graphics and images (the "Materials"), are the copyrighted works and other forms of intellectual property of Marcel Dekker, Inc., or its licensors. All rights not expressly granted are reserved.

Get permission to lawfully reproduce and distribute the Materials or order reprints quickly and painlessly. Simply click on the "Request Permission/Reprints Here" link below and follow the instructions. Visit the U.S. Copyright Office for information on Fair Use limitations of U.S. copyright law. Please refer to The Association of American Publishers' (AAP) website for guidelines on Fair Use in the Classroom.

The Materials are for your personal use only and cannot be reformatted, reposted, resold or distributed by electronic means or otherwise without permission from Marcel Dekker, Inc. Marcel Dekker, Inc. grants you the limited right to display the Materials only on your personal computer or personal wireless device, and to copy and download single copies of such Materials provided that any copyright, trademark or other notice appearing on such Materials is also retained by, displayed, copied or downloaded as part of the Materials and is not removed or obscured, and provided you do not edit, modify, alter or enhance the Materials. Please refer to our Website User Agreement for more details.

Order now!

Reprints of this article can also be ordered at
http://www.dekker.com/servlet/product/DOI/101081SS120002217