



# ***Organophilic nanofiltration to separate solvent mixtures***

Dipl.-Ing. L. Wessely

o.Univ.-Prof. Dr. W. M. Samhaber

Institute of Process Engineering, Johannes Kepler University Linz

## Abstract

Main goal of this investigation is a comparison of different commercially available solvent resistant membranes in regard to the possibilities to separate specific mixtures of organic liquids by solvent resistant nanofiltration (SRNF, ONF). It could be found that all the used binary mixtures were basically separable but with quite different retention coefficients and fluxes. One can draw the conclusion that in principle SRNF can be applied to recycle used or purify contaminated solvents but the achievable performance lies within a broad range. For systems with fairly small separation coefficients a combination (hybrid system) of SRNF with conventional techniques (distillation) can be seen as possible expedient.

## Introduction

Based on the progress in organophilic nanofiltration (SRNF, ONF) during the last few years this technique seems to be one of the most promising to replace conventional separation or at least complement it <sup>[1,2,3,4]</sup>. In contrary to the thermal separation processes (distillation, extraction, adsorption) SRNF holds the benefit of sparing phase transition and therefore increasing energy efficiency, thus reducing CO<sub>2</sub> emission.

Especially mixtures which demand high energy input using conventional techniques or even resist them are predestined to be processed using solvent resistant nanofiltration. Short term investigations of different groups have shown that the separation performance of selected membranes is quite different concerning the solvent systems examined. <sup>[5,6,7,8]</sup>

In this investigation the focus is directed at the separation of organic solvent mixtures without dissolved species. Solvent resistant membranes are applied in laboratory tests to separate different organic solvents (acetonitrile, benzene, cyclohexane, ethanol, ethyl acetate, toluene) in binary mixtures of different compositions. Some of the mixtures consist of solvents with quite similar physical properties (benzene/cyclohexane) while others are rather different (ethanol/toluene).

## Experimental

Commercially available solvent stable nanofiltration membranes of different manufacturers are used in this investigation. The experiments were conducted over weeks to ensure the constancy of the obtained data (especially the reproducibility of the retention coefficients and fluxes). All the chemicals had at least p.A. grade and were purchased by different suppliers.

### *Chemicals*



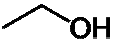
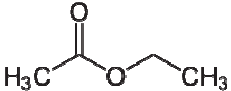
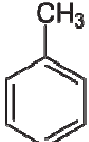
The different chemicals used for his investigation, their purity and the respective source are found in table 1.

table 1 - used solvents and combinations

	No.	purity	manufacturer	combined with
Acetonitrile	1	HPLC grade	J.T.Baker	2
Benzene	2	p.A. (>99,9%)	Merck	1, 3
Cyclohexane	3	Suprasolv	Merck	2
Ethanol	4	p.A. (> 99,9%)	Merck	5, 6
Ethyl-Acetate	5	> 99,9%	J.T.Baker	4
Toluene	6	p.A. (> 99,9%)	VWR	4

Common organic solvents were used for the investigations on binary mixtures and their separability. The used pairs and their properties can be found in table 3. On the one hand there are binary mixtures found with components of quite similar characteristics (molar mass, density,...) and on the other hand ones with quite different features concerning physical and/or chemical properties of the ingredients (table 3).

table 2 - properties of the used chemicals <sup>[9]</sup>

	structure	molecular mass [g/mol]	boiling point [°C]	density [g/cm <sup>3</sup> ]	viscosity [mPas]	dipole moment [D]
Acetonitrile	$\text{H}_3\text{C}-\text{C}\equiv\text{N}$	41,05	81,6	0,79	0,34	3,92
Benzene		78,11	80,0	0,88	0,65	0
Cyclohexane		84,16	80,7	0,78	0,98	0
Ethanol		46,07	78,2	0,79	1,07	1,69
Ethyl Acetate		88,11	77,1	0,9	0,46	1,78
Toluene		92,14	110,6	0,87	0,59	0,37

Criterion for the chosen mixtures was their ability to form azeotropes what limits the separability by conventional (thermal) separation processes. The used azeotropes and their properties can be seen in table 2.

table 3 - used azeotropes

	mass ratio	boiling point [°C]	density [g/cm <sup>3</sup> ]
Acetonitrile/ Benzene	0,34/0,66	73,0	0,85
Benzene/ Cyclohexane	0,55/0,45	77,8	0,84
Ethanol/ Toluene	0,68/0,32	76,7	0,82
Ethanol/ Ethyl acetate	0,32/0,68	72,0	0,86

### Membranes

Five commercially available membranes of different manufacturers, with different properties and made of different materials were used for the examinations. One main aspect was the long term solvent stability which was analysed by storing the membranes in the respective solvent for at least six weeks before starting the experiments. The experiments were then conducted over weeks to check the stability of the membranes' performance.

The main properties of the membranes as given by the manufacturer are shown in table 4. All of them were basically of polymeric nature with anisotropic polyimide based membranes obtained from Evonik and MET and silicon based membranes obtained from GMT/Borsic and Koch. The manufacturer's information about the MWCO (molecular weight cut-off) was spared for this investigation as it is normally determined in aqueous surroundings and therefore can't be compared with or transferred to organic solvent systems [10].

table 4 – used membranes

membrane	manufacturer	nature	material of active layer	applied pressure [bar]
P-84	Evonik	organophilic	Polyimide	20/30
STARMEM 122	(MET)	organophilic	Polyimide	20/30
ONF-1	GMT/Borsic	organophilic	PDMS	20/30
ONF-2	GMT/Borsic	organophilic	PDMS	20/30
MPF-50	Koch	organophilic	PDMS	20/30

### Set-up

The used set-up can be seen in figure 1. It basically consists of four membrane cells which are operating in a cross flow mode. Each membrane cell contains a membrane with an active area of 50 cm<sup>2</sup>. The feed tank featured a volume of approximately 1,8 L and the applied transmembrane pressure was chosen to be 20 or 30 bars depending on the different systems and their permeabilities and fluxes. The temperature was held constant at 20°C using a double pipe heat exchanger located in the retentate pipeline.

The permeabilities and fluxes were obtained by measuring the mass of permeate which was separated within five minutes. Every reading point was done several times to gain a reliable average value.

For every combination of solvents not only the azeotropic mixture was investigated but the system over the whole range of composition. The membranes were not changed within the investigation of one system.

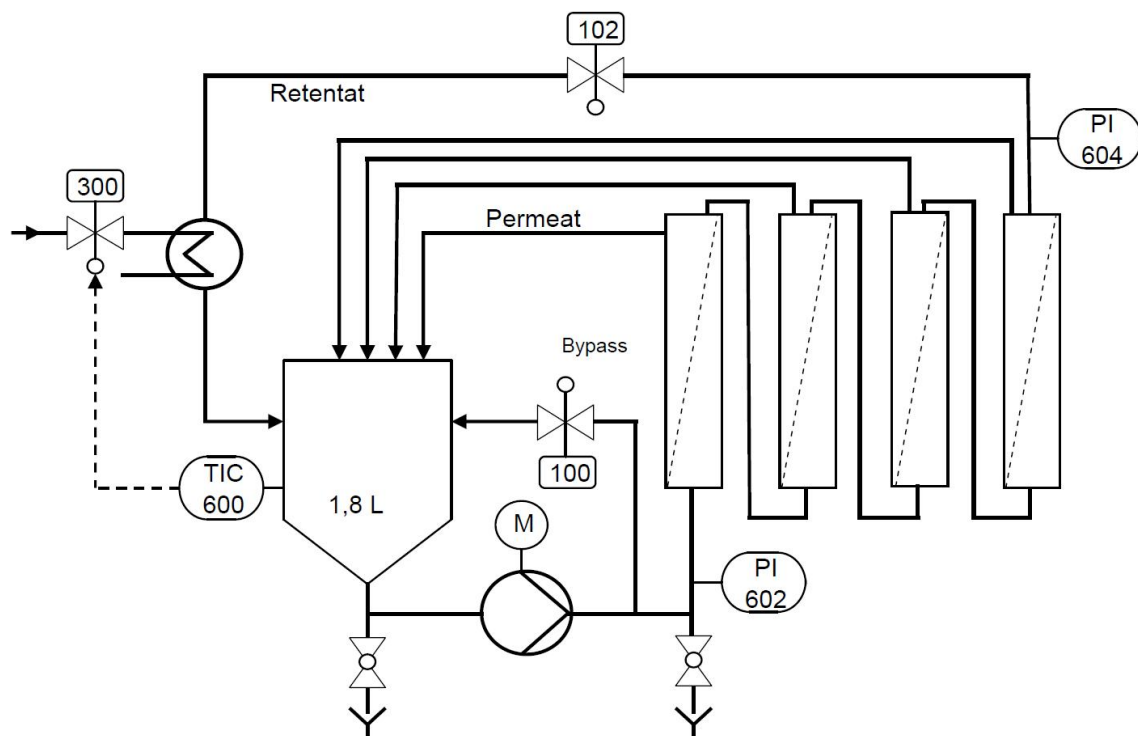


figure 1 - Set-up of the membrane comparison equipment

### *Analytics*

Due to different diffusion velocity through the polymers of the used membranes the components of the mixtures were found in different ratios in the feed/retentate and permeate. There are several possibilities to describe these effects. For this work the so called separation factor  $\alpha$  and the retention  $R$  were used. As seen in equation (1) this coefficient is defined as fracture of permeate and retentate composition with  $y_A$  and  $y_B$  as permeate ratios,  $x_A$  and  $x_B$  as retentate ratios and both in amounts of moles, mass or volume.

$$\alpha_{A/B} = \frac{y_A / y_B}{x_A / x_B} \quad (1)$$

Usually the separation factor is chosen to reach a value bigger than one. This means that component A permeates preferentially. A separation factor of exactly one means that the mixture is not separable at all.

The retention  $R$  of one component through a membrane is defined by equation (2)

$$R = 1 - \frac{y_A}{x_A} \quad (2)$$

with  $y_A$  meaning the concentration of component A in the permeate and  $x_A$  meaning the concentration of component A in the retentate, both in mass fraction.

Beneath the retention the normalized retention is found to describe the possibility to separate mixtures using membrane based separation processes. It is defined according to equation (3)

$$R_{norm} = \frac{R}{flux} \quad (3)$$

To determine the composition of feed and permeate an HP5890 series II gas chromatograph with a J&W Scientific column (DB-XLB, 30m, 0,25 $\mu$ m film) and a mass selective detector (HP 5971 MSD) was used. The method of external standards was applied to determine the exact composition of the samples.

## Results

### Acetonitrile/Benzene

The membrane fluxes of the different compounded mixtures of acetonitrile and benzene are found in figure 2 (left axis). It can be seen that there are differences in fluxes and differences in the development of the fluxes as some of them increase (ONF-1, ONF-2) with increasing amount of benzene and others decrease (P-84) with rising benzene.

On the right axis of figure 2 one can find the normalized retention of the different mixtures. The azeotropic composition (66 weight% benzene) is marked in red.

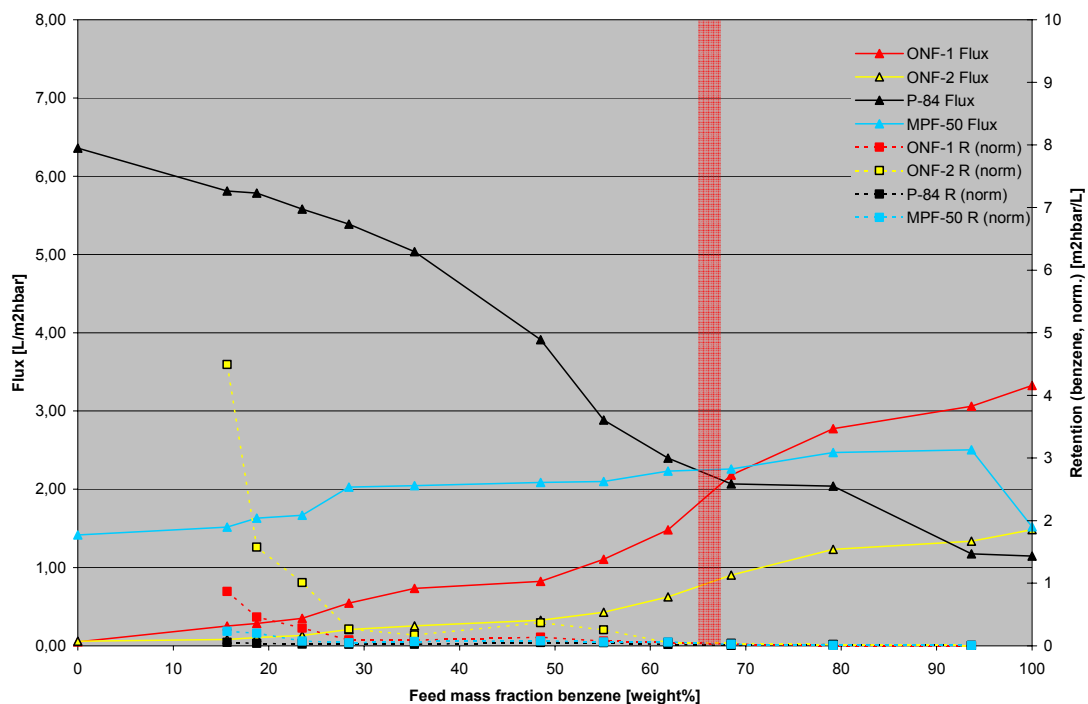


figure 2 - fluxes and normalized retention of the different acetonitrile/benzen mixtures

### Benzene/Cyclohexane

The membrane fluxes of the different mixtures consisting of benzene and cyclohexane can be seen in figure 3 (left axis). Fluxes of the various membranes differ and there are also differences in the development of the fluxes as some of them decrease (ONF-1, MPF-50) with increasing amount of cyclohexane while the others remain constant.

On the right axis the normalized retention of the different mixtures can be found. The azeotropic composition (45 weight% cyclohexane) is marked in red.

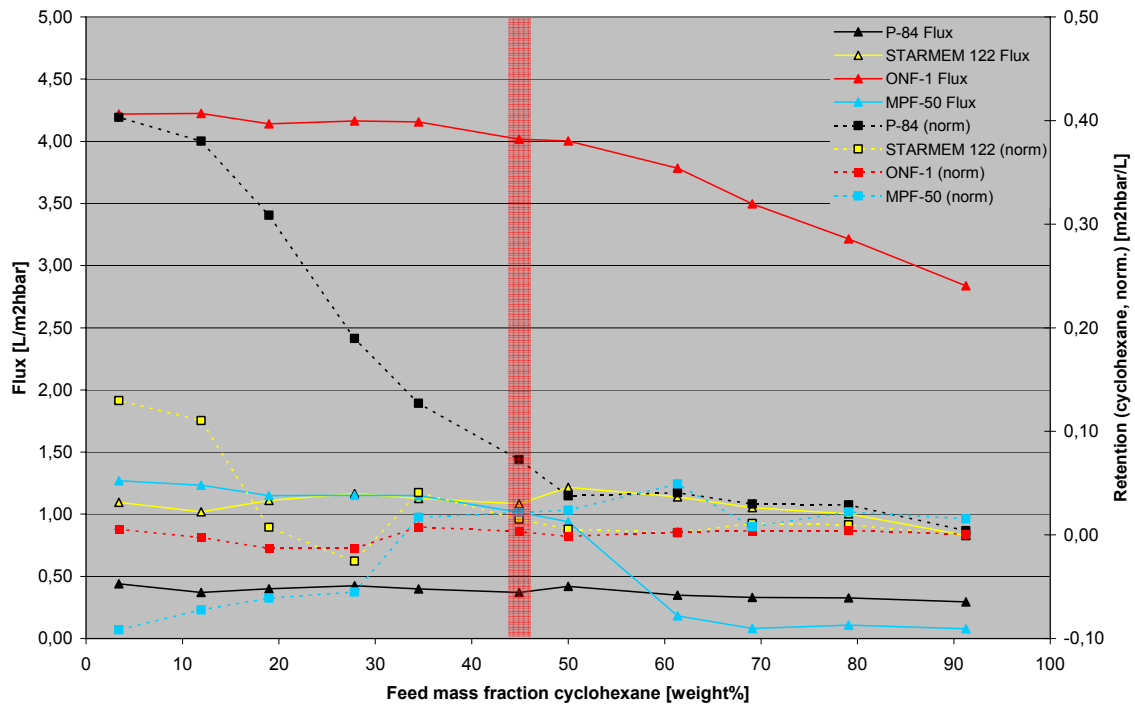


figure 3 - fluxes and normalized retention of the different benzene/cyclohexane mixtures

### Ethanol/Toluene

The differences in fluxes (left axis) and normalized retention (right axis) of the used ethanol/toluene mixtures can be seen in figure 4. As the normalized retentions are quite stable over the range of composition, the fluxes of some membranes (ONF-1, MPF-50) decrease with increasing amount of ethanol while the others increase slightly. The azeotropic composition (68 weight% ethanol) is marked in red.

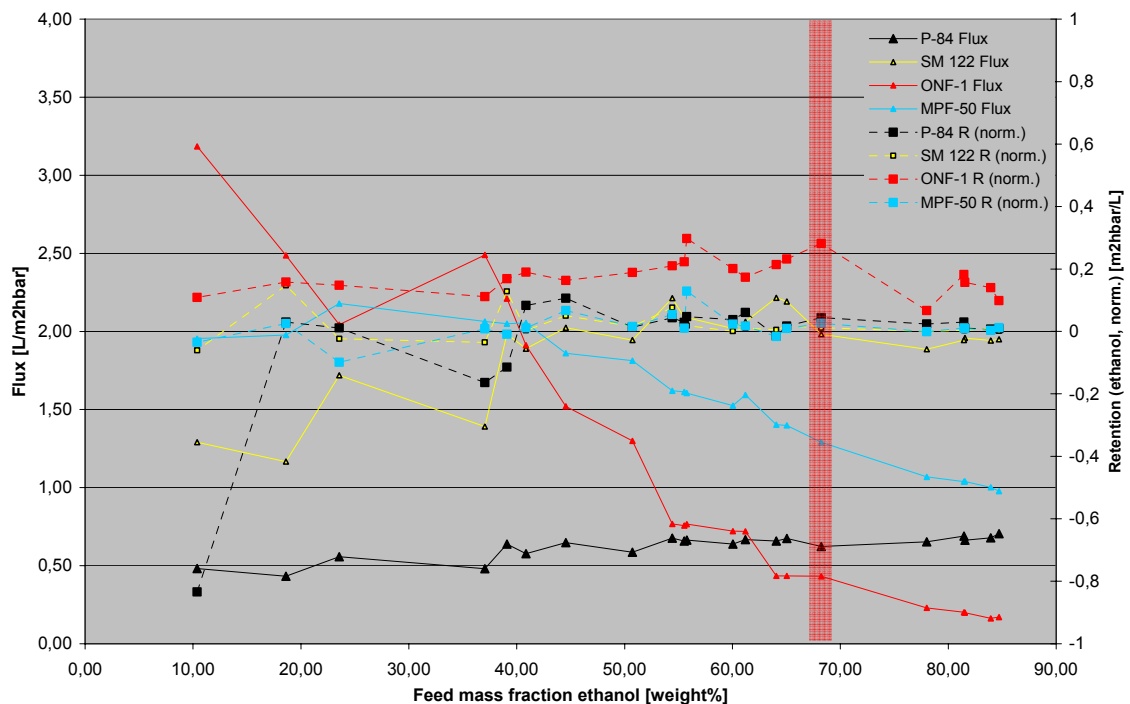


figure 4 - fluxes and normalized retention of the different ethanol/toluene mixtures



### Ethanol/Ethyl acetate

One can see the varieties in fluxes (left axis) and normalized retention (right axis) of the used ethanol/ethyl acetate mixtures in figure 5. As the normalized retentions are quite the same over the range of composition, the fluxes of more or less all membranes (except P-84) decrease with increasing amount of ethanol. The azeotropic composition (32 weight% ethanol) is marked in red.

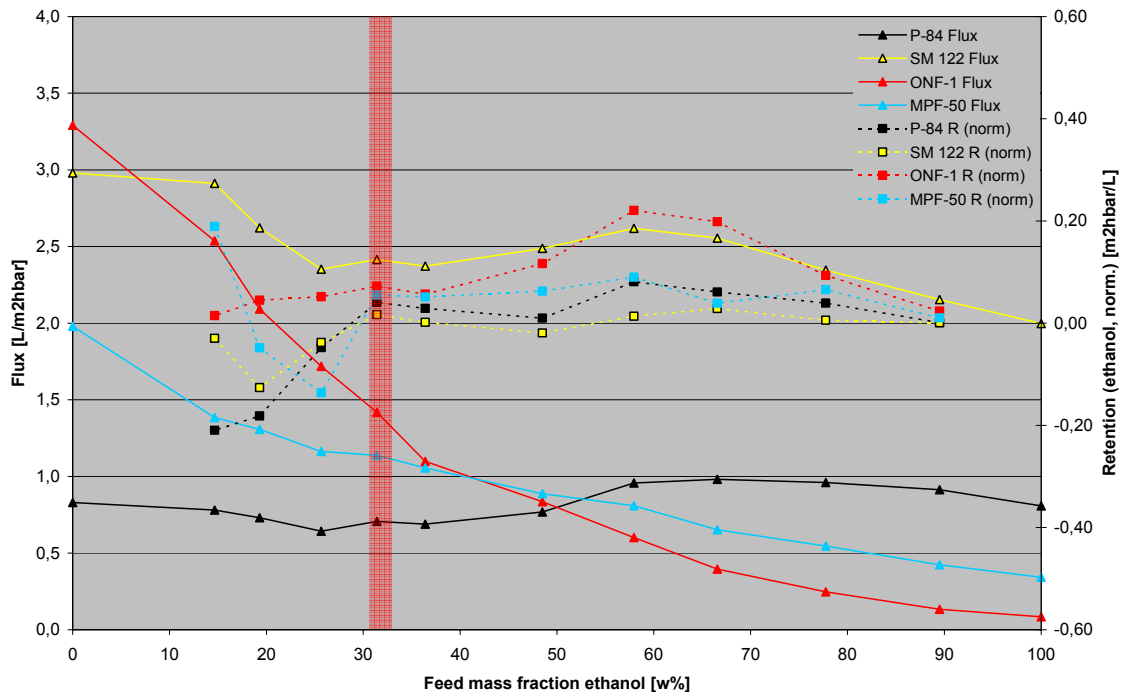


figure 5 - fluxes and normalized retention of the different ethanol/ethyl acetate mixtures

### Discussion

The first system (figure 2) of acetonitrile/benzene showed a quite weak separability with the used membranes. The quite high values for mixtures of low benzene contents have to be considered discordant values as they result from the very low membrane fluxes (see equation (3) where the flux is found in the denominator). Normalized retention for the azeotropic point was found in a range slightly above zero (depending on the membrane) so the system was basically separable but with poor quality and therefore the need of a multi-stage process which will not be feasible in a technical application.

The second mixture, consisting of benzene and cyclohexane (figure 3) showed quite various fluxes and retentions. Some of the membranes had considerable fluxes (ONF-1) but more or less no separation performance (as the retention was close to zero) while other had relatively low fluxes but a separation with retentions about fifteen percent. Regarding the azeotropic mixture the P-84 membrane was best performing although the normalized retention was just about 10% and the corresponding flux lay below 0.5 [L/m²hbar].

Figure 4 shows the separation data for the system consisting of ethanol and toluene. One can see that there are big differences in the performance of the used

membranes as normalized retention in a range between zero and more than thirty percent can be reached. The same is found for the fluxes which vary between 0.5 and 2 [L/m<sup>2</sup>hbar]. At this particular system the azeotropic point is of special interest. The azeotropic mixture consisting of 68 weight% ethanol and 32 weight% toluene can be separated with a normalized retention of nearly 30 % and a flux of about 0.5 [L/m<sup>2</sup>hbar] using a GMT ONF-1 membrane. Although this performance is not sufficient to provide a total separation using SRNF, it gives the possibility to combine SRNF and conventional techniques (e.g. distillation) to form a hybrid process and separate mixtures of the two solvents with higher efficiency, less energy consumption and less CO<sub>2</sub> emission.

The system consisting of ethanol and ethyl acetate (shown in figure 5) is similar to the system of ethanol/toluene in relation to its separability using an ONF-1 membrane. Normalized retention of 20 % and more and fluxes between 0.5 and 3 [L/m<sup>2</sup>hbar] are found. A really interesting fact for this system occurs using MPF-50 or P-84 membranes. It can be seen that those membranes offer retention for ethyl acetate in compositions with a low amount of ethanol. When the ratio changes to higher amounts of ethanol these membranes provide retention for the ethanol as well. The retention characteristics more or less depend on the composition of the feed. This gives the possibility to purify either one or the other component.

The investigation showed that there are considerable differences not only in the fluxes itself but also in their constancy over the range of composition. Some of the membranes showed more or less constant fluxes regardless of the feed composition while others offered an increase or decrease depending on the amount of the solvents. In some cases this could be correlated to the separation performance as expected. A good flux but a bad normalized retention can be seen in the case of benzene/cyclohexane and the ONF-1 membrane while the same system showed a quite low flux but good separation performance with the P-84 membrane.

## Conclusion

In summary it can be stated that the organophilic nanofiltration is capable of separating the used organic solvent mixtures as all used membranes were stable over the entire period of experiments and fluxes/retentions were actually constant. The quality of the separation or more precisely the quality of the obtained permeates is quite different as the normalized retention is found to be in a range between almost zero and up to 30 %. There are systems which can be separated more effectively than others and there are membranes which are more efficient than others.

The cause for the quite different results can be found in differences in structure and properties (physical / chemical) of the used solvents (as seen in table 2) and in the different properties and materials of the membranes (table 4). There was no pattern found in the course of this investigation to predict the best match for various solvent systems and membranes. This could be possible topic of ongoing research as could be the membrane modification to custom-fit membranes to specific separation problems or solvent systems.

## References

---

- [1] D. Bhanushali, S. Kloos, C. Kurth, D. Bhattacharyya, *Journal of Membrane Science* 2001, 189, 1.
- [2] K. Ebert, J. Koll, M.F.J. Dijkstra, M. Eggers, *Journal of Membrane Science* 2006, 285, 75.
- [3] P. Silva, S. Han, A. G. Livingston, *Journal of Membrane Science* 2005, 262, 49.
- [4] D.F. Stamatialis, N. Stafie, K. Buadu, M. Hempenius, M. Wessling, *Journal of Membrane Science* 2006, 279, 424.
- [5] L.P. Raman, M. Cheryan, N. Rajagopalan, *Journal of American Oil Chemists' Society*, 1996, 73, 219–224.
- [6] S.S. Koseoglu, J.T. Lawhon, E.W. Lusas, *Journal of American Oil Chemists' Society*, 1990, 67, 315–322.
- [7] M. Schmidt, S. Mirza, R. Schunert, H. Rodicker, S. Kattanek, J. Malisz, *Chemie Ingenieur Technik*, 1998, 71, 199.
- [8] X.J. Yang, A.G. Livingston, L. Freitas dos Santos, *Journal of Membrane Science*, 2001, 190, 45–55.
- [9] R. Lide, *CRC Handbook of Chemistry and Physics*, 78th edition, 1997, New York.
- [10] X.J. Yang, A.G. Livingston, L. Freitas dos Santos, *Journal of Membrane Science*, 2001, 190, 45.