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A comparison of nanofiltration with aqueous and organic solvents

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Abstract

This paper reports rejection of organic solutes with molecular weight (MW) in a range of 180–600 in aqueous and organic solvents through several commercial solvent resistant nanofiltration membranes (SRNF). The organic solutes investigated include charged and neutral molecules and the selected solvents are water, water–methanol mixture, methanol, ethanol, acetone and ethyl acetate. The higher rejection in water than in organic solvents was observed for Desal-DK, MPF-44 and STARMEM^{TM} series membranes. However, MPF-50 showed "uncommon" rejection characteristics of higher rejection in organic solvents (methanol, ethanol and acetone) than in water for neutral molecules compared to charged molecules. The rejection was analysed in accordance with the charge effect and hydration/solvation mechanism.

Keywords: Nanofiltration; Organic solvents; Rejection

1. Introduction

In recent years, nanofiltration (NF) has been applied in organic solvents more and more widely [1–15]. It has been observed that the NF performance is much less predictable with organic solvents than with aqueous solutions [1–5]. Whu et al. [1] studied NF of larger organic microsolutes safranin O, brilliant blue R and Vitamin B_{12} in methanol solutions and reported that the manufacturer-specified molecular weight cut-off (MWCO) is an insufficient indicator of separation capabilities of the membranes. Yang et al. [2] observed significantly lower rejections in organic solvents than in water for a wide range of commercial polymeric NF membranes including MPF membranes (MPF-44 and MPF-60) and Desal membranes (Desal-5 and Desal-DK). Van der Bruggen et al. [3] reported the lower rejection in organic solvents (ethanol and *n*-hexane) than in water for N30F, NF-PES-10, MPF-44 and MPF-50 and Geens et al. [4] observed lower rejection of raffinose in methanol than in water for Desal membranes and N30F. After demonstrating that the membranes were still stable after exposed to the organic solvents in which lower rejections than in water were observed, Yang et al. [2] suggested that the higher rejection in water is likely due to larger size of the solutes in water via the coordination of water molecules with the solute molecules. Van der Bruggen et al. [3] proposed an assumption that the enhanced mobility of polymeric chains in organic solvents increased the effective membrane pore size, thus leading to lower rejection in organic solvents than in water.

It appears that the lower rejection in organic solvents than in water is a common belief in NF. However, significantly higher rejection of raffinose in methanol than in water for MPF-50 was recently observed by Geens et al. [4], who commented that Yang et al.'s observation that rejections are generally lower in organic solvents than in water is applicable to hydrophilic membranes only but not to hydrophobic membranes. They proposed a "hydration/solvation" mechanism to explain higher rejection of raffinose in methanol than in water for hydrophobic MPF-50 and lower rejection in methanol than in water for hydrophilic Desal-DK and N30F. MPF-50 is highly hydrophobic and thus the interaction with water molecules is very low (hydration of membrane is almost non-existing); solvation of the membrane pore wall with methanol decreases the effective pore size, leading to higher rejection in methanol than in water. Desal-DK and N30F are hydrophilic and the hydration of the membrane polymer is more important than solvation, leading to smaller effective pore size in water than in organic solvents. However, the hydration/solvation mechanism does not hold for a hydrophilic inorganic silica–zirconia NF membrane, which showed significantly higher rejection of PEG600 in methanol than in water [5].

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It is noted that Geens et al.'s "hydration/solvation" mechanism was based on the observation of higher rejection of one solute (raffinose) in methanol for one hydrophobic membrane (MPF-50). Therefore, further experimental evidences for a variety of membranes and organic solvents are required to support this mechanism. Yang et al.'s work was lack of rejection data in water and organic solvents for the neutral molecule solvent blue 35, which is insoluble in water. Van der Bruggen et al.'s assumption was based on the rejections of different solutes dissolved in water and organic solvents: 2,2′-methylenebis-(6-*tert*-butyl-4-methyl phenol) (MW 341) dissolved in ethanol and *n*-hexane compared to maltose (MW 342) dissolved in water; DL-alpha-tocophenol hydrogen succinate (MW 531) dissolved in ethanol and *n*-hexane compared to raffinose (MW 504) dissolved in water. Since the use of MW as a measure of molecular size, in particular for different solutes dissolved in different solvents, could be unreliable and different solutes may interact with the membrane differently, further experimental evidences are also required to support Yang et al.'s observation [2] and Van der Bruggen et al.'s assumption [3]. Therefore, in this study we investigated the rejection of the same molecules dissolved in water and different organic solvents for a variety of polymeric SRNF membranes.

2. Experimental

2.1. Membranes and membrane pretreatment

Table 1 shows membrane properties. Desal-DK is polyamide and STARMEM™ series membranes are polyimide. MPF membranes are polydimethylsiloxane (PDMS)-based. Desal-DK membrane and STARMEM™ series membranes (120, 122, 228 and 240) were supplied in a "dry" form. MPF-44 and MPF-50 were supplied in a "wet" form in a preserving solution of 0.7% Roccal and 50% ethanol/water, respectively. Subsequently, 50% methanol/water and 50% ethanol/water are referred to as 50% methanol and 50% ethanol for convenience. The membrane was cut in a disc of 49 mm diameters. In a previous study [6], it has been shown that membrane pretreatment has significant effects on the performance of Desal-DK and STARMEM™ membranes and 50% ethanol is a moderate treatment solvent. In addition, MPF-50 is preserved in 50% ethanol and showed "uncommon" rejection properties (higher rejection in methanol than in water). Therefore, in this study we employ 50% ethanol to pre-treat the membranes (soaked for 3 days).

2.2. Solvents

Four organic solvents, methanol, ethanol, ethyl acetate and acetone (AR grade), were selected for this study as these solvents are commonly used in pharmaceutical and chemical industries. The solvents were obtained from Beijing Chemicals (Beijing, China). High purity water (18 MΩ cm) was also tested for comparison. Table 2 lists the physical properties of these solvents used in this work.

Table 1
Membrane properties (MWCO and hydrophilicity/hydrophobicity) provided by the manufacturers

Manufacturer	Membrane type	MWCO	Nature
Osmonics	Desal-DK	300[a]	Hydrophilic
KOCH	MPF-44	200[b]	Hydrophilic
	MPF-50	700[c]	Hydrophobic
W.R. Grace[d]	STARMEM™ 120	200	Hydrophobic
	STARMEM™ 122	220	Hydrophobic
	STARMEM™ 228	280	Hydrophobic
	STARMEM™ 240	400	Hydrophobic

[a] Based on rejection of pesticides in water.
[b] Based on rejection of glucose in water.
[c] Based on rejection of Sudan IV (MW 384) dissolved in ethyl acetate.
[d] STARMEM™ is a trademark of W.R. Grace & Co. (Colombia, USA) and the membranes were purchased from Membrane Extraction Technology (MET) Ltd. (London, UK). The MWCO was based on rejection of normal alkanes dissolved in toluene.

Table 2
Physical properties of the solvents at 20 °C [16]

Solvent	MW (g/mol)	Viscosity ($\times 10^{-3}$ Pa s)	Surface tension (mN m^{-1})	Dielectric constant
Water	18	0.89	72.75	80.1
Methanol	32	0.59	22.55	32.70
Ethanol	46	1.17	22.27	24.55
Acetone	58	0.32	23.70	20.7
Ethyl acetate	88	0.45	23.75	6.02

2.3. Solutes

The principal characteristics of the solutes tested in this study are given in Table 3, and the structures of some solutes are presented in Fig. 1. The purity of all the solutes is greater than 95%. Crystal violet (dye content >95%) was purchased from Amresco (Cleveland, OH, USA). Glucose, maltose, acid blue and puerarin were obtained from Beijing Chemicals (Beijing, China). Soybean daidzin and genistin were kindly provided by the Centre for Natural Product Separation of Beijing University of Chemical Technology. The solubility of soybean daidzin in different solvents is given in Table 4.

Table 3
Principal characteristics of the solutes used

Solutes	Crystal violet	Acid blue 25	Soybean daidzin	Puerarin	Soybean genistin	Glucose	Maltose
MW	408	411	416	416	432	180	342
Charge[a]	Positive	Negative	Neutral	Neutral	Neutral	Neutral	Neutral

[a] The charge status of the solutes is referred to water as the solvent.