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Performance of Nanofiltration Membranes in Ethanol

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Abstract: Several nanofiltration membranes were tested for flux and rejection of selected solutes in ethanol. The membranes were initially conditioned with pure solvent containing increasing concentrations of ethanol. Flux decreased with increase in ethanol concentration and increased at higher temperatures and pressures. The type of solute had an influence on membrane rejection profiles. The DK membrane showed increasing rejection of polyethylene glycols (PEG) dissolved in ethanol from 29% at a molecular weight (MW) of 200 to 80% at MW 1000. However, the MW of sugars and lipids had little or no effect on rejection with the DK membrane; their rejection averaged 87%. In contrast, the TFC-SR1 membrane showed higher rejections with higher MW compounds: lipid rejection increased from 19% to 71%, sugars from 35% to 85%, and lipids from 77% to 89%. The TFC-SR2 membrane was much more open and showed the lowest rejections of all these compounds. Flux generally showed opposite trends, with the DK showing the lowest flux and the SR2 the highest.

Keywords: Nonaqueous, nanofiltration, lipids, sugars, PEG, corn oil, ethanol

INTRODUCTION

Studies of membrane use with organic solvents have continued with the promise that successful separations of solutes in nonaqueous systems would

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open the door to a wide range of applications. New membranes have been developed for their use in these systems, though the characterization and performance of the membranes with any particular nonaqueous system are left up to the user of the membranes. There is usually a difference in solute rejection and flux in organic solvents when compared with performance in aqueous environments (1–8). In most cases, rejection of the same molecule in an organic solvent is significantly lower than in aqueous solution for the same membrane (2, 3, 7). In addition to solute size and shape being important, the affinity of the solvent and the solute for the membrane material is also important (8). Flux with nonaqueous systems through membranes containing hydrophilic sites would be considerably lower than water due to the limited (alcohols) and no (alkanes) hydrogen bonding capability of the organic solvents (1). The permeability is influenced by these factors as well as molecular size and hydrophobicity.

The behavior of the membranes in organic solvents has been described using several different models with varying degrees of success, taking into account characteristics of the solvent such as viscosity, molar volume, and surface tension as well as characteristics of the membranes and solutes (1–5). Swelling and deformation of the membranes when exposed to organic solvents is common and is dealt with by conditioning the membranes through gradual solvent change (6, 7). Once conditioned, the membrane's performance may be significantly different from that in an aqueous system and may have to be described for each individual solute-solvent-membrane system.

The nonaqueous application being considered in our laboratory is in the vegetable oil industry. Membrane technology may be substituted into nearly all stages of vegetable oil refining (9–13). Potential applications include degumming by ultrafiltration (UF), solvent recovery by reverse osmosis/nanofiltration (RO/NF), deacidification by NF, dewaxing by microfiltration (MF), recovery of hydrogenation catalyst by MF, nitrogen production for packaging by gas separation (GS), and wastewater treatment by UF/NF/RO. The advantages include separating molecules in a customized manner, minimization of thermal damage, recycling solvents, lower emissions, lower energy consumption, decreased oil losses, and reduction in bleaching earth requirements.

There is increasing interest in using less toxic and renewable solvents such as ethanol for the extraction of oil instead of petroleum-derived hexane. However, low-cost and low-energy methods will have to be used instead of evaporation or distillation to recover and recycle the solvent to compensate for ethanol's higher latent heat and higher boiling point. We focused on extraction of oil from corn (maize) using absolute ethanol followed by nanofiltration (NF) and/or reverse osmosis (RO) for recovering the ethanol (13, 14).

This paper describes the screening and characterization of selected NF and RO membranes in terms of their ability to reject various solutes dissolved in absolute ethanol. These solutes were polyethylene glycols (PEG), sugars and lipids of various known molecular weights (MW) to

simulate crude corn oil components that are co-extracted with ethanol, such as free fatty acids, phospholipids, carbohydrates, pigments, waxes, and insolubles (15). Pure corn oil is primarily triacylglycerols, with a molecular weight of approximately 900 g per mole, varying with the particular fatty acid side chains. The selection of a membrane for the concentration of corn oil in ethanol extracts will depend on the flux and rejection of selected components.

MATERIALS AND METHODS

Membranes

The membranes listed in Table 1 were evaluated in initial trials. All were hydrophilic flat sheet membranes, except for the MPF-60 which was a hydrophobic flat sheet, and the Hydranautics 7450 flat sheet which had an unknown degree of hydrophilicity. Screening experiments were carried out in a SEPA-ST model membrane test cell (Osmonics Inc., Minnetonka, MN) with a magnetic stirrer and a nitrogen gas cylinder to provide pressure. The cell is capable of withstanding pressures up to 6.9 MPa (1000 psig) and holds a 5-cm-diameter membrane disc (effective membrane area of 17.35 cm^2). The test cell was immersed in a water bath to control temperature.

The membrane coupons were conditioned by methods described by Shukla and Cheryan (6) and Tsui and Cheryan (7). The membrane coupon was exposed to an increasing concentration of ethanol in stages. The coupon was first rinsed under running deionized water and then soaked in the first solvent (e.g., 10% ethanol) overnight. It was then placed in the test cell, the cell was filled with 150–200 mL of the 10% ethanol solvent and

Table 1. Membranes screened during initial trials

Membrane	MWCO (Da) or NaCl rejection[a]	Manufacturer
NF-45	200 Da	Dow-FilmTec
SW-30	99.2% NaCl rej.	Dow-FilmTec
MPF-44	250 Da	Koch
MPF-60	400 Da	Koch
TFC-S	60% NaCl rej.	Koch
TFC-SR1	88% NaCl rej.	Koch
TFC-SR2	95% NaCl rej.	Koch
DK	300 Da	GE-Osmonics
G-5	$<$1000 Da	GE-Osmonics
7450	NF	Hydranautics

[a]Manufacturer's specifications.

the cell, and its contents were allowed to reach the temperature of the water bath. The cell was pressurized to the desired pressure (1.38, 2.76, or 4.14 MPa) and the solvent permeated until the flux had reached a steady value. The membrane was removed and placed in the next higher ethanol concentration (e.g., 20% ethanol) overnight and the procedure repeated until the membrane had been exposed to 100% ethanol. Conditioning was at ambient temperature (22°C) and pressure of 1.38 MPa.

Materials

Potable ethanol (anhydrous, 200 proof containing 0.1–0.2% water as determined by Karl-Fischer titration) was obtained from Aaper Alcohol and Chemical Company (Shelbyville, KY). Ethanol and deionized water were microfiltered through a 0.2 μm filter for use in all experiments. Ethanol solutions were prepared as a binary mixture on a volume basis as necessary.

Rejection profiles of the membranes were determined using polyethylene glycols (PEG), sugars, and lipids purchased from Sigma-Aldrich (St. Louis, MO). The molecular weights (MW) of PEG were 200, 400, 600, and 1000 g/mol. They were made up to 10 g/L in absolute ethanol. Data were taken at 2.76 MPa and 22°C. The rejection profiles were developed with sugars and lipids based on anticipation of their presence in future applications. PEG's were used based on their availability and common use as molecular weight markers.

The sugars were prepared in ethanol at a concentration of 200 ppm. They were glucose (MW 180), maltose (MW 342), maltotriose (MW 504) and maltotetraose (MW 666). Rejection and flux were measured at 1.38 MPa and 24°C.

The lipids were oleic acid (MW 282 at a concentration of 2000 ppm), monoolein (MW 352, 760 ppm), diolein (MW 621, 400 ppm), and triolein (MW 885, 560 ppm). Flux and rejections were measured at 1.38 MPa and 24°C. Commercially refined corn oil was purchased from a local grocery store and made up to 4 g/L in ethanol. Flux and rejections were measured at 1.38 MPa and 24°C.

Analytical Methods

Polyethylene glycols were measured by total organic carbon (TOC) analyzer. Samples were dried in an 80°C oven overnight and reconstituted in 10 mL water prior to TOC analysis. Sugars were measured by HPLC using a Supelcogel Ca carbohydrate column isocratically with a refractive index detector. The column temperature was 80°C and the mobile phase was deionized water at a flow rate of 0.6 mL/min. Concentration of the sugars was determined by using a standard curve created with solutions of different sugars in water. Lipid and corn oil concentrations were determined

gravimetrically. Liquid samples were placed in fume hood while the solvent evaporated, and the desolventized residue was dried in an oven at 103°C to remove the moisture. The weight of the residue after drying and the volume of the original liquid sample were used to determine the concentration.

Flux is expressed as the volume of permeate (L) per unit membrane area (m^2) per unit time (h) or LMH. Rejection (R) is defined as ($1 - C_P/C_R$) where C_P and C_R are the concentrations of solute in permeate and retentate, respectively.

All measurements were performed in duplicate. An independent estimate of error was determined for flux through each membrane with absolute ethanol and was used to distinguish the membranes when selecting a few for further study. Error bars on all graphs represent 95% confidence intervals.

RESULTS AND DISCUSSION

The results of conditioning are shown in Fig. 1 for selected nanofiltration membranes. All of them showed a decline in flux with increasing ethanol concentration, similar to what has been observed by others (6, 7). The membranes that had a higher flux in water (TFC-S, SR1, SR2, and 7450) had steeper initial decreases in flux than other membranes. These results are in agreement with other conditioning studies done in ethanol on several membranes (7).

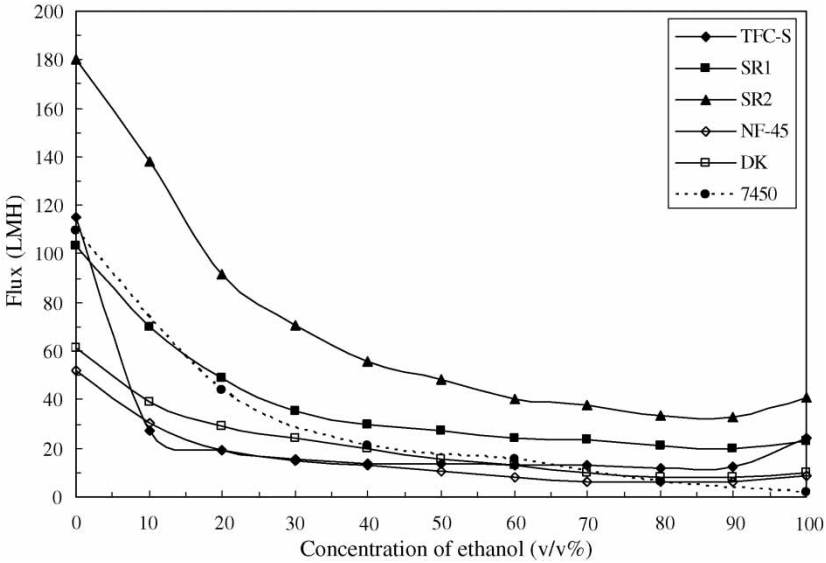

Figure 1. Conditioning of nanofiltration membranes with increasing concentrations of ethanol. Effect of ethanol concentration on flux at 22°C and 1.38 MPa.

Flux of the MPF-44 and MPF-60 membranes between 80% and 100% ethanol fluctuated greatly and were not considered further in this study. Of the 10 membranes screened, 3 were chosen for further studies based on their high flux in pure ethanol and prior experience in separating ethanol-soluble solutes (16): DK, SR1, and SR2.

Flux can also be expressed in terms of the Darcy convective transport model

$$J_v = \frac{L_p P_T}{\mu}$$

where J_v is the solvent flux, L_p is the permeability coefficient of the membrane, P_T is the transmembrane pressure, and μ is the viscosity of the permeate. Using this equation, a plot of flux vs. the reciprocal of viscosity should be linear if the membranes were unaffected by the solvent. A nonlinear plot would indicate that the solvent had an effect on the membrane, e.g., swelling of the polymer, dilation of membrane pores, pore dehydration or deformation (1, 4–7, 17).

Darcy plots of the three membranes (DK, SR1, SR2) are shown in Fig. 2. A nonlinear relationship is observed for all three membranes with the inflexion point at about 50% ethanol, which is the point of maximum viscosity for ethanol : water solutions (6, 7). Viscous effects may be the dominant mechanism that describes the data at low ethanol concentrations (less than 50%), while

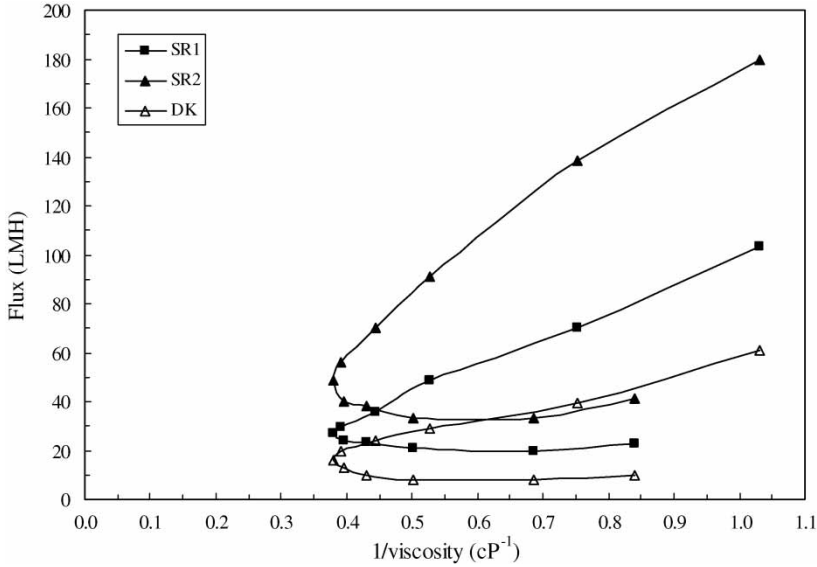

Figure 2. Darcy plot for DK, SR1, and SR2 membranes at 22°C and 1.38 MPa with ethanol solutions.

other physicochemical properties such as molar volume of the solvent and surface tension, and effects such as pore dehydration and swelling, may govern transport at higher ethanol concentrations (greater than 50%).

To extend the Darcy model to account for solvent effects, Bhanushali et al. (1) incorporated molar volume (V_m) into the viscosity term, with the assumption that membranes that are not affected by the solvent will have a flux proportional to the ratio of molar volume/viscosity of solvent (V_m/μ). However, the plot of flux vs. molar volume/viscosity again shows a non-linear relationship over the entire range of ethanol concentration (Fig. 3). Interestingly, the minimum value of the molar volume/viscosity ratio occurs at 40% ethanol, which is where the redirection of the curve occurs. Similar plots were also reported by Tsui and Cheryan (7).

Higher temperature and pressure results in higher fluxes throughout the range of ethanol concentrations as can be seen by comparing the data in Fig. 4 with Fig. 1. Another side effect of the higher temperature and pressure was the flattening of the membrane coupons. At lower temperatures and pressures, an increase in ethanol concentration would cause the membranes to curl convexly. After exposing it to higher temperatures and pressures, the membrane would have no curvature at all. This effect appeared to be permanent as long as the membrane was kept in contact with liquid, even subsequently at room temperature.

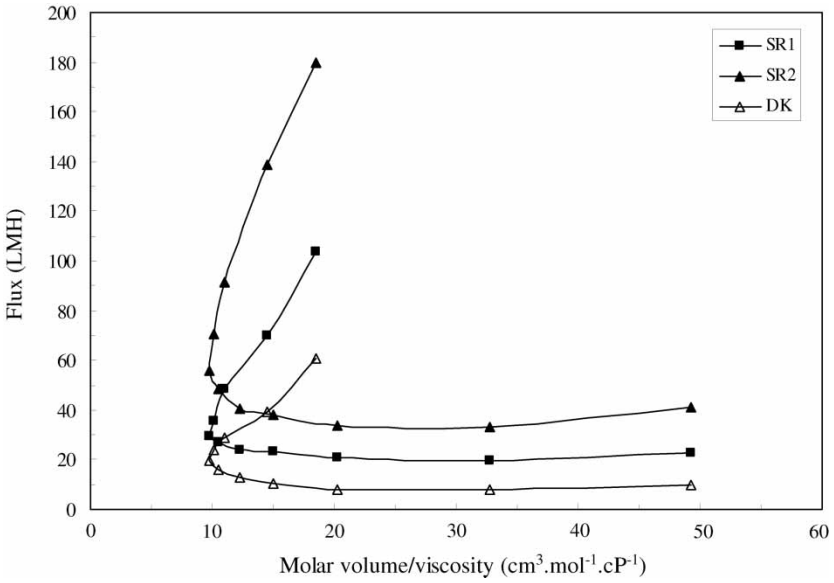

Figure 3. Relationship between molar volume/viscosity ratio and flux for nanofiltration of ethanol solutions at 22°C and 1.38 MPa.

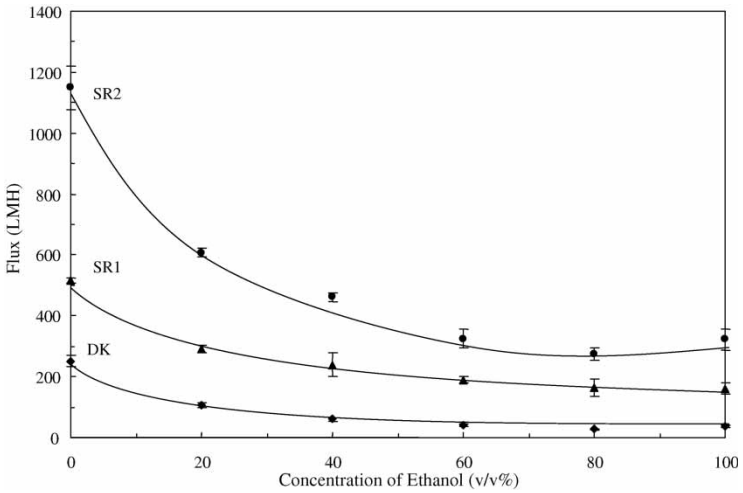

Figure 4. Effect of ethanol concentration in the conditioning solvent on flux at 50°C and 2.76 MPa. Error bars represent a 95% confidence interval.

Rejection and Flux Profiles

The flux and rejection of various lipids in ethanol is shown in Fig. 5. The rejection of all lipids by the DK membrane was just below 90%. The SR1 membrane showed a slight increase in rejection with increasing molecular

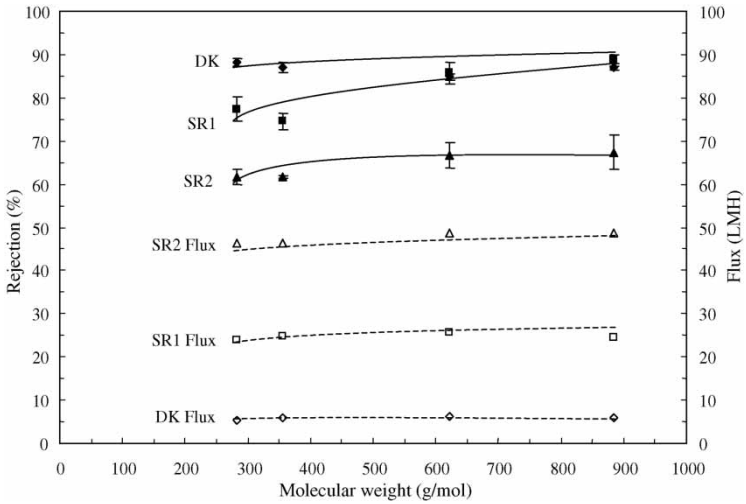

Figure 5. Rejection and flux of lipids by nanofiltration membranes at 22°C and 1.38 MPa. Full points are rejections, open points are flux. Error bars represent a 95% confidence interval.

weight of the lipids, from 77% at MW 282 to 88% at MW 885. The SR2 membrane rejection increased slightly from 62% to 67% in that same MW range. The flux order was reversed as expected: the high-rejection membrane (DK) had the lowest flux (~5 LMH) while the low-rejection SR2 had the highest flux (~47 LMH). The SR1 had much better flux (~22 LMH) than the DK membrane even though its rejection was comparable.

The performance of the membranes with sugars in ethanol is shown in Fig. 6. The rejection with the DK membrane was just under 90% for all sugars. The SR1 membrane showed increasing rejection, from 34% at MW 180 to 85% at MW 666. The SR2 membrane showed the lowest rejection of sugars; the decrease in rejection of the SR2 membrane at MW 666 cannot be explained, even though it was reproducible. Once again, the flux was fairly constant throughout the range of molecular weights for each membrane, with a similar trend of lowest flux/highest rejection and highest flux/lowest rejection seen in the lipid experiments. Flux of the DK membrane averaged 5 LMH while the SR1 and SR2 had average fluxes of 27 LMH and 50 LMH, respectively.

The three membranes did not perform as expected with polyethylene glycols as shown in Fig. 7. The DK rejection at 2.76 MPa increased from 28% with PEG 200 to 80% with PEG 1000. The SR1 saw an increase in rejection from 19% with PEG 200 to 71% with PEG 1000, while the SR2 performed poorly throughout with a maximum rejection of 20% with PEG

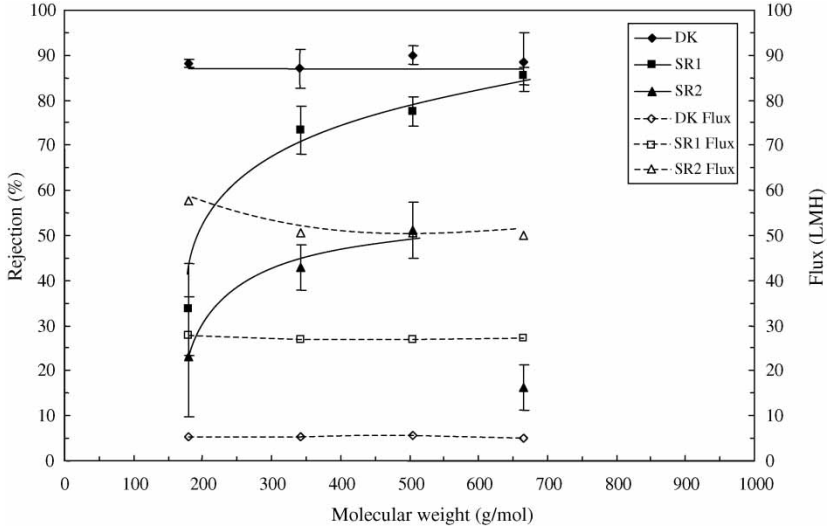

Figure 6. Flux and rejection of sugars in ethanol at 22°C and 1.38 MPa by nanofiltration membranes. Full points are rejection values, open points are flux. Error bars represent a 95% confidence interval.

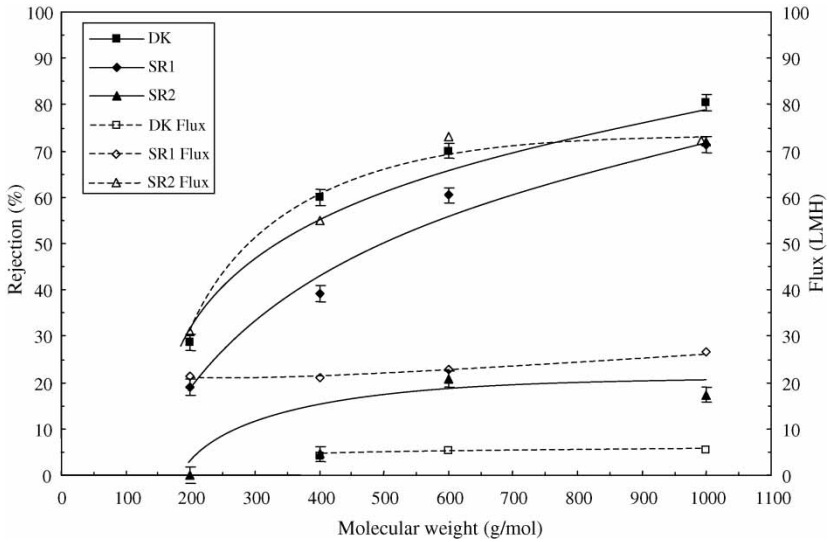

Figure 7. Rejection of 10000 ppm polyethylene glycols in ethanol at 22°C and 2.76 MPa. Error bars represent a 95% confidence interval.

600. The flux was steady at all PEG concentrations with the DK and SR1 membranes at 5 LMH and 22 LMH, respectively. On the other hand, the flux of the SR2 membrane actually increased from 31 LMH to 72 LMH with increasing molecular weight of the PEGs.

Corn Oil

As shown in Table 2, the DK and SR1 membranes had over 90% rejection of corn oil dissolved in ethanol at 1.38 MPa. The SR2 membrane was not able to satisfactorily reject corn oil in ethanol at any pressure.

Table 2. Rejection of corn oil in absolute ethanol by nanofiltration membranes as a function of transmembrane pressure at 22°C

	Rejection (%)		
Membrane	1.38 MPa	2.76 MPa	4.14 Mpa
DK	98.8^a	90.0^b	88.9^b
SR1	93.1^a	89.7^a	81.6^b
SR2	27.1^a	16.5^b	9.7^b

Means with the same letter are not significantly different from each other ($\alpha = 0.05$) for each membrane.

Based on the data presented here, the DK or SR1 membrane should be able to successfully concentrate oil in ethanol extracts of corn. Additionally, it has been shown that the MWCO or rejection profiles specified by the manufacturer or determined using aqueous solutions may not be sufficient to characterize the membrane's performance in nonaqueous solvents. Each solute-solvent combination will have to be experimentally tested to obtain a good estimate of the performance of the membrane in organic solvents.

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