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Effects of ethanol concentration on flux and gel formation in dead end ultrafiltration of PEG and dextran[☆]

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Abstract

The phenomenon of concentration polarization and gel formation plays an important role in ultrafiltration of macromolecules from water. However, there is lack of studies on similar phenomena for macromolecule ultrafiltration from blends of aqueous and non-aqueous solvents. This paper reports the effect of ethanol concentration on flux in ultrafiltration of polyethylene glycol and dextran with a solvent resistant polymeric membrane. Transient filtration data, collected after steady state, was utilized to determine actual filtration resistance and contribution of polarization using the osmotic pressure model. It was observed that both steady state flux and gel formation were significantly influenced in the ultrafiltration of both PEG and dextran from blended solvents. It was also observed that the onset of gel formation for PEG and concentration polarization for dextran in blended solvents occurred at significantly higher bulk solute concentrations than in water alone.

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Keywords: Ultrafiltration; Polarization; Gel layer; Ethanol; PEG; Osmotic pressure; Filtration resistance

1. Introduction

Membrane ultrafiltration (UF) is widely regarded as low energy process compared to the other conventional chemical engineering filtration processes. The application of membrane separation is growing very rapidly in pharmaceutical, chemical and food industries. Twin phenomena of concentration polarization and gel formation play an important role when separating macromolecular solutes from water. The effects of various operating parameters on ultrafiltration flux, concentration polarization (CP) and gel formation have been studied extensively, however, the effects of non-aqueous and aqueous solvent blends on the behavior of flux, CP and gel formation has received very little attention in reported literature. Certain organic solvents such as ethanol are widely used in extraction and refining of natural products, drug intermediates and fine chemicals using membrane technology. In recovering solvents and/or concentration of products in

above applications ultrafiltration could be increasingly used. There are very few studies available in literature on ultrafiltration of blends of solvents. Most of the reported work on organic solvents has been on nanofiltration membranes. Nguyen et al. [1] studied organic solvent permeabilities and observed that, in the absence of solutes, membrane permeability of several commercial UF membranes increased with some solvents (ethanol, methanol) and decreased with others (chloroform, decane, benzene). Lencki and Williams [2] reported effects of non-aqueous solvents on flux behavior. They concluded that those solvents with solubility parameter similar to that of membrane cause the greatest change in flow resistance. In addition, solvents with similar solubility parameter but low hydrogen bonding capabilities can actually disrupt the structure of anisotropic polysulfone membrane to such an extent that a dramatic drop in flow resistance was observed. It was further observed [3] that flux is greatly affected by alcohols and this flux reduction could be explained by an increase of viscosity due to ethanol. The concentration polarization layer during protein UF was analyzed by Elysee-Collen and Lencki [4,5] using ternary phase diagram. They have also studied the effect of added ethanol and ammonium sulfate on CP layer resistance by measur-

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ing the flux decline index (FDI) and concluded that methods such as turbidity, intrinsic viscosity analysis are useful in characterizing the state of protein on the membrane surface. The addition of ethanol to solution of hydrophobic proteins such as gelatin could be novel for improving UF flux and system productivity.

Machado et al. [6,7] studied the effect of solvent properties on permeate flow through nanofiltration membranes. They have proposed a resistance in series approach for predicting results and used several parameters like viscosity and surface tension to predict the influence on flux data. Whu et al. [8] studied performance of nanofiltration membrane with methanol and reported that membranes initially exhibit considerable time dependence for change in flux and rejection while becoming time invariant later on. Recently, Shukla and Cheryan [9] reported studies on UF of organic solvents. They reported a significant effect of membrane conditioning on performance of UF membrane in ethanol–water solution and subsequently suggested a conditioning scheme.

A review of the published literature showed that none of the previous studies revealed any information on separation, concentration polarization and gel formation in the presence of organic solvents for standard solutes such as PEG and dextran. We have reported [10,11] gel formation with PEG and analysis of concentration polarization with dextran along with a procedure for differentiating between concentration polarization and gel formation with pure water. However, the effects of solvent on CP and gel formation have not been studied. This work is the extension of our previous studies and reports the effects of ethanol–water blends on flux, gel formation and polarization time [10,11]. The effect of initial solute concentration to form a gel in ultrafiltration of PEG was also studied. Using unsteady state filtration data, a procedure for determining actual filtration resistance is also described. The major focus in this paper is on PEG but analysis was extended to dextran in order to verify the validity of above observation for other macromolecular solutes.

2. Theory

Using Darcy's law flow of liquid through UF membrane can be expressed as follows [12]:

$$J_s = \frac{\Delta P}{\mu R_m} \quad (1)$$

where J_s is the flux of solvent, ΔP the pressure difference, R_m the membrane filtration resistance and μ the solvent viscosity.

In case the membrane retains the solute, the driving force and the flow resistance would be modified due to concentration polarization or gel layer formation. Permeate flux for such a case can be obtained using the osmotic pressure model reported by Wijmans et al. [13,14]:

$$J_s = \frac{\Delta P - \Delta \pi}{\mu R_f} \quad (2)$$

where J_s is the solute flux, ΔP the applied pressure, R_f the total filtration resistance, which is the sum of membrane (R_m) and polarization layer (R_p) resistances and $\Delta \pi$ the osmotic pressure difference across the membrane.

In ultrafiltration of macromolecules, the resistance of membrane might be calculated using Eq. (1). However, this equation is not valid for estimating total filtration resistance R_f for those solutes that exert osmotic pressure. After steady state was achieved, the transient filtration data were obtained by reducing the applied pressure as a function of time. Actual filtration resistance was subsequently calculated using the slope of a J_s versus ΔP graph by utilizing Eq. (2).

3. Experimental

3.1. Membrane materials and UF solution preparation

The commercial G-Series (G-20 and G-50) solvent resistant UF membranes used in this work, had a nominal MWCO of 6 and 8 kDa, respectively, and were supplied by GE-Osmonics, USA. Polyethylene glycol (Fluka chemie AG, Switzerland) with 35 kDa molecular weight and dextran T40 (Polysciences, Inc., USA) with 39 kDa molecular weight were used as standard solutes. Feed solution comprised of water, ethanol and PEG or dextran with varying concentrations. Analytical grade ethanol was supplied by Commercial Alcohols, Toronto, Canada. RO water was used for making blended solutions. As both PEG and dextran are not directly soluble in ethanol, required amount of PEG or dextran was first dissolved in water and then ethanol was added to get the desired concentrations. Polyethylene glycol and ethanol concentrations in feed were varied from 1 to 18 kg/m³ and 0–90% (w/w), respectively while dextran was tested for a solute concentration of 5 kg/m³ only.

3.2. Apparatus

The experimental set-up used in this work is shown in Fig. 1. All experiments were performed with a commercial ultrafiltration stirred cell unit (Amicon, USA). A detailed description of experimental set-up is given elsewhere, Zaidi and Kumar [11]. Initially, pure water permeation (PWP) was measured for new membrane followed by solvents that were blends of ethanol and water. Mass of permeated solvent was recorded every 2 s through data acquisition software LabVIEW (National Instruments Corporation, USA). An error of less than 0.1% in measuring solvent flux was observed. The membrane resistance was calculated using Eq. (1). For a given feed solution, flux versus time data was collected at constant feed pressure till a steady state had reached. A steady state was assumed when the recorded flux values were varying within $\pm 0.2\%$. Once steady state was achieved, bypass valve (item 3 in Fig. 1) was opened slightly to let the applied pressure decay as a function of time. This transient

Fig. 1. A schematic diagram of the experimental set-up.

filtration data was continuously recorded using the data acquisition system.

4. Results and discussions

Experiments were performed to determine the effects of pressure, solute and ethanol concentration on permeate flux. Fig. 2 shows the permeate flux as a function of time for three different feed pressures (135, 270 and 405 kPa) for a PEG bulk concentration of 8 kg/m^3 in water. As expected, there

is an initial sharp drop in the permeate flux from the initial value for short filtration times. At longer filtration times, the flux gradually reduces and eventually attains steady state. The initial drop in permeate flux is due to the sudden formation of CP layer, however, subsequent rate of flux decline also depends on the bulk solute concentration of the solution. The membrane used in our experiments retained the solute completely. Consequently, the concentration at membrane surface was rising sharply, which led to gel formation and osmotic pressure build up at the membrane surface, which has been clearly demonstrated by Zaidi et al. [10].

Fig. 2. Variation of permeate flux as a function of time for various feed pressures without added ethanol at a bulk PEG concentration of 8 kg/m^3 .

Fig. 3. Steady state permeate flux as a function of feed pressure for different feed concentration of PEG without added ethanol.

Fig. 3 shows the steady state flux for a PEG concentration of 1, 5 and 8 kg/m³ as a function of feed pressure. It is clear from this figure that permeate flux becomes independent of pressure above 250 kPa for a feed concentration of 8 kg/m³. The pressure range was restricted to 405 kPa due to the limitations of the test cell. After steady state was reached at

a constant feed pressure, the bypass valve (see Fig. 1) was opened slightly. This resulted in reduction of applied feed pressure as time passed. A plot of unsteady flux and feed pressure is shown in Fig. 2. It is noted from this figure that the osmotic pressure at membrane surface was constant due to the existence of gel during experiment. At one stage dur-

Fig. 4. Steady state permeate flux as a function of feed pressure for different feed concentration of PEG at a constant ethanol concentration of 10%.

Fig. 5. Steady state permeate flux as a function of feed pressure for different PEG and ethanol concentrations in feed.

ing pressure reduction this osmotic pressure exceeded the applied pressure, which caused negative flux as observed by reduction in weight recorded by the balance. This negative flux could only be due to the formation of gel layer at membrane surface. In the absence of any ethanol, this gel layer formation was observed when PEG concentration in feed was 8 kg/m^3 . Once ethanol was added the steady state

flux was not observed for this concentration. Fig. 4 shows the permeate flux versus applied pressure for different concentration of PEG when 10% ethanol was added to the feed solution. It is clear from this figure that the steady state flux value was now observed at 10 kg/m^3 instead of 8 kg/m^3 with water alone (Fig. 3). The effects of ethanol concentration on steady state flux are more clearly shown in Fig. 5.

Fig. 6. Polarization time as a function of various ethanol and PEG feed concentrations at different feed pressure.

Fig. 7. Effects of ethanol concentration on permeate flux and viscosity of feed with and without PEG.

As can be seen from this figure that once ethanol concentration is increased from 10 to 30%, a higher, initial feed concentration of PEG is required for the onset of a pressure independent flux. Obviously, the process of gel formation is

delayed by the presence of ethanol, in other words, ethanol has been able to shift the formation of gel to a higher initial bulk concentrations than usually required in water alone. The possible reason could be the change in cumulative phys-

Fig. 8. Variation of permeate flux as a function of reducing feed pressure for different PEG and ethanol concentrations in transient filtration after the steady state.

ical properties of bulk feed solution such as density. Since increase in ethanol concentration leads to the decrease in density while the increase in PEG concentration leads to increase in density. The polarization time, t_p , defined as the time of flux decay necessary to reach 50% of the initial flux J_s , was compared for the various bulk solute concentrations and pressures. Fig. 6 shows the polarization time for various ethanol and PEG concentrations and applied pressures, it is clear from this figure that an increase in ethanol concentration increased the polarization time, which is a clear indication of delayed gel formation. The polarization time was found to decrease with increase in applied pressure also. In the absence of PEG, the effect of ethanol concentration on permeate flux at constant pressure of 405 kPa was shown in Fig. 7. This figure shows that viscosity of ethanol first increases then it decreases as the concentration of alcohol is increased. This corresponds to the flux decreases with increase in concentration till 50% and then increases again. It is obvious that viscosity of solvent has directly influenced the permeate flux. It can be further noted from this figure that viscosity of solution increases further with the addition of PEG in solution, which had additional influence on the flux values.

After each experiment with different concentration of ethanol and PEG, membrane was washed and pure water permeation was checked, it was found that 97–99% PWP was recovered. Recovery of PWP indicates that there is no pore plugging in membrane and moreover there is no permanent swelling caused by ethanol. The membrane stability is important [15] usually when membrane is exposed to organic solvents. Fortunately, in our case the membrane was very stable during the experiments.

Since the membrane is fully retentive, a higher initial bulk concentration leads to additional deposition of solute at

Table 1

Osmotic pressure as a function of different PEG and ethanol concentration in feed

Ethanol–water concentration (w/w, %)	PEG concentration (kg/m ³)	Osmotic pressure, π_s (kPa)
10–90	10	131.6
30–70	12	132.3
50–50	14	133.0
70–30	16	133.5
90–0	18	132.8
		132.6 ± 0.7

membrane surface thereby offering higher resistance, which would lead to lowering of flux. Further, higher concentration might be giving higher polarized layer resistance, which is also inversely proportional to flux. The actual filtration resistance was calculated as described in Section 3. A typical plot of applied pressure versus flux is shown in Fig. 8. In case of gel formation at membrane surface, it is obvious that there is a very good linear correlation for each value of starting pressure. Using the slope values of these straight lines the filtration resistance (R_f) was calculated. The actual filtration resistances for feed solution of different ethanol, water and solute concentrations are shown in Fig. 9. Utilizing this estimated filtration resistance the osmotic pressure (π_s) of the solute accumulated at the membrane surface, was calculated by using intercept and slope values of plots of pressure difference versus flux (e.g. Fig. 8). Considering that the membranes are fully retentive in our studies, $\Delta\pi$ in Eq. (2) will be equal to π_s . These calculated π_s values are given in Table 1. It is clear from this table that the osmotic pressure at the membrane surface is independent of the initial solute concentration of the feed solution. This implies that the gel

Fig. 9. Effects of ethanol concentration on various resistances in ultrafiltration of PEG.

Fig. 10. Steady state permeate flux of dextran T40 (concentration 5 kg/m^3) as a function of feed pressure for different ethanol concentrations in feed.

concentration remains constant regardless of initial feed concentration, however, due to the presence of alcohol, a higher initial solute concentration was required to form a gel.

A similar analysis was also applied to the case of ultrafiltration of dextran solution. In our previous study [11] it was shown that dextran T40 at feed concentration of 5 kg/m^3 forms CP layer and does not form gel. In order to verify the effects of ethanol concentration on CP layer, we blended

ethanol at various concentrations in dextran–water solution. The steady state flux was pressure dependent and increased with increase in pressure as found in case of osmotic limited ultrafiltration. However, as shown in Fig. 10, the steady state flux decreases due to the effects of viscosity as the concentration of ethanol was increased. The formation of CP layer was delayed due to the presence of ethanol as shown in Fig. 11, which further verifies that the effect of ethanol

Fig. 11. Polarization time of dextran T40 as a function of various ethanol concentrations for different feed pressure (solute concentration 5 kg/m^3).

on flux appears to be valid for dextran, which does not make a gel but only forms a concentration polarization layer.

5. Conclusions

It was observed that the presence of alcohol plays an important role during ultrafiltration of macromolecules such as PEG and dextran. It was concluded that ultrafiltration of PEG is influenced by the formation of gel at higher pressures and concentrations while for dextran concentration polarization controls UF. As ethanol concentration in solvent was increased, observed polarization time was longer while gel formation was delayed. Furthermore, a higher initial solute concentration was required to get the steady state flux. It was also observed that presence of ethanol affected filtration resistance mainly due to variation in feed solution viscosities. Using transient filtration data after the steady state was attained, filtration resistances and osmotic pressures exerted by gel for ethanol–water–PEG and ethanol–water–dextran solutions could be calculated. It was also concluded that the osmotic pressure of gel remained independent of the initial feed concentrations for PEG. A similar effect on the concentration polarization in ultrafiltration of dextran–water–ethanol system was observed.

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