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The influence of pH, salt and temperature on nanofiltration performance

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Abstract

The influence of pH, KCl and temperature on the performance of an Alfa Laval NFT-50 nanofiltration membrane was evaluated by glucose and KCl retention measurements at constant flux. It was found that at constant temperature an increase in pH in the absence of KCl reduced the water permeability, and this was correlated to the electroviscous effect. The selectivity decreased with increasing KCl concentration and the decrease became more evident with increasing pH. The decrease in selectivity could be related to membrane swelling, and it appears that pH had no effect on swelling other than enhancing the effect of KCl. The influence of KCl and pH on membrane performance was evaluated as a function of temperature after reaching steady state at 50 °C. The degree of swelling was higher at 50 °C than at 20 °C, due to an increase in polymer flexibility with increasing temperature. The decrease in selectivity with increasing temperature was less for KCl than for glucose, showing that the charge effect was influenced less by temperature than diffusion through the membrane.

1. Introduction

Nanofiltration (NF) is an established process in many industries for the separation and purification of aqueous solutions. Operation at high process temperatures close to the limits of the membrane can have a significant effect on the performance of the membranes. Three-layer, thin film (TF) polyamide (PA) membranes are composite membranes formed using interfacial polymerisation [1], where the top layer, or the active PA layer, is added to a porous support, typically an ultrafiltration membrane, which rests on a non-woven material, often of polypropylene or polyester. The active PA layer is cross-linked, which stabilises the structure. The maximum operating temperature of commercial three-layer TF-PA NF membranes is often quoted as being 50–60 °C.

In NF, separation is achieved by charge and size exclusion. The charge on the membrane is positive below the iso-electric point and negative above it. The charge exclusion of ions is dependent on the charge of the membrane, the ionic strength and the valence of the ions, the latter two influencing both the membrane charge density and the iso-electric point. The size exclusion is dependent on the membrane structure; a more dense structure leading to lower permeation.

Previous studies have found both increasing [2,3] and decreasing [4–6] permeability in the presence of salts due to changes in the membrane structure. The fact that the results are inconsistent shows that the salt–membrane interaction is complex. Bouchoux et al. [7] found when using three different samples of the Desal-5DK membrane (3 cm × 137 cm), that the retention of glucose decreased or was unaffected in the presence of NaCl, which shows that the same polymer material could behave differently in the presence of salt. Such differences could be due to variations in the polymer rigidity [6]. Two mechanisms are often proposed to explain the change in flux and selectivity: electroviscous effect/friction and membrane swelling. A change in Stokes radius of the solute, can in some specific cases be an alternative explanation [8]. The electroviscous effect is expected to be rapid [9] while swelling, which involves reorientation of

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large polymers, is slower. Freger [6] found using atomic force microscopy measurement that the addition of a 15% NaCl solution decreased the thickness of the polypiperazine layer in NF membranes. The decrease was greater at pH 3 than at pH 9. The results are in accordance with permeability data obtained using 9% NaCl [5]. Freger et al. [5] explained that such changes could be due to hydration swelling and/or charge screening by NaCl. Bargeman et al. [3] found increasing pore radius and membrane thickness with increasing salt concentration that followed the Hoffmeister series ($CaCl_2 < NaCl < KCl$), where KCl had the largest influence. These effects were related to the salt concentration inside the membrane. As a result of that it was proposed that the average pore size could be increased due to higher repulsion forces between the double layers in the pores as the concentration of ions and therefore the membrane charge, as predicated by their model, was increased. A similar mechanism was also proposed by Bouchoux et al. [7]. However, this explanation contradicts charge screening by the salt. As an alternative explanation Bargeman et al. [3] proposed a pore size distribution, and that the salt reduces the flux through the small pores to a larger degree than that through larger pores and that the retention of neutral solutes thus may decrease.

The influence of temperature on the permeation through a membrane typically follows an Arrhenius type of relation, where the activation energy and permeability coefficient are different for each solute or solvent. A significant decrease in retention of neutral solutes with increasing temperature has been found at both constant pressure and constant flux [10]. The increase in salt permeation and water flux with increasing temperature was found to be approximately the same at constant pressure, while at constant water flux an increase in temperature reduced the salt retention [11].

Changes in the membrane performance have been found to be dependent on the temperature [12], which was explained by polymer reorientation due to an increase in flexibility of the molecular chains with increasing temperature. After processing at elevated temperatures (65 °C) the flux decreased and the glucose retention increased [13]. A change in the membrane structure will have the greatest effect on uncharged solutes, but could also have an important influence on charged solutes if the charge effect is low, i.e. when operating at high ionic strengths or close to the iso-electric point. The enhancing effect of temperature on the change in the membrane performance makes it important to improve our knowledge of the mechanisms behind these changes and how they arise, in order to simplify the implementation of NF at elevated temperatures.

The aim of this study was to evaluate the influence of pH, a salt (KCl) and temperature on the performance of a TF-PA NF membrane to elucidate the mechanisms influencing the membrane performance at ambient and elevated temperatures.

2. Theory

2.1. Calculation of osmotic pressure in the feed

The interaction between KCl and glucose is neglected, and the contributions of KCl and glucose to the total osmotic pressure are assumed to be additive. The osmotic pressure of glucose and KCl was calculated according to Eq. (1) [14]:

$$\pi = \frac{vRTM_A}{V_A}\phi m \tag{1}$$

where v is the number of moles of ions (solute) formed from 1 mol of electrolyte (solute), R is the gas constant, T is the temperature, M_A is the molecular weight of the solvent, V_A is the partial molar volume of the solvent, ϕ is the molal osmotic coefficient and m is the molality. A molal osmotic coefficient of 1 was used for glucose and extrapolated tabulated values were used for KCl [14].

2.2. Debye screening length

The Debye screening length, κ^{-1}, is a characteristic length that describes the ionic environment near a charged surface. The Debye screening length quantifies the distance from a charged surface at which there is no interaction between the surface and the electrolytes in the bulk solution. According to Eq. (2), the Debye screening length depends only on the properties of the surrounding electrolytes and is independent of surface properties [15].

$$\kappa^{-1} = \left(\frac{\varepsilon_0\varepsilon_r kT}{\sum_i (z_i e)^2 C}\right)^{1/2} \tag{2}$$

Here, ε_0 is the permittivity in vacuum, ε_r the relative dielectric permittivity, k is Boltzmann's constant, T is the temperature, z_i is the ion valency, e is the charge on an electron and C is the electrolyte solution concentration.

2.3. Diffusivity in liquids

The diffusion coefficient of the solute in the bulk can be estimated using the Stokes–Einstein equation [16], which uses a rigid spheres model to describe the solute diffusivity in the solvent as:

$$D = \frac{kT}{6\pi\mu R_s} \tag{3}$$

where D is the diffusivity, μ is the dynamic viscosity of the solvent and R_s is the solute radius.

2.4. Water permeability

The water permeability is defined as:

$$P_0 = \frac{J_w}{(\Delta P - \Delta \pi)} \tag{4}$$

where, J_w is the water flux, ΔP is the pressure difference and $\Delta \pi$ is the osmotic pressure difference.