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Unusual trend of increasing selectivity and decreasing flux with decreasing thickness in pervaporation separation of ethanol/water mixtures using sodium alginate blend membranes

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ABSTRACT

Pervaporation membranes were produced comprising a 4:1 sodium-alginate:poly(vinyl-alcohol) polymer blend selective layer with a plasticizing agent (glycerol). Membranes were supported on a poly(acrylonitrile) mesoporous support layer and non-woven fabric base. Pervaporation separation of ethanol/water mixtures was carefully followed as a function of film thickness and time. It was found, contrary to what might be expected from literature, that these films showed increased selectivity and decreased flux as film thickness was reduced. It is argued that the morphology and structure of the polymer blend changes with thickness and that these structural changes define the efficiency of the separation in these conditions.

1. Introduction

Pervaporation is a membrane separation technology used industrially for solvent dehydration and separation of organic mixtures and has a significant advantage over other separation methods in that it can be used to effectively separate azeotropic mixtures. Because of this, pervaporation may have considerable importance in water–ethanol separation and thus, allow low water content, fuel grade ethanol to be generated [1]. Sodium alginate (NaAlg), a naturally occurring polysaccharide, is a suitable choice of membrane for water/ethanol separation because it is partially soluble in water whilst it is insoluble in ethanol [2]. When exposed to a water–ethanol mixture the membrane will swell with water molecules, and in pervaporation, water will permeate through the membrane allowing separation. Because of the vacuum on the permeate side of the membrane, there will be a diffusion profile across the membrane as shown in Fig. 1. On the retentate side of the membrane, swelling will be almost complete and the glass transition temperature (T_g) of the polymer will be significantly lowered to a point where the feed side of the membrane is above the effective T_g ensuring that it is in a rubbery state. On the permeate side of the membrane, the water content is lower so that the temperature is below T_g and so in a glassy state. Between, the two sides of the membrane there will be a region where there is a transition between the two polymer states.

Whilst NaAlg has an almost ideal chemistry for this separation, it is mechanically unstable and thin membranes cast from solutions of pure NaAlg are brittle and prone to cracking [3], while pervaporation membranes suffer from a loss in performance over time due to *relaxation* [1,4]. This limits the practicality of the use of these systems in industrial environments. Relaxation is the process by which residual stresses in a polymeric glass are released changing the polymer's physical and mechanical properties [5]. These residual stresses are a result of non-equilibrium derived from changes in structure and mobility of the polymer chain matrix at the glass transition temperature (T_g) [6].

As a polymer is cooled through the T_g the structural changes required to maintain thermodynamic equilibrium cannot occur in the time scale of cooling and residual stress is present. In a pervaporation process, the membranes are particularly prone to relaxation related damage because of the variation in the effective T_g and Young's modulus across the membrane. It is important to note that relaxation would occur almost instantly in the rubbery state and very slowly in the glass state resulting in stress variation across the membrane.

The focus of our work described here has been to reduce membrane thickness, thus minimising relaxation effects by limiting the thickness of the glassy phase. This should enable development of a membrane synthesis procedure whereby efficient separations can be achieved over long periods. The use of pristine sodium alginate was the experimental ideal, but initial testing proved that the mechanical and chemical stabilities of pristine sodium alginate membranes are too poor to permit long periods of testing required for the membrane system to reach equilibrium. This lack of

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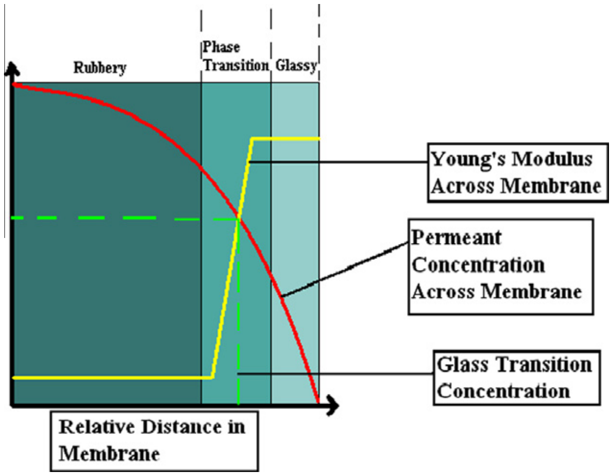

Fig. 1. Schematic of a diffusion profile across a pervaporation membrane.

stability becomes more of a problem as membrane selective layer thickness decreases. As such, in order to achieve suitably thin membrane layers it is necessary to use polymer blends and composition modifications as well as membrane supports to provide mechanical robustness. This means that the approach contrasts many academic studies of these systems but the methodology is applicable to use in commercial environments. In this paper, it is demonstrated that this membrane type produces highly unexpected results, with high performance characteristics, while expected trends in pervaporation performance and film thickness were not observed.

2. Experimental

2.1. Materials

Sodium alginate (NaAlg), 0.03% hydrolysed dimethylsulphoxide (DMSO) and glycerol (85%) were purchased from Sigma-Aldrich. Poly(vinyl alcohol) (PVA), molecular weight approximately 78,000 g mol^{-1}, was purchased from Polysciences Inc. Poly(acrylo nitrile) (PAN) was obtained from Scientific Polymer Products Inc. as a fine powder. Pure ethanol (100% HPLC grade) was purchased from the Carbon Group (Irl.). All chemicals were used without further purification. Non-woven polyester fabric (CraneCU414) was supplied by Crane & Company Inc. and used as a membrane support. The thickness of the non-woven fabric used in this study was ~120 μm.

2.2. Membrane processing

Pervaporation experiments were conducted using a laboratory bench test unit – the Sulzer Chemtech Laboratory 6″ Test Cell produced by Sulzer Chemtech. All parts in contact with the feed mixture were stainless steel, polytetrafluoroethylene (PTFE), the membrane or appropriate elastomeric seals. Membranes were placed inside the test cell which was clamped closed and feed solution (90 wt% ethanol solution in deionised water) was circulated continuously at 60 °C above the membrane. To minimize concentration polarization, static mixers in the form of spacers were placed inside the cell in contact with and perpendicular to the membrane surface. On the permeate side of the membrane a permanent vacuum was maintained to drive diffusion of feed molecules. All pervaporation tests were run for a period of 5 h with hourly sampling. The flux was calculated from $J = W/At$, here J is flux of the membrane, W is the mass of permeate, A is the area of the membrane and t is the time interval between samples. The membrane selectivity, α, was calculated from $\alpha = (Y_i/Y_j)/(X_i/X_j)$, where Y_i is the weight percentage water in the permeate, X_i is the weight percentage water in the retentate, Y_j is the weight percentage ethanol in the permeate and X_j is the weight percentage ethanol in the retentate.

2.3. Membrane preparation

As described above, NaAlg membranes were found to be too brittle for use in pervaporation and the mechanical stability of the membrane was improved by combination of the NaAlg with PVA and plasticizers [7]. This polymer blend adds elasticity to the system. Membrane supports were still required and were produced by attaching the non-woven fabric to a glass plate. A solution of PAN in DMSO was then cast onto the fabric using a film coater (K202 Control Coater, RK Printcoat Instruments Ltd.). This is an automated coater utilizing coating bars using spiral wound stainless steel and provides a highly reproducible and uniform coating due to controlled bar pressure and drawdown speed. This cast layer was then immersed in a water bath for 20 min to induce phase inversion of the PAN solution to form a macroporous layer. This layer was dried in air to ensure that it had fully solidified, and SEM analysis showed that a non-porous skin layer had formed on the surface, this skin layer ensured that no impregnation of the selective polymer layer into the support layer was possible. Using the film coater, a NaAlg based casting solution was cast onto the PAN and non-woven fabric support. The casting solution (unless otherwise stated) comprised of 4 g of NaAlg, 1 g of PVA, 5 g of glycerol plasticizer and 90 g deionised water. The solution was cast at various thicknesses and allowed to dry in air for 24 h to form the selective membrane layer.

2.4. Membrane characterisation

Differential Scanning Calorimetry, DSC, (DSC Q1000 version 9.9 build 303 instrument from TA instruments, with a Mettler Toledo Microgram balance) was used to examine the sodium alginate polymer. Analysis was conducted in a temperature range of −40.0 °C to 397.0 °C, with a temperature gradient of 20 °C min^{-1}, and conducted under nitrogen at 50 ml min^{-1} flow rate. The morphologies of the cross sections and top surfaces of the membranes were characterised using a Jeol model FEI FP 2031/11 Inspect F field emission scanning electron microscope (SEM). All images of membranes were obtained under similar resolutions. All membrane samples were prepared for imaging by the Cryo-Rupturing Image Sample Preparation (CRISP) method, whereby a section of membrane was immersed in liquid nitrogen and subsequently broken to preserve the structural integrity of the broken edge (which is usually compromised by simple cutting). All polymer membrane samples required gold-coating (45 nm) to provide a conductive surface to allow imaging. The ethanol content of both feed and permeate was measured (accuracy of 10^{-4} g cm^{-3}) using a Mettler -Toledo DE40 Density Meter, produced by Mettler-Toledo Ltd. Temperature control was via a built-in Peltier thermostat. The calculation of the ethanol concentration was performed by the programme "Alcodens" version 2.1. copyright 2003–2009 Katmar Software.

3. Results and discussion

The aspects of solution diffusion theory concerning diffusion in polymers have not been fully explained in literature due to the difficulties with calculation of diffusion coefficients in polymer membranes [4]. Observed decreases in flux with membrane thickness