



Ethylene glycol as bore fluid for hollow fiber membrane preparation



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ABSTRACT

We proposed the use of ethylene glycol and its mixture with water as bore fluid for the preparation of poly(ether imide) (PEI) hollow fiber membranes and compared their performance and morphology with membranes obtained with conventional coagulants (water and its mixture with the solvent N-methylpyrrolidone (NMP)). Thermodynamics and kinetics of the systems were investigated. Water and 1:1 water:EG mixtures lead to fast precipitation rates. Slow precipitation is observed for both pure EG and 9:1 NMP:water mixture, but the reasons for that are different. While low osmotic driving force leads to slow NMP and water transport when NMP:water is used, the high EG viscosity is the reason for the slow phase separation when EG is the bore fluid. The NMP:water mixture produces fibers with mixed sponge-like and finger-like structure with large pores in the inner and outer layers; and hence leading to a high water permeance and a high MWCO suitable for separation of large-sized proteins. As compared to NMP:water, using EG as bore fluid provides fibers with a finger-like bilayered structure and sponge-like layers near the surfaces, and hence contributing to the higher water permeance. It also induces small pores for better protein rejection.

1. Introduction

Along with membrane chemistry, membrane pore characteristics such as surface pore size, porosity and pore size distribution are crucial factors in ultrafiltration process because they contribute to determine water flux, solute rejection and even resistance to fouling [1]. In the phase inversion process, a versatile technique for fabrication of asymmetric ultrafiltration membranes, membrane pore structures can be tailored by changes in polymer dope composition, solvent evaporation temperature and duration, and the chemistry and temperature of the coagulation bath. The addition of pore-forming agents is an important strategy in membrane preparation to enhance permeation properties. These additives can be inorganic (e.g. water [2,3], LiCl [3–6], ZnCl₂ [7] or phosphoric acid [8]), small organic molecules (alcohols [3,9], acetone [10], ethylene glycol [11] or glycerol [3,8]) or organic macromolecules (e.g. poly(vinyl pyrrolidone) (PVP) [12–15] or poly(ethylene glycol) (PEG) [16–19]). Their action mechanism combines thermodynamic and kinetic aspects, such as coagulation capability, viscosity, phase separation mechanism and rate, diffusion coefficient, etc. For example, LiCl, glycerol and phosphoric acid are known to increase the viscosity of poly(vinylidene fluoride) (PVDF) dope solution, because of their stronger interactions with the solvent or polymer [4,8],

and the addition of PVP in the PVDF dope solution is reported to increase the precipitation rate in water due to its hydrophilic nature [12].

It is accepted that the fabrication of hollow fiber membranes involves additional factors to those involved in the flat-sheet membrane formation because of the large number of spinning parameters (polymer dope chemistry and flow rate, bore fluid composition and flow rate, spinneret design, air gap, take-up speed, etc.). Similar to the formation of flat-sheet membranes, many efforts have been made to investigate the introduction of additives in dope solutions to improve membrane pore characteristics. On the other hand, it has also been reported that the presence of additives in the bore fluid (i.e. internal coagulant) has significant effects on membrane pore structure. Most studies have used volatile solvents (e.g. ethanol [20]) or non-solvent (water) [21] as such additives to control the pore formation in the lumen of the hollow fiber and adjust the internal skin. This method mostly changes the pore size of the internal surface and overall cross-sectional morphology, while the external skin (selective layer) remains unchanged when the strong non-solvent (water) is used as the external coagulant. In this study, we demonstrate that ethylene glycol added to the bore fluid can be used to tailor also the pore size of the external selective layer. Its similar compounds (e.g. diethylene glycol, glycerol and polyethylene glycol)

Abbreviations: HAC, acetic acid; BSA, bovine serum albumin; DEG, diethylene glycol; DMAc, (2-dimethyl amino) ethyl methacrylate-co-butyl methacrylate; EG, ethylene glycol; FESEM, field emission scanning electron microscope; MWCO, molecular weight cut-off; NG, nucleation and growth; NMP, N-methyl-pyrrolidone; PEG, poly(ethyleneglycol); PEI, polyetherimide; PEO, poly(ethylene oxide); PVDF, poly(vinylidene fluoride); PVP, poly(vinyl pyrrolidone); pI, isoelectric point; SD, spinodal decomposition

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Nomenclature			
A_m	effective membrane area (m^2)	c_f	solute concentration in the feed (ppm)
ID	inner diameter (μm)	l	length (cm)
OD	outer diameter (μm)	m	weight (mg)
Q	water permeation volumetric flow rate (L/h)	t	time (s)
R_T	solute rejection (%)	ΔP	transmembrane pressure (bar)
c_p	solute concentration in the permeate (ppm)	Δv	volume (L)
		ε	porosity (%)
		ρ	density (g/cm^3)

have been known as pore-forming agents when added to polymer dope solutions, due to their high viscosity and hydrophilicity [3,5,22,23]. However, to the best of our knowledge, there are no studies on the effects on ethylene glycol as a bore fluid component on membrane pore structure.

Aromatic poly(ether imide) (PEI) (Fig. 1) was used for the fabrication of ultrafiltration hollow fiber membranes. PEI is a high performance membrane material for various applications. Its aromatic imide units offer high separation performance, while its flexible ether linkages facilitate good processability [23,24]. We believe this approach will be very useful for the optimization of spinning process for high-performance hollow fiber membrane preparation.

2. Experimental

2.1. Materials

Polyetherimide (PEI) Ultem® 1000, provided by Sabic (Saudi Arabia), diethylene glycol (DEG, 99%, Alfa-Aesar), ethylene glycol (EG, 99.8%, Sigma-Aldrich) and N-methyl-2-pyrrolidinone (NMP, ≥99.5%, Merck) were used to prepare the dope solution and bore fluids for the fabrication of hollow fiber membranes. Poly(ethylene glycol) (PEG) and poly(ethylene oxide) (PEO) with different molecular weights from Sigma-Aldrich were used for pore size analyses. Myoglobin from equine skeletal muscle (95–100%), bovine serum albumin (BSA, ≥96%) and γ -globulin from bovine blood (≥99%) for protein rejection tests were also obtained from Sigma-Aldrich. The information on their molecular weights and isoelectric points (pIs) are listed in Table 1 (from Sigma-Aldrich).

2.2. Phase diagram

The phase diagram of the PEI/NMP/DEG/EG/water system was estimated by cloud point tests. A series of PEI solutions with different polymer concentrations was prepared in DEG/NMP (13/70). Their cloud points were determined by adding different non-solvents (NMP:water (9:1), water, water:EG (1:1) and EG) at 60 °C (temperature at which PEI can be completely dissolved in NMP) until turbidity was observed. The amounts of PEI, DEG/NMP, and non-solvent for each cloud point were plotted in a ternary diagram.

2.3. Phase inversion kinetics

The phase inversion kinetics was studied by light transmittance experiments in different non-solvents. The polymer solution was cast on a glass plate, forming a solution layer of 1 mm and then the glass plate was immediately immersed in a cuvette, containing non-solvent. The changes in light transmittance were monitored at 600 nm (water, NMP and EG have no absorbance peak at this wavelength) using a Cary 5000 UV-vis-NIR, Agilent. The transmittance curves were plotted as a function of time.

2.4. Hollow fiber spinning

PEI hollow fiber membranes were fabricated by non-solvent-in-

duced phase-separation process, using a dry-jet wet spinning line, as described in Fig. 2. The detailed procedure can be found elsewhere [25] and spinning conditions are listed in Table 2. All spinning parameters were kept unchanged while different bore fluid compositions were used. The membrane modules were prepared with 2–3 fibers per module and their effective length was around 13.4 cm.

2.5. Membrane characterizations

The cross-sectional and surface morphologies of PEI hollow fiber membranes were observed on a field emission scanning electron microscope (FESEM, Quanta 200 or Nova Nano). Before imaging, the membranes were fractured in liquid nitrogen and then coated with iridium, using a coater.

The water contact angle on the hollow fiber membrane surfaces, which characterizes their hydrophilicity, was measured by a Sigma 701 Tensiometer from KSV Instruments Limited. The hollow fibers were sealed at one end and then immersed into distilled water. Their advancing contact angles were calculated with the help of a computer software. Five readings were recorded and an average was obtained.

The porosity of hollow fiber membranes was determined by weight and volume measurements. Wet fibers were taken out from the water bath and cut into 5 cm in length (l) and then freeze dried overnight before weighed (m) with 5 samples for each measurement. The overall porosity ε (%) was calculated using the following equation:

$$\varepsilon = \frac{\frac{1}{4}\pi l \rho (OD^2 - ID^2) - m}{\frac{1}{4}\pi l \rho (OD^2 - ID^2)} \times 100 \quad (1)$$

where OD and ID are the outer and inner diameters of the fiber, respectively. ρ is the polymer density (1.28 g/cm^3).

The pore structural characteristics of PEI hollow fiber membranes, including pure water permeance, molecular weight cut-off (MWCO), pore size, and pore size distribution were analyzed, by using nanofiltration experiments in a lab-scale circulating filtration unit, as previously described [23]. Since the selective layer locates on the outer surface of the fibers, the feed solutions were circulated into their shell side, while the permeate solution were collected from their lumen side. The pure water permeance PWP ($L \text{ m}^{-2} \text{ bar}^{-1} \text{ h}^{-1}$) was measured by circulating water into the module at a constant flow rate of 0.1 L min^{-1} under a pressure of 1 bar and then calculated using the equation:

$$PWP = \frac{Q}{\Delta P \times A_m} \quad (2)$$

where Q is the water permeation volumetric flow rate (L/h), A_m is the effective area (m^2), and ΔP is the transmembrane pressure (bar).

The pore size, pore size distribution, and MWCO of PEI hollow fiber membranes were evaluated via solute rejection experiments with

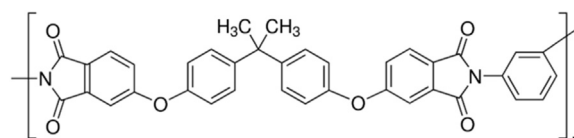


Fig. 1. Chemical structure of PEI.

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