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Thin-film composite bicontinuous cubic lyotropic liquid crystal polymer membranes: Effects of anion-exchange on water filtration performance

Blaine M. Carter [a], Brian R. Wiesenauer [b], Richard D. Noble [a,*], Douglas L. Gin [a,b,*]

[a] Department of Chemical and Biological Engineering, University of Colorado, Boulder, CO 80309, USA
[b] Department of Chemistry and Biochemistry, University of Colorado, Boulder, CO 80309, USA

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ABSTRACT

The effects of anion-exchange on the filtration performance of thin-film composite (TFC) membranes with an active layer consisting of a nanostructured, lyotropic (i.e., surfactant) liquid crystal (LLC) polymer were investigated. These TFC LLC membranes are made by the in situ cross-linking of reactive amphiphiles (i.e., surfactants) that self-organize in the presence of glycerol into a type I bicontinuous cubic (Q_I) phase that contains a uniform, 3D-interconnected pore network lined with tethered cationic moieties and free mobile anions in the pores. In this study, a systematic series of experiments were performed to independently investigate how monovalent cations and anions affect transport in these TFC Q_I membranes. TFC Q_I membranes exposed to feed solutions that contain different cations (i.e., $Li^+_{(aq)}$, $Na^+_{(aq)}$, and $K^+_{(aq)}$) but have the same monovalent anion as the free mobile anion in the membrane (i.e., $Br^-_{(aq)}$) have a constant flux and a high rejection ($>98\%$). When the cation is kept constant (i.e., $Na^+_{(aq)}$) and the anion in the feed is varied (i.e., $Cl^-_{(aq)}$, $Br^-_{(aq)}$, $NO^-_{3(aq)}$, and $I^-_{(aq)}$) and allowed to partially anion-exchange with the membrane, a high rejection is maintained ($\geq 96\%$), but the flux significantly changes depending on the anion in the feed solution. The flux of the TFC Q_I membranes can also be repeatedly be cycled by contacting the membranes with different anions. Control experiments with completely anion-exchanged TFC Q_I membranes (i.e., with $Cl^-_{(aq)}$, $Br^-_{(aq)}$, $NO^-_{3(aq)}$, and $I^-_{(aq)}$) showed that the rejection of sodium salts and uncharged organic solutes was virtually the same for all of the completely anion-exchanged membranes. As a whole, these results demonstrate that the flux of these TFC Q_I membranes can be tuned by changing the anion with little to no change in the rejection performance. The unique performance characteristics of TFC Q_I membranes may offer advantages over conventional NF and RO membranes for water purification applications or other aqueous separations.

1. Introduction

Inadequate access to clean water is a significant worldwide problem [1–5]. Over 1 billion people lack access to safe drinking water and this number is expected to increase [1]. Not only is clean water essential for survival, but it also significantly impacts food and energy production as well as industrial output and the quality of the environment [2–4]. As the demand for clean water intensifies, it is imperative to be able to efficiently remove salts, organic solutes, and other impurities from contaminated sources of water. Membrane technology is currently utilized in numerous processes to efficiently generate clean water [1–3,5].

In order to remove virtually all dissolved salt ions and small organics from water, reverse osmosis (RO) membranes can be employed. RO membranes are typically thin-film composite (TFC) or asymmetric membranes consisting of an ultrathin (ca. ≤ 0.1–$0.2\ \mu m$ thick) dense polymer layer (i.e., the active layer) on top of a porous support [6–8]. Because the active layer in RO membranes is dense and does not contain discrete pores, the transport is described by the solution-diffusion model [3,9]. In this model, solutes and water in the feed dissolve in the active layer and then diffuse through the membrane. Solutes are rejected by the membrane due to the differences in the solubility and mobility of the feed components in the active layer. The permeability of dense RO membranes is typically much lower than that of membranes with discrete pores.

Another type of membrane commonly used to purify water to a high degree is nanofiltration (NF) membranes [6,8,10]. These porous membranes can remove almost all divalent ions and large uncharged solutes from water but only partially reject monovalent

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[*] Corresponding authors at: Department of Chemical and Biological Engineering, University of Colorado, Boulder, CO 80309, USA.
E-mail addresses: nobler@colorado.edu (R.D. Noble), gin@spot.colorado.edu (D.L. Gin).

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ions and very small organics. NF membranes are also typically TFC or asymmetric membranes, but the active layer contains discrete pores that are about 1 nm in diameter [6,10,11]. Rejection of neutral solutes in NF membranes is well described by a pore flow model where separation is achieved by molecular size-exclusion [3,10,11]. However, due to the extremely small pore size, any surface charge on NF membranes can result in appreciable rejection of ions that would normally pass through based solely on size [3,11]. The transport of ions through a charged material is often qualitatively described by the Donnan exclusion mechanism [9,10,12,13]. Co-ions (same sign charge as the fixed membrane charge) are repelled by the charged membrane; and due to the requirement of electroneutrality on a macroscopic scale, their counterions are rejected as well.

Although current NF and RO membranes are capable of efficiently producing large amounts of high purity water, they face a number of challenges. One of the inherent difficulties in the construction of NF and RO membranes is the inability to control the average size and distribution of the effective pores or interstitial polymer voids on the molecular size scale in the active layer [10,14,15]. Current production methods such as phase inversion and interfacial polymerization offer little control over the effective pore size and pore size distribution of the membrane [10,15]. A wide pore size distribution limits rejection selectivity and the ability to cleanly fractionate solutes of different size. Other inherent challenges that face conventional NF and RO membranes based on polyamide or cellulose acetate chemistries are limited resistance to chlorine or strong pH feed solutions, as well as a lack of control over the charge character and charge density of the membrane [10,16–19]. Membrane charge significantly impacts and often improves rejection and permeability performance [10,17–21]. The study and development of polymer materials or processes to create polymer membranes with uniform pores on the molecular size scale, tunable charge characteristics, and improved resistance to harsh chemical feeds would offer significant improvements over conventional NF and RO membranes.

Our research team previously developed a unique type of polymeric NF membrane material that contains uniform, sub-1-nm pores that are lined with tethered cationic moieties and free mobile anions [22–24]. This new NF membrane material is made by the in situ cross-linking of reactive amphiphiles (i.e., surfactants) that self-organize in the presence of a solvent (e.g., most commonly water) into ordered lyotropic liquid crystal (LLC) phases. The best LLC phase that has been utilized for this new type of NF material is a cross-linkable type I bicontinuous cubic (Q_I) phase (Fig. 1). Consisting of an ordered (i.e., cubic symmetry) 3D-interconnected annular pore network, Q_I phases do not require any sort of phase alignment for the best transport characteristics, unlike lower dimensionality hexagonal (H) and lamellar (L) LLC phases. Water is transported through the Q_I phase by the interconnected, annulus-like water channels, but due to their small dimensions and charged character, larger solutes and ions are excluded.

Initial studies of supported Q_I-phase polymer membranes have shown they have performance characteristics in-between those of conventional RO and NF membranes [24]. These Q_I-phase LLC membranes reject neutral solutes like a porous NF membrane but reject monovalent and divalent salts comparable to a RO membrane at brackish water feed concentrations. Although initial studies involving supported Q_I-phase membranes demonstrate these materials have significant potential as a new type of uniform, nanoporous NF membrane, the only viable method found for membrane fabrication involves heating and pressing the monomer/water mixture into a porous support and subsequently photo-cross-linking to covalently lock in the Q_I-phase. In this process, the support is fully infused with the Q_I-phase material and as a result the active layer is as thick as the support itself (ca. 40 μm). Due to the extremely thick active layer, the water flux of the supported Q_I-phase membranes is far too low for any extensive testing or practical application. Even though the flux of the melt-infused Q_I-phase membranes is much lower than commercial NF and RO membranes, the thickness-normalized pure water permeance is comparable to a commercial RO membrane [24]. This suggests that it is possible for Q_I-phase membranes to obtain fluxes comparable to commercial RO membranes if the active layer of the Q_I-phase membranes can be reduced to the same approximate 0.1 μm thickness as commercial RO membranes.

The major problem in trying to process thin films of Q_I phases (prior to cross-linking) on top of a support is the fact that these LLC phases are particularly sensitive to changes in composition and temperature [25]. A specific composition of reactive LLC monomer and water must be maintained at a specific elevated temperature range until the desired Q_I phase is completely polymerized. As a result, solution-based processing techniques are not possible for narrow-composition, water-based Q_I-phases, since any evaporative loss of water that occurs during processing will result in disruption of the Q_I-phase monomer assembly.

To overcome the processing limitations of the previous water-based Q_I phases, our research team recently developed a new imidazolium-based monomer (**1**) that forms a cross-linkable Q_I-phase with glycerol instead of water (Fig. 1) [26]. Due to the low volatility of glycerol (which is also water-miscible and non-toxic), minimal evaporative loss occurs during solution-based thin-film processing. As a result, a thin film of a cross-linked Q_I

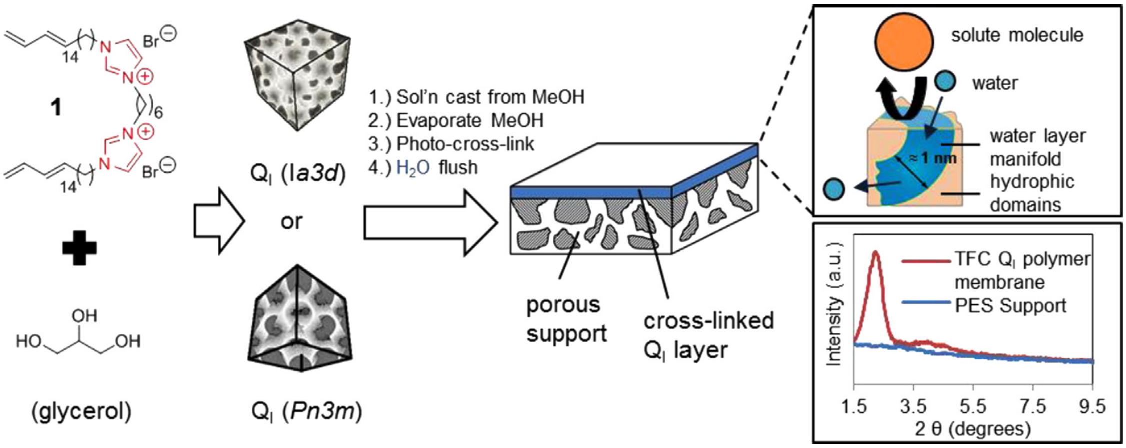

Fig. 1. Imidazolium-based monomer **1** that forms a Q_I phase with glycerol, and the formation of cross-linked TFC Q_I membranes.