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Design and evaluation of CO_2-switchable polymers as forward osmosis draw solutes

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Clean water is necessary for every aspect of human life. Contaminated water is unusable, and its consumption or improper disposal can be catastrophic to human health and the environment. Unfortunately, standard water purification techniques, such as reverse osmosis are energy intensive, especially for concentrated wastewater.
Forward osmosis (FO) is a promising purification method, with much lower energy demands than conventional methods. FO uses a concentrated draw solution to pull clean water from contaminated water though a membrane. While the initial filtration requires minimal energy, the subsequent removal of the draw solute from the clean water is energy intensive due to the high osmotic pressures they exert. In order for FO to be a viable alternative to the standard purification methods, the energy required to remove the draw solute must be minimized. This can be accomplished by the selection and design of the draw solute.
CO_2-switchable materials are promising FO draw solutes[1]. These materials contain tertiary amines ("B" in the equation below) which are protonated in carbonated water, producing one bicarbonate anion per protonated nitrogen. Upon heating (~60 °C), CO_2 is released, and the amines are returned to its neutral state.

$$\mathbf{B} + nH_2O + nCO_2 \underset{\Delta}{\rightleftharpoons} \mathbf{B}_nH^{n+} + nHCO_3^-$$

In the presence of CO_2 the materials exert a high osmotic pressure, ideal for filtration, while in the absence of CO_2 the osmotic pressure is reduced, ideal for removal. Several CO_2-switchable materials have already been considered as potential FO draw solutes, including dimethylcyclohexylamine[2], 1-cyclohexylpiperidine[3], trimethylamine[4] and poly(N,N-dialkylaminoethyl methacrylate)[1,5]. Polymers such as poly(N,N-dimethylaminoethyl methacrylate) have been explored as a FO draw solute because of a low reverse salt flux and a low osmotic pressure in air allowing easy removal. However, to date none of the polymers reported have produced osmotic pressures which rival that of trimethylamine.
In this work, we investigate and design water soluble polymeric draw solutes with a high osmotic pressure in the presence of CO_2 and a low osmotic pressure in air. To begin, a range of polymers were designed, focusing on maximizing the concentration of bicarbonates in solution. Following the synthesis and purification of the polymers, osmotic pressures were measured using membrane osmometry under air and CO_2. With thoughtful design, osmotic pressures of our CO_2-switchable polymers now exceeded 60 bar.
The osmotic pressure results demonstrate the balance that must be achieved between a high osmotic pressure in CO_2 and a low osmotic pressure in air. The pK_{aH}, structure, molecular mass, hydrophilicity, and intermolecular interactions of the polymers are key to producing a favorable balance. The results of this work indicate that CO_2-switchable polymers are viable FO draw solutes and may one day be capable of purifying concentrated wastewater streams.

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