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Doped Soap Membranes Selectively Permeate a Chiral Isomer

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Abstract: Soap films can not only be made with sub-μm thickness, they can have intrinsic permeabilities comparable to many commercial membranes, permitting very high transmembrane flux. Soap films readily incorporate a wide range of modifiers to allow highly tailored selectivity: We show that incorporating α-cyclodextrin in an 890 nm thick Triton-X-100 film allows, in a single stage, a high degree of chirally selective transport (1.6:1) of α(+)-pinene over α(−)-pinene.

Soap bubbles and soap films (SFs) have fascinated scientists and nonscientists alike for ages. An SF is a ultrathin liquid membrane: a micelle solution sandwiched between layers of surfactant. Previously we showed the ready ability of a H_2O_2-containing SF to collect and conductometrically sense sub-ppb levels of SO_2.[1] Soap solutions can dissolve a large range of substances of varying polarity that can be used to tailor the film reactivity and permeability. Permeability is the product of solubility and diffusivity. Although adding a surfactant or selector can increase viscosity and thereby decrease diffusivity, this can potentially be offset by increased solubility.[2] SF permeabilities have not generally been studied. However it is known that in common soap film flow meters gas permeation through the film can cause errors at low flow rates.[3] In the only reported study, on heptane transport, although permeabilities were not quantitatively measured, transport was found to depend on both the surfactant type and its concentration.[2] With sodium dodecyl sulfate (SDS), heptane is transported only above its critical micelle concentration (CMC), the flux increasing with [SDS] past the CMC.

We introduce here the concept that SFs can be not only used as membranes for selective transport but also readily doped with a chiral selector to carry out chirally selective transport. Membrane-based processes increasingly play a major role in industrial gas separations. Although a single stage rarely brings about sufficient separation, multistep separations are common: the scale is getting ever larger.[4] Chiral separations (CSs) are industrially important; sales of chiral drugs crossed the $100 billion mark in 2000. Preparative separation of the racemic anesthetic Halothane has been reported.[5] Many chiral primary amines of significant vapor pressure are used as drug precursors; membrane-based chiral gas separations have never been reported. Cyclodextrins (CDs) occupy a uniquely important place in CS.[6] Aqueous CD-bearing liquid membranes for enantiomeric/isomeric enrichment were proposed early.[7]

Our experimental set up is shown in Figure 1. Benzene (Bz), toluene (Tol), α(+)Pinene, and α(−)Pinene (α(±)P) vapor were separately generated from gravimetrically calibrated diffusion tubes; the diluted test streams contained 1.56, 0.16, 0.18, and 0.18 mg/L

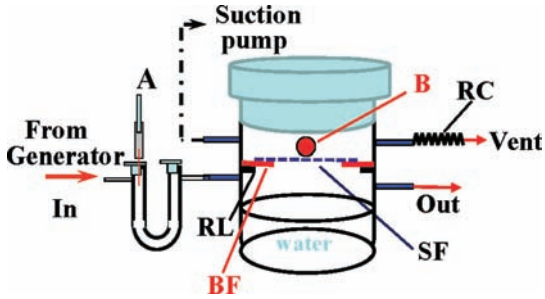

Figure 1. A sealable cylindrical chamber is fitted with a ring-shaped ledge RL. Atop RL is a bubble frame BF with a rectangular opening (area 30 cm^2) on which the film SF is formed (see SI for details of film-forming). The donor stream passes though a U-tube, where inlet concentration is measured under static conditions (position A), below the SF and out. The permeated concentration is measured at position B through a septum port. RC is a vent capillary that keeps the receiver chamber at atmospheric pressure. The suction pump is turned on to clean the chamber.

(STP) of Bz, Tol, α(+)P, and α(−)P, respectively. Quantitation was made by a 30 s static uptake on a solid phase microextraction fiber followed by capillary chiral GC-FID that afforded baseline separation of either Bz/Tol or α(±)P. SF solution viscosity was measured with an Ostwald viscometer. SF thickness was measured by putting a blue dye in the SF and laser transmissometry and ranged from 0.70 ± 0.30 to 1.63 ± 0.37 μm for different films. See the Supporting Information (SI) for details.

SF stability depends on composition, flow geometry, flow rate, and gas stream relative humidity. Our SF was nonionic (0.05−5% v/v Triton-X-100 (TX)) with 0−30% v/v glycerol (Gly). The latter, both a humectant and a film thickener, prolongs film life. With 10% Gly, either with no flow or with a moist gas stream, the SF is stable for >30 min. In a vertical SF orientation liquid runs to the bottom; in the horizontal orientation used here, donor flow on the bottom side promotes film liftup, inhibits the flow of excess liquid to the SF center, and prolongs SF life (Figure 2 shows SF lifetime data).

The intrinsic membrane property of interest is the permeability, given in barrers, that already accounts for membrane thickness. Illustrative values for benzene are 1100, 6000, 4100, 1500−2300 (all at 50 °C), 2900 (25 °C), 3665 (35 °C) barrer for polyvinyl alcohol (PVA),[8a] PVA-γ-glycidyloxypropyl trimethoxysilane,[8a] PVA-graphite,[8b] polyamide grafted poly(dimethyl)siloxane,[8c] low-density polyethylene,[8d] and poly(vinyl) acetal,[8e] respectively. For a 2% TX100-10% Glycerol membrane, benzene permeability was >3000 barrer at 23 °C. An ultrathin SF will effectively provide a far greater flux than these membranes.

For an SF containing 0.05−5% TX-10% Gly, the flux of either αP isomer increased with log[TX] content ($n = 6$, $r^2 = 0.999$):

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$$\text{Flux (nmol/cm}^2\cdot\text{min)} = 0.229 \pm 0.001 + 0.102 \pm 0.002 \log[\text{TX}]$$

The solubility of αP in various surfactants has been examined;[9a] it increases linearly with surfactant concentration for both nonionic and ionic surfactants. However, the concomitant increase in film thickness and viscosity (0.84 ± 0.37 μm, 1.185 ± 0.002 cP for 0.05%TX-10% Gly to 1.49 ± 0.24 μm, 2.095 ± 0.002 cP for 5%TX-10% Gly) leads to a less than linear increase in overall flux; the excellent linear correlation with log[TX] may be fortuitous. The effect of viscosity can be judged from the fact that the permeation flux of either αP isomer for a 0.05% TX-10% Gly SF (1.18 cP) was 42.8 ± 0.4% of that of a 0.05% TX SF (0.91 cP).

To make an SF chirally selective, a chiral modifier is needed. Chiral surfactants have been available for sometime, but just adding a chiral selector to the SF solution is sufficient. Indeed, this is a boon to the synthesis-challenged. α-CD is known to preferentially bind α(−)P.[10] We observed that while α-CD freely dissolves in water, the solubility drastically decreases with increasing [TX]. In 5%TX-10% Gly, little more than 3% w/v α-CD can be dissolved. When such an SF was used with 1% α-CD, we observed no enantiomeric selectivity (*s*). With 3% α-CD, a nonunity selectivity ($s = 1.1 \pm 0.1$, $n = 7$) was barely discernible.

Although the solubility of αP in mixed α-CD-surfactant systems is not known, the solubility of αP has been found to be greater in either a pure surfactant solution (whether nonionic, cationic or anionic) or a pure α-CD solution than in an α-CD-surfactant mixture.[9b] A film with only α-CD is not stable; some soap is needed to make a stable film. We used 0.05% TX. For an SF containing 0.05% TX-10% Gly and 0, 5, and 10% α-CD, respectively, *s* increased 1.0 ± 0.0→1.2 ± 0.1→1.6 ± 0.1; a soap membrane can clearly be rendered chirally selective. The binding constant between α-CD and the two αP isomers differ by 1.9×;[10b] the presently attained single stage *s* value by this high flux 0.89 ± 0.43 μm thick SF bearing 10% α-CD is thus remarkable.

What is interesting is that although α-CD preferentially binds α(−)P, in the present experiments, it is α(+)P that is preferentially transported. The gaseous feed flows at a slow rate; essentially all αP molecules reaching the SF from the donor side is taken up. In the film, the TX and the α-CD competitively bind the αP isomers. Because α-CD selectively binds α(−)P, it follows that in the nonselective TX-bound form, α(+)P dominates. The observed selectivity is due to kinetic reasons: The

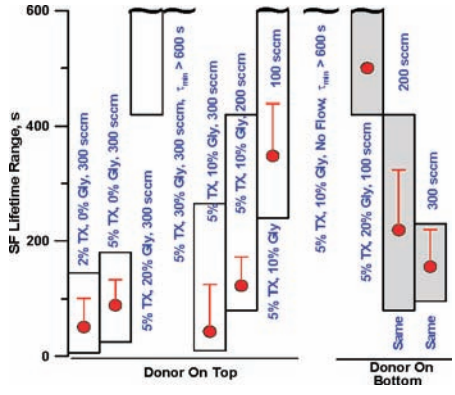

Figure 2. Lifetime of soap films under different conditions. The bars span the minimum to maximum values observed. Either the minimum (τ_{min}) or maximum exceeds 10 min under some conditions. Each bar has the average (+1SD) shown as an inset. The hollow bars on left have receiver on bottom; the filled triad on right has receiver on top.

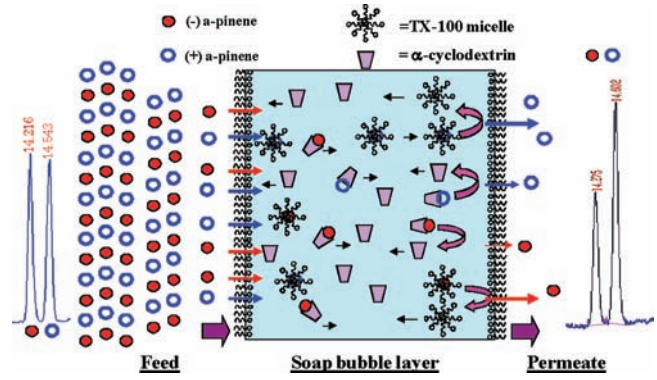

Figure 3. Cartoon showing selective carrier action of a doped soap film. Note that, in a transport process where mobile carriers must be recycled across the membrane, membrane thickness is critical in governing transport flux.

combined process of transport to the other side of the film and release into the gas phase will appear to be substantially faster for the micelle-bound form compared to the α-CD bound form. Unlike the case for β-CD,[11a] complexation kinetics with α-CD can be slow;[11b,c] chromatography of α(±)P on α-CD bonded column leads to broad tailing peaks unless additives that strongly compete for α-CD are added.[10a] Also, under our conditions, the αP-α-CD adduct likely involves 2 α-CD molecules rather than just one, slowing transport further,[10b,12a,b] while micelles may actually help the transfer of αP across the interfacial layer into the gas phase.[12c] Figure 3 graphically summarizes these findings. In principle, ternary complex formation between α-CD, TX, and αP may play some role in governing selectivity. However, the overwhelming evidence is that there is little, if any, interaction between α-CD and TX; the α-CD cavity is too small to accommodate the hydrophobic end of TX.[13]

We have demonstrated that soap solutions are readily modified with specific selectors that still allow ultrathin soap films to be formed. Extraction into an SF is akin to extraction from an inner fluid drop to an outer, immiscible fluid shell;[14] to achieve continuous extraction, one or both phases must continuously flow. In the present case, evaporation from the soap film to the receptor side provides for continuous transfer in a similar manner. These films permit highly selective transport while simultaneously allowing very high transmembrane flux. While SFs are thought to have only a limited lifetime, very long lifetimes are possible with appropriate humidity control. Continuously flowing large area grid supported SFs, including tubular/tunnel forms, have been demonstrated;[15] the practical use of SF membranes may be more than an evanescent thought.

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Supporting Information Available: Permeability measurements of benzene and toluene, description of test chamber and making soap film, analyte vapor generation and measurement of analyte by solid-phase microextraction—chirally selective gas chromatography and measurement of soap film thickness. This material is available free of charge via the Internet at http://pubs.acs.org.

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