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Electromodulated Molecular Transport in Gold-Nanotube Membranes

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We have developed a new class of synthetic membranes that contain monodisperse Au nanotubes with inside diameters that can be of molecular dimensions ($<$1 nm).[1,2] The Au nanotubes span the complete thickness of the membrane and can act as conduits for molecule and ion transport between solutions placed on either side of the membrane. We have demonstrated three important transport-selectivity paradigms with these Au nanotube membranes (Au-NTMs). First, because the nanotubes can have inside diameters of molecular dimensions, Au-NTMs can be used to cleanly separate small molecules on the basis of molecular size.[1a] Second, chemical transport selectivity can be introduced by chemisorbing thiols to the Au nanotube walls.[1b] Of particular relevance to the work reported here, we showed that when hydrophobic thiols are chemisorbed in this way, the Au-NTM preferentially transports hydrophobic molecules. Finally, because Au-NTMs are electronically conductive, they can be charged electrostatically in an electrolyte solution. This introduces ion-transport selectivity, and the Au-NTM can be electromodulated between ideal-cation and ideal-anion transporting states.[2]

We have recently become interested in the more challenging problem of *electromodulating neutral molecule transport* across Au-NTMs.[3] We have developed a system that is a hybrid between the thiol chemisorption route for introducing chemical transport selectivity and the electrostatic charging route for controlling ion-transport selectivity. This approach makes use of an anionic surfactant which, when a positive potential is applied to the Au-NTM, partitions into the nanotubes to charge the solution side of the electrical double layer at the tube walls (Figure 1). Because of the hydrophobic tail of the surfactant, this renders the nanotube interior hydrophobic, and the membrane now preferentially extracts and transports hydrophobic molecules.[1b] Because the anionic surfactant can be expelled from the nanotubes by applying a negative potential, this provides a route for reversibly electromodulating neutral molecule transport in the Au-NTMs.

To prove this concept, the transmembrane fluxes of four different neutral "permeate" molecules (Table 1) were investigated as a function of potential applied to Au-NTMs in the presence of the anionic surfactant sodium dodecylsulfonate (SDS). The relative hydrophobicities of the permeate molecules were gauged by the magnitude of the octanol/water partition coefficient (Table 1).[8] Au-NTMs with an effective inside nanotube diameter[1b] of 2.8 nm were used. The membrane was mounted between the two halves of a U-tube permeation cell.[1,2] The feed half-cell contained 5 mL of an aqueous solution that was 5 mM in one of the permeant molecules and 1 mM in SDS; the permeate half-cell initially contained 5 mL of 1 mM aqueous SDS. It is important to point out that SDS is the only electrolyte present and that there are no micelles present in this solution. The rate of *diffusive* transport of the permeant molecule through the Au-NTM was monitored by periodically measuring the UV absorbance of the permeate solution. The potential of the membrane was controlled with a potentiostat versus a Ag/AgCl wire immersed in the feed solution.[9]

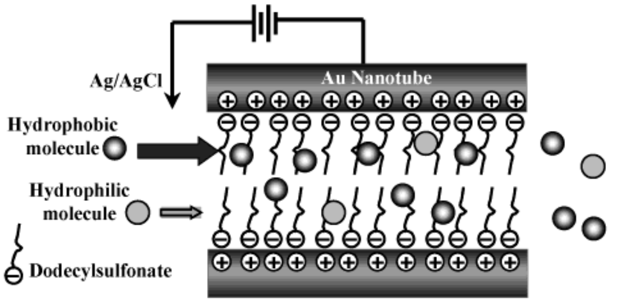
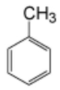
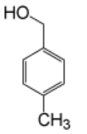
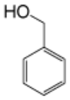
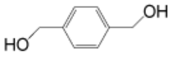


Figure 1. Schematic illustration of surfactant/double-layer-charging approach for electromodulating neutral molecule transport in Au nanotube membranes. At the potential applied, there is excess positive charge on the nanotube walls, and the anionic surfactant dodecylsulfonate is incorporated into the nanotubes to charge the double layer.

Table 1. Chemical Structures and Octanol/Water Partition Coefficients ($P_{o/w}$) for the Permeant Molecules Investigated

				
	Tol	**MBA**	**BA**	**BDM**
$P_{O/W}$	630[a]	40[a]	13[a]	3[b]

[a] Partition coefficient. See ref 8. [b] Measured at 23 °C.

Because Tol is the most hydrophobic of the permeate molecules (Table 1), it seemed to be the most likely candidate for demonstrating the electromodulated-transport concept. If the model summarized in Figure 1 is correct, we would expect the flux of toluene to be low at negative applied potentials, where SDS is electrostatically excluded from the nanotubes, and high at positive applied potentials, where SDS is electrostatically partitioned into the nanotubes. Plots of moles Tol transported per cm^2 of membrane surface area versus permeation time (flux plots) as a function of potential applied to the Au-NTM show that these results are, indeed, observed experimentally (Figure 2a). In the presence of SDS, the flux of Tol at $+0.74$ is $\sim$4 times higher than that at -0.46 V. When this experiment is repeated with the more hydrophilic molecule methylsulfonate instead of SDS, the flux of Tol increases by only a factor of 1.2 over this same potential range.

The slope of the flux plot line provides the flux of permeate molecule across the Au-NTM. Flux data versus applied potential

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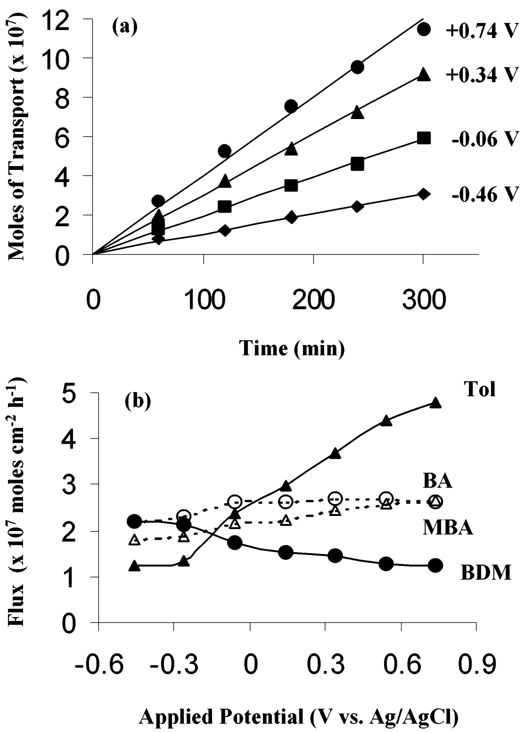

Figure 2. (a) Flux plots (see text) for Tol transport as a function of potential applied to the Au-NTM. (b) Plots of flux versus applied potential for all of the permeate molecules. All data show less than 10% relative deviation as deduced from three replicate measurements for each permeate molecule; error bars were omitted for clarity.

for all of the permeate molecules are shown in Figure 2b. Because BA and MBA are less hydrophobic than Tol (Table 1), these molecules should be less susceptible to the potential-dependent partitioning of SDS into the membrane, and this is also observed experimentally. While BDM is the most hydrophilic of the permeate molecules investigated, its octanol/water partition coefficient is still greater than unity (Table 1). This suggests that, in analogy to the other permeate molecules, BDM might show a slight increase in flux with increasing applied potential or perhaps show fluxes that are invariant with potential. Instead, the opposite trend is observed with BDM, a decrease in flux with increasing applied positive potential (Figure 2b).

These data show that as SDS is incorporated into the nanotubes, BDM is rejected by, rather than preferentially partitioned into, the Au-NTM. One way to interpret this result is to posit that incorporation of SDS into the Au-NTM creates a local microenvironment within the nanotubes that, in fact, has a lower effective dielectric constant than that of octanol. For example, the measured hexane/water partition coefficient for BDM is 0.15, meaning that because of its relative hydrophilicity, BDM is preferentially partitioned into water rather than hexane. If the microenvironment within the SDS-containing Au nanotubes is closer to that of hexane (dielectric constant, $\epsilon = 1.8$) than octanol ($\epsilon = 10$), then SDS incorporation would cause the membrane to reject BDM, as is observed experimentally. These results suggest that such studies might provide a route for investigating the local dielectric constant inside the Au nanotubes.

For any electrode and electrolyte, there is a potential called the potential of zero charge (pzc) where there is no excess charge on the electrode surface and therefore no compensating excess ionic charge in the solution layer adjacent to the surface.[2] In terms of this experiment, the Tol flux should be independent of applied potential at potentials negative of the pzc (where SDS is electrostatically rejected by the Au-NTM) and should increase with applied potential at potentials positive of the pzc (where SDS is electrostatically partitioned into the Au-NTM). While this trend is observed, the Tol data (Figure 2b) would suggest that the pzc is at the rather negative potential of -0.26 V. In contrast, in our prior investigation of electromodulated ion transport in such membranes, we showed that in *an electrolyte that contains no specifically adsorbing anions*, the pzc is very close to 0 V. This indicates that, as might be expected, SDS is specifically adsorbed to the Au nanotube surfaces and a potential of -0.26 V is required to remove all of this specifically adsorbed anion. These results suggest that such experiments might provide a way for investigating specific adsorption of ions at metal surfaces.

In conclusion, we have demonstrated a new approach for electromodulating the rate of transport of neutral hydrophobic molecules across a synthetic membrane. This approach is reversible and makes use of simple nonfaradaic electrochemistry. While we have demonstrated only the most rudimentary form of electromodulated transport selectivity here (selectivity based on the hydrophobic effect), it seems likely that more sophisticated forms of transport selectivity might be possible. For example, by making ionic versions of molecule-specific complexing agents (e.g., cyclodextrins), it might be possible to electromodulate transport of the molecules that bind to these agents. We are currently investigating this possibility.

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References

(1) (a) Jirage, K. B.; Hulteen, J. C.; Martin, C. R. *Science* **1997**, *278*, 655. (b) Jirage, K. B.; Hulteen, J. C.; Martin, C. R. *Anal. Chem.* **1999**, *71*, 4913.
(2) Nishizawa, M.; Menon, V. P.; Martin, C. R. *Science* **1995**, *268*, 700.
(3) While there are a number of examples of the electromodulation of transport for organic and inorganic ions,[2,4−6] few reports have focused on the electromodulation of neutral molecule transport.[7]
(4) (a) Burgmayer, P.; Murray, R. W. *J. Am. Chem. Soc.* **1982**, *104*, 6140. (b) Burgmayer, P.; Murray, R. W. *J. Electroanal. Chem.* **1983**, *147*, 339. (c) Burgmayer, P.; Murray, R. W. *J. Phys. Chem.* **1984**, *88*, 2515.
(5) (a) Partridge, A. C.; Milestone, C. B.; Too, C. O.; Wallace, G. G. *J. Membr. Sci.* **1999**, *152*, 61. (b) Zhao, H.; Price, W. E.; Wallace, G. G. *J. Membr. Sci.* **1998**, *148*, 161. (c) Partridge, A. C.; Milestone, C. B.; Too, C. O.; Wallace, G. G. *J. Membr. Sci.* **1997**, *132*, 245. (d) Zhou, D.; Zhao, H.; Price, W. E.; Wallace, G. G. *J. Membr. Sci.* **1995**, *98*, 173.
(6) (a) Miller, L. L.; Zinger, B.; Zhou, Q.-X. *J. Am. Chem. Soc.* **1987**, *109*, 2267. (b) Zhou, Q.-X.; Miller, L. L.; Valentine, J. R. *J. Electroanal. Chem.* **1989**, *261*, 147. (c) Miller, L. L.; Lynch, L. E. *J. Electroanal. Chem.* **1990**, *296*, 141.
(7) Feldheim, D. L.; Elliott, C. M. *J. Membr. Sci.* **1992**, *70*, 9.
(8) Hansch, C.; Leo, A. *Substituent Constants for Correlation Analysis in Chemistry and Biology*; Wiley: New York, 1979.
(9) This wire functions as a quasi reference electrode whose potential is stable and was measured to be +0.14 V versus a saturated Ag/AgCl reference electrode. Applied potentials reported in this paper have been corrected to those corresponding to a saturated Ag/AgCl reference electrode. We waited ~5 min after application of a new applied potential before taking transport measurements.

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