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Communications to the Editor

Introducing Chemical Transport Selectivity into Gold Nanotubule Membranes

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We recently described polymeric membranes that contain a collection of monodisperse Au nanotubules with inside diameters of molecular dimensions <1 nm.[1,2] These membranes can be used to cleanly separate small molecules on the basis of molecular size,[1] and they can show charge-based transport selectivity.[2] Chemical interactions between the membrane material and the molecule to be transported can also be used to control transport selectivity. The introduction of chemically based transport selectivity into our Au nanotubule membranes is described here. This was accomplished by chemisorbing thiols (RSH) to the Au tubule surfaces.[3,4] Membranes derivatized with two different R groups, the hydrophobic R = $-C_{16}H_{33}$ and the more hydrophilic R = $-C_2H_4-OH$, were prepared. The rate and selectivity of transport in these membranes is dramatically altered by the chemical identity of the R group.

The electroless plating procedure described previously[1,2,5] was used to plate the Au nanotubules into the pores of commercially available polycarbonate track-etch filters [Osmonics, 6 μm thick, pore diameter = 50 nm (28 nm diameter Au tubules) or 30 nm (all other Au tubules), 6 × 10^8 pores cm^{-2}]. This plating method yields an Au tubule within each pore, and an Au surface layer on each face of the membrane. The Au surface layers are less than 150 nm in thickness, and thus are a negligible contribution to the total membrane thickness. As discussed in detail in our previous paper, this plating procedure yields "bottleneck" tubules.[1]

The inside diameter (*d*) of the nanotubes was varied by varying the plating time, and a gas-flux method was used to obtain approximate *d* values for each membrane.[1,2] Because these tubes are bottleneck in shape,[1] the *d* values are approximate and really only provide a relative measure of the effective tube diameter. In addition, the *d* values reported here were measured before chemisorption of the thiol, and this will clearly result in further constriction of the pore. However, the decrease in the measured *d* value after incorporation of the thiol is not as dramatic as might be expected on the basis of the length of the thiol. For example, a membrane that contained Au nanotubules with a measured *d* value of 2.6 nm before chemisorption showed a *d* value of 1.9 nm after chemisorption of the R = $-C_{16}H_{33}$ thiol. No change in *d* could be detected after chemisorption of the R = $-C_2H_4-OH$ thiol.

Transport properties were determined by mounting the membrane between the two halves of a U-tube permeation cell.[1,2] The feed half-cell contained 5 mL of an aqueous solution (5 mM) of the molecule to be transported (the permeant molecule); the permeate half-cell initially contained 5 mL of pure water. The transport of the permeant molecule into the permeate half-cell was monitored by periodically assaying (via UV absorbance spectroscopy) the permeate solution. These membranes showed reproducible fluxes for periods of at least 10 days.

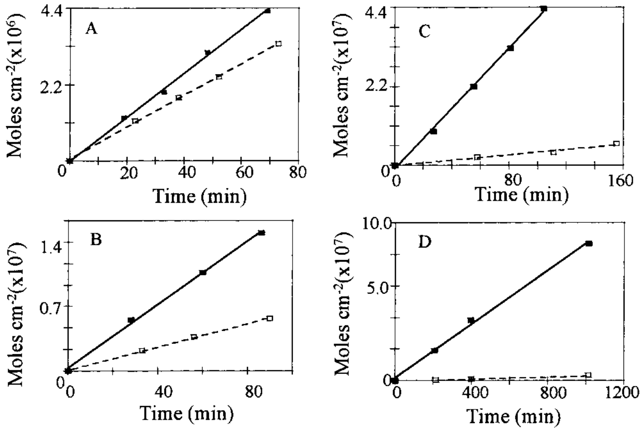

Figure 1. Pyridine permeation data for membranes containing Au nanotubes with approximate inside diameters of (A) 28 ± 1, (B) 7.0 ± 0.1, (C) 1.9 ± 0.1, and (D) 1.5 ± 0.2 nm. In each case, the upper solid line is for the R = $-C_2H_4-OH$ membrane and the lower dashed line is for the R = $-C_{16}H_{33}$ membrane.

Table 1. Pyridine and Toluene Flux and Selectivity Data

		flux in the membranes ($mol\ cm^{-2}\ h^{-1}$)			
permeant molecule	nanotube diameter (nm)	R = $-C_2H_4OH$	R = $-C_{16}H_{33}$	$\alpha_{OH/C16}$	$\alpha_{C16/OH}$
pyridine	7	9.7×10^{-7}	3.5×10^{-7}	2.8	
pyridine	1.9	2.5×10^{-7}	2.2×10^{-8}	11	
pyridine	1.5	1.2×10^{-7}	5.2×10^{-9}	23	
toluene	7	2.7×10^{-6}	5.5×10^{-6}		2.0
toluene	1.9	1.3×10^{-6}	3.6×10^{-6}		2.8
toluene	1.5	4.2×10^{-7}	2.1×10^{-6}		5.0

We begin by comparing fluxes of the permeant molecule pyridine in untreated and thiol-treated nanotubule membranes. An untreated membrane that contained tubules with diameters of approximately 2.6 nm showed a pyridine flux of 1.8 × 10^{-7} mol cm^{-2} h^{-1}. After chemisorption of the R = $-C_2H_4-OH$ thiol the flux increased to 4.2 × 10^{-7} mol cm^{-2} h^{-1}. In contrast, after chemisorption of the R = $-C_{16}H_{33}$ thiol, the pyridine flux dropped to 2.7 × 10^{-8} mol cm^{-2} h^{-1}. These data clearly show that thiol chemisorption has a dramatic effect on permeant flux in these nanotube membranes.

Au nanotube membranes with the following approximate nanotube diameters were used to obtain the majority of the data reported here: *d* = 28 ± 1, 7.0 ± 0.1, 1.9 ± 0.1, and 1.5 ± 0.2 nm. Figure 1 shows permeation data for transport of pyridine through these various membranes. Data for membranes derivatized with both the R = $-C_2H_4-OH$ (upper solid curve) and the R = $-C_{16}H_{33}$ (lower dashed curve) thiols are shown. The corresponding flux data are shown in Table 1. As would be expected,[6] the flux of pyridine decreases with decreasing tubule diameter for both the R = $-C_2H_4-OH$ and R = $-C_{16}H_{33}$

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(1) Jirage, K. B.; Hulteen, J. C.; Martin, C. R. *Science* **1997**, *278*, 655−658.

(2) Nishizawa, M.; Menon, V. P.; Martin, C. R. *Science* **1995**, *268*, 700−702.

(3) Porter, M. D.; Bright, T. B.; Allara, D. L.; Chidsey, C. E. D. *J. Am. Chem. Soc.* **1987**, *109*, 3559−3568.

(4) Chemisorption was accomplished by immersion for 12 h into a 1 mM solution of either mercaptoethanol or hexadecanethiol; the solvent was absolute ethanol.

(5) Menon, V. P.; Martin, C. R. *Anal. Chem.* **1995**, *67*, 1920−1928.

S0002-7863(98)00045-6 CCC: $15.00

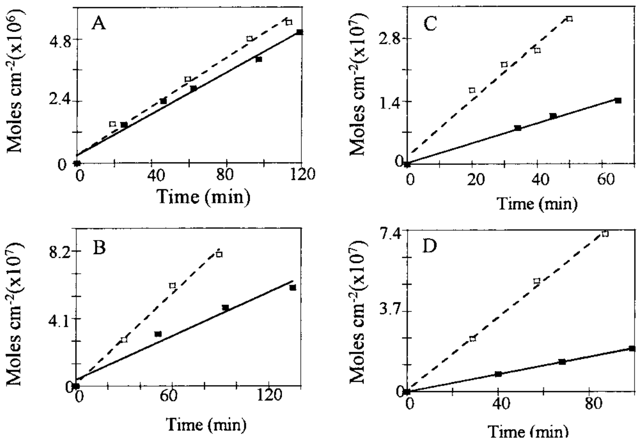

Figure 2. Toluene permeation data. Membranes as per Figure 1. In each case, the upper dashed line is for the R = $-C_{16}H_{33}$ membrane and the lower solid line is for the R = $-C_2H_4-OH$ membrane.

membranes. However, for any nanotube diameter, the pyridine flux in the R = $-C_2H_4-OH$ membrane is greater than that in the R = $-C_{16}H_{33}$ membrane. In addition, as the tubule diameter decreases, the difference in flux between the R = $-C_2H_4-OH$ and the R = $-C_{16}H_{33}$ membranes becomes more dramatic.

This last point can be illustrated by defining a selectivity coefficient, $\alpha_{OH/C16}$, which is the flux of pyridine in the R = $-C_2H_4-OH$ membrane divided by the flux of pyridine in the corresponding R = $-C_{16}H_{33}$ membrane. As shown in Table 1, this selectivity coefficient increases with decreasing tubule diameter. The smallest tubule diameter R = $-C_2H_4-OH$ membrane showed a factor of 23 higher selectivity for pyridine transport than the corresponding R = $-C_{16}H_{33}$ membrane. Similar large $\alpha_{OH/C16}$ values were obtained for two other relatively hydrophilic organic molecules—benzoic acid ($\alpha_{OH/C16} = 28$) and phenol ($\alpha_{OH/C16} = 15$).

Results of analogous permeation studies for the hydrophobic toluene molecule are shown in Figure 2. Now the opposite selectivity pattern is observed; i.e., toluene is preferentially transported in the R = $-C_{16}H_{33}$ membranes. This can be illustrated by defining the alternative selectivity coefficient $\alpha_{C16/OH}$ (Table 1). As was the case for $\alpha_{OH/C16}$, the $\alpha_{C16/OH}$ values increase with decreasing tubule diameter. In addition to toluene, $\alpha_{C16/OH}$ values were determined for *p*-xylene and naphthalene in the d = 1.9 nm membranes. The $\alpha_{C16/OH}$ values obtained were as follows: toluene 2.8, *p*-xylene 6.2, and naphthalene 16.

We suggest the following interpretation for these various data: Note first that of all the flux values reported in Table 1, the toluene fluxes in the R = $-C_{16}H_{33}$ membranes are, in general, the highest. This may, at first glance, seem surprising because the long C_{16} thiol might be expected to hinder diffusion in these membranes.[7] However, flux is proportional to both the diffusion coefficient and *the partition coefficient* for the permeant molecule in the membrane.[8] The comparison of $\alpha_{C16/OH}$ values for toluene, *p*-xylene, and naphthalene clearly shows that the hydrophobic effect causes preferential partitioning of hydrophobic molecules into these hydrophobic membranes. Hence, we suggest that flux for hydrophobic molecules in the R = $-C_{16}H_{33}$ membranes is driven by favorable partitioning of such molecules from water (the feed solution) into the membrane.

This hypothesis is supported by the fact that the expected[6] decrease in flux with tubule diameter is not, in general, observed for toluene in the R = $-C_{16}H_{33}$ membranes (Table 1). This hypothesis also is supported by the fact that the next largest group of flux values in Table 1 is for toluene in the R = $-C_2H_4-OH$ membranes. Water can still lower its free energy by partitioning the hydrophobic toluene molecule into these membranes, but much of the advantage is lost due to the lower hydrophobicity of the R = $-C_2H_4-OH$ group relative to R = $-C_{16}H_{33}$.

The next highest set of fluxes is for pyridine in the R = $-C_2H_4-OH$ membranes (Table 1). Clearly, the hydrophobically driven partitioning of this molecule is greatly diminished relative to toluene, and this accounts for the lower pyridine (vs toluene) fluxes in the R = $-C_2H_4-OH$ membranes. Finally, the lowest fluxes are for pyridine in the R = $-C_{16}H_{33}$ membranes. Now the relatively hydrophilic pyridine molecule pays an enthalpic penalty (loss of hydration) upon entering these hydrophobic membranes. We suggest that this results in a low partition coefficient and correspondingly low fluxes.

Finally, the ratio of the fluxes for toluene vs pyridine transport in the d = 1.5 nm R = $-C_{16}H_{33}$ membrane is greater than 400 (Table 1). This suggests that this membrane might be useful for separating mixtures containing hydrophobic and hydrophilic molecules, with the hydrophobic molecules being preferentially transported to the permeate. To explore this point we did a mixed molecule experiment in which the feed solution was 7 mM in toluene and 5 mM in pyridine. The ratio of the toluene to pyridine fluxes (corrected for the difference in feed concentrations) was 100. While not as high as predicted by the single molecule permeation experiments, this datum does confirm that these membranes show promise for separating hydrophobic and hydrophilic molecules.

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(6) Deen, V. M. *AIChEJ* **1987**, *33*, 1409−1425.

(7) The mechanism of diffusion of these permeant molecules in these membranes is an issue that must be explored in detail. We have shown that the R = $-C_2H_4-OH$ derivatized nanotubes flood when immersed in water. In contrast, permeation experiments with inorganic salts suggest that the R = $-C_{16}H_{33}$ nanotubes do not flood with water. Hence, in these membranes the permeate molecule is partitioned into and diffuses through the C_{16} phase within the tubes.

(8) Veith, W. R. *Diffusion in and Through Polymers*; Hanser Publishers: Munich, 1991; pp 19 and 20.