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Perforated Monolayers: Porous and Cohesive Monolayers from Mercurated Calix[6]arenes[1]

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Membrane filtration methods represent the most energy efficient means currently available for chemical separation and concentration.[3,4] While engineering approaches have proven useful in creating new classes of permeable membranes, relatively little progress has been made in the rational design and control of pore structure at the molecular level.[5] In this paper we introduce the concept of a two-dimensional network of molecular pores, i.e., "*perforated monolayers*". Such arrays are intended to serve as a basis for fabricating thin-film composite membranes bearing uniform, oriented, and adjustable micropores. Preliminary studies reported herein employ a series of calix[6]arene-derived surfactants as first-generation prototypes.[6]

Alkylation of calix[6]arene with a homologous series of n-alkylbromides afforded the corresponding ether derivatives 1a–d.[7] Subsequent mercuration in CDCl$_3$, using 1 equiv of mercury trifluoroacetate (1.2 mM, 48 h at 23 °C), was quantitative.[8] Resulting solutions of 2a–d were diluted with hexane, spread directly onto a pure water subphase (25 °C) of a MGW Lauda film balance, and compressed at a rate of 60 cm^2/min.[9]


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        OR
        |
( ——⟨benzene ring⟩—CH2 )6
        |
        X
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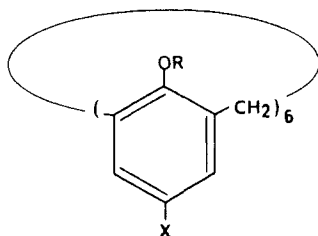
1a, R = C$_2$H$_5$; X = H   2a, R = C$_2$H$_5$; X = HgO$_2$CCF$_3$
 b, R = n-C$_4$H$_9$; X = H   b, R = n-C$_4$H$_9$; X = HgO$_2$CCF$_3$
 c, R = n-C$_8$H$_{17}$; X = H   c, R = n-C$_8$H$_{17}$; X = HgO$_2$CCF$_3$
 d, R = n-C$_{16}$H$_{33}$; X = H   d, R = n-C$_{16}$H$_{33}$; X = HgO$_2$CCF$_3$

Surface pressure–area isotherms measured for 2a–d readily establish their surfactant behavior. Each calixarene produced a stable monolayer having a limiting area of ca. 150 ± 8 Å^2/molecule (Figure 1); within experimental error, monolayers formed from 2a–d were identical.[10] Transfer of compressed monolayers (20 dyn/cm, 25 °C) to glass microscope slides by single passage from water into air (0.8 cm/min) resulted in transfer ratios[11] of
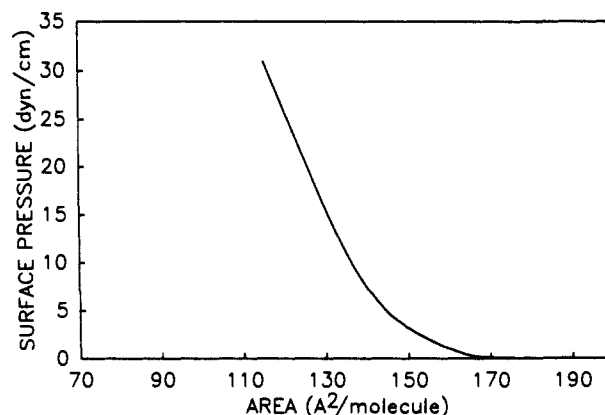
(1) Supported by the Division of Basic Energy Sciences of the Department of Energy (DE-FG02-85ER-13403).

(2) On leave from the Institute of General Chemistry, Agricultural University of Warsaw, Poland.

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(6) Review: Gutsche, C. D. In Synthesis of Macrocycles: The Design of Selective Complexing Agents; Izatt, R. M., Christensen, J. J., Eds.; Wiley-Interscience: New York, 1987; p 93.

(7) Procedures used were similar to those previously described: Gutsche, C. D.; Lin, L.-G. Tetrahedron 1986, 42, 1633. All calixarenes gave satisfactory ^{1}H NMR and IR spectra; mp 323–324, 236–238, 110.5–112, and 85–86 °C for 1a–d, respectively.

(8) In each case, the integrated ^{1}H NMR spectra showed the loss of six aromatic protons per calixarene.

(9) Actual calixarene concentrations (typically 2 mg/mL; 4/1 hexane/CDCl$_3$,v/v) were determined by ^{1}H NMR analysis with CH$_3$OH as an internal standard.

(10) Compression of 1b, "spread" at the air–water interface, showed an apparent limiting area of ca. 25 Å^2/molecule.

(11) The transfer ratio is defined as the decrease in monolayer area at the gas–water interface divided by the geometrical surface area of the substrate passing through the interface.

Figure 1. Surface pressure–area isotherm for 2b.

0.85, 0.99, 0.94, and 0.96 for 2a–d, respectively; corresponding advancing contact angles for water on these surfaces were 57°, 64°, 82°, and 83°.[12]

The limiting areas observed for 2a–d are in excellent agreement with that which is predicted from CPK models (155 Å^2/molecule), if it is assumed that the calixarenes lie at the air–water interface in a hexagonally packed array and that all of the mercury ions are in contact with water. The fact that 2a–d exhibit the *same limiting area*, in and of itself, provides compelling evidence for such an orientation. For a hydrophilic glass surface bearing a thin porous monolayer of surfactant, one expects a somewhat hydrophilic surface due to penetration of water through the film.[13] The relatively high surface hydrophilicity that is observed for transferred monolayers of 2a and 2b is consistent with a porous film structure. The precise reason for the decrease in wettability that is found, as the alkoxy groups are extended, is not clear at present; likely possibilities include the following: (i) the alkyl chains are "filling in" the molecular and interstitial pores, by assuming one or more gauche conformations or (ii) open pores are maintained via an all-anti configuration of the alkyl chains, but the distance to the hydrophilic subphase is too great to be detected by contact angle measurements.[14]

In an attempt to stabilize a monolayer prepared from 2b, we have examined the influence of malonic acid on the cohesiveness of 2b. In principle, replacement of trifluoroacetate by a bridging malonato ligand could lead to a cross-linked and stable calixarene network. A monolayer of 2b was compressed to 20.6 dyn/cm, with a movable barrier which was positioned directly behind a second barrier that contained a 5-mm slit (canal viscometer). Subsequent movement of only the former, in the expansion direction, resulted in a decrease in surface pressure to 6.1 dyn/cm after 11 min (time required for full expansion); after a total of 25 min, the pressure fell to 0 dyn/cm. Analogous experiments carried out in which malonic acid (10 μM) was introduced into the subphase after compression resulted in a pressure decrease from 20.3 to 18.8 dyn/cm after 72 min and to 16.1 dyn/cm after 140 min.[15] Transfer of these monolayers to glass slides (water to air) resulted in a transfer ratio and contact angle of 1.40 and 66°, respectively. Attempted stabilization with oxalic acid (10 μM) failed to produce a cohesive monolayer; i.e., the surface pressure decreased, precipitously, to 0 dyn/cm upon expansion of the solid movable barrier. CPK models strongly suggest that oxalic acid, but not malonic acid, may have difficulty in spanning

(12) Contact angles were measured immediately and were unchanged upon storage in air for 12 h. Reported values are the average from at least six water droplets on each sample, at different locations.

(13) Popovitz-Biro, R.; Hill, K.; Landau, E. M.; Lahav, M.; Leiserowitz, L.; Sagiv, J.; Hsiung, H.; Meredith, G. R.; Vanherzeele, H. J. Am. Chem. Soc. 1988, 110, 2672. Maoz, R.; Sagiv, J. Langmuir 1987, 3, 1034, 1045.

(14) Recent contact angle studies for alkyl thiol derivatized gold suggest that wetting is dominated by short-range interactions (≤5 Å): Troughton, E. B.; Bain, C. D.; Whitesides, G. M.; Nuzzo, R. G.; Allara, D. L.; Porter, M. D. Langmuir 1988, 4, 365.

(15) Similar experiments carried out with succinic acid in the subphase showed a pressure drop from 19.6 to 14.9 dyn/cm after 2.5 min, which remained unchanged after a total of 60 min.

adjacent mercurated calixarenes at the air–water interface. The fact that malonic and not oxalic acid is capable of increasing the cohesiveness of the calix[6]arene monolayer strongly suggests that bridging is, in fact, responsible for this stabilization.[16]

Direct evidence for the porous character of compressed monolayers of **2b** (before and after treatment with malonate) has been obtained by measurement of water evaporation through the film.[17] Placement of a Ni/Cr wire basket, containing 200 mg of dried (170 °C) 6–12 mesh silica desiccant, 5 mm above a monolayer of **2b** for 1 h (20 dyn/cm; 20 μM sodium trifluoroacetate subphase, maintained at 25 °C), resulted in water evaporation which was 92.4 ± 5.6% of that found with use of a clean surface; with a 10 μM malonic acid subphase, the percentage was 88.4 ± 3.6%.[18,20] Similar experiments that were carried out by using a monolayer of 1-hexadecanol (20 dyn/cm; 20 μM sodium trifluoroacetate subphase) showed a water evaporation of 64.0 ± 3.5%. Thus, monolayers of **2b**, compressed to a surface pressure of 20 dyn/cm, maintain a pore structure which offers relatively little resistance toward the permeation of water.[21]

Studies that are now in progress are aimed at fabricating composite membranes based on perforated monolayers derived from **2a–d**, defining their permeability characteristics, and synthesizing related "porous surfactants" for use in the construction of other perforated monolayers.

(16) Monolayers of **2b** have also been stabilized using dithiothreitol (10 μM). In this case, surface pressures fell from 25.4 to 24.7 dyn/cm after 71 min and remained unchanged after 131 min. Transfer of these monolayers to glass slides, however, gave irreproducible transfer ratios that ranged between 0 and 0.9.

(17) Adamson, A. W. *Physical Chemistry of Surfaces*, 4th ed.; John Wiley: New York, 1982; p 143.

(18) The percentage of water evaporation relative to bare surface is defined as $[(A - C)/(B - C)] \times 100$, where A and B are the percent weight gains in the presence and absence of the monolayer, respectively, and C is the percent weight gain in the laboratory ambient.[19]

(19) Archer, R. J.; LaMer, V. K. *J. Phys. Chem.* **1955**, *59*, 200.

(20) All evaporation data are reported as averages of at least four independent experiments, carried out with a MG Lauda film balance.

(21) CPK models predict a maximum pore diameter of 6.4 Å, when each of the aromatic rings are approximately perpendicular to the air–water interface. Rotation about the bridging methylenes can further reduce the effective pore size.

The Preparation and Crystal Structures of New Platinum/Phosphonate Complexes

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Certain phosphonates [e.g., phosphonoformic acid (PFA), phosphonoacetic acid (PAA), some derivatives of methylene diphosphonate (MDP), and others] are known to inhibit Herpes, influenza, and other viruses.[1–3] Their anti-viral activity is associated with their inhibition of viral polymerases and transcriptases,[4–6] dication-dependent enzymes which catalyze the

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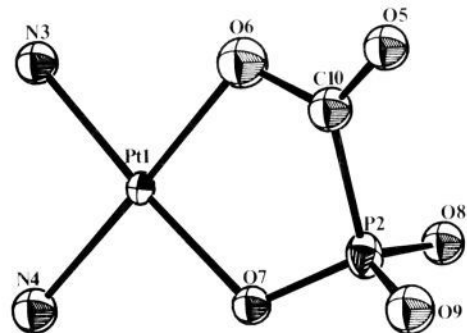
Figure 1. Structure of the [*cis*-Pt(NH$_3$)$_2$(PFA)]$^-$ anion. Average distances around the periphery of the Pt atom are normal: Pt–N = 2.09 (2), Pt–O(C) = 2.08 (1), C–O = 1.26 (2), C–P = 1.85 (2), P–O = 1.56 (2), and Pt–O(P) = 2.05 (2) Å. Na$^+$[*cis*-Pt(NH$_3$)$_2$Pt(PFA)$^-$·3H$_2$O crystallizes in the triclinic space group P1, with a = 6.366 (8) Å, b = 13.00 (2) Å, c = 6.933 (6) Å, α = 93.30 (9)°, β = 114.22 (8)°, γ = 93.96 (10)°, ρ_c = 2.703 g cm^{-3} for Z = 2. The structure was solved by standard heavy atom techniques and refined a final agreement factor of R = 3.4%, $R(w)$ = 5.8% for 833 reflections. A listing of final atomic coordinates is available.[15]
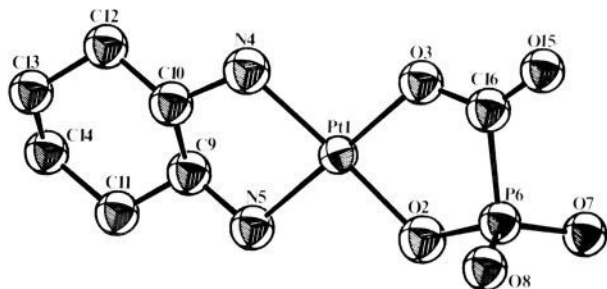

Figure 2. Structure of Na$^+$[Pt(*trans-l*-dach)(PFA)]$^-$. The compound crystallizes in the cubic space group P432, with a = 21.631 (8) Å, V = 10120 (7) Å^3, Z = 24. The structure was solved by using direct methods to locate the platinum atom and refined to present agreement factors of R = 9.9% and $R(w)$ = 7.7% for 842 reflections.

formtion of a complementary strand of polynucleotide from a single-stranded parent polynucleotide.[6–9] The molecular basis of phosphonate action has not been unambiguously established, but it is strongly suspected tht the phosphonates bind either to an endogenous metal of the enzyme (e.g., Zn^{2+}) or the exogenous coenzymes (e.g., Mg^{2+} or Mn^{2+}) required for enzymatic activity. Thus, the paucity of information about the ligand properties of these compounds, and the structures of their complexes, is somewhat surprising. Only a few structures of MDP[10] and py-

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(8) Several *non-viral* DNA polymerases are now believed not to contain constitutive Zn (ref 9a–f), although metal-binding site(s) are present; on the other hand, Zn has been clearly demonstrated in at least two non-viral RNA polymerases (ref 9g,h).

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