Permeation Control by a Phase Transition of the Dialkylsilane Monolayer immobilized on a Porous Glass Plate

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The polymeric monolayer of dialkylsilane amphiphiles was covalently bonded onto a porous glass plate by the Langmuir–Blodgett technique, and the permeability of NaCl could be controlled by the phase transition of the immobilized monolayer.

Permeability-controllable membranes have been developed as models to study the transport properties of biological membranes.[1] We have reported that signal-receptive, permeability-controllable, bilayer-immobilized nylon capsule membranes[2] and polyion complex films,[3] where the bilayers are supported on a polymer membrane, act as a permeation valve responding to external stimuli. Kajiyama and co-workers have prepared a porous filter membrane covered with Langmuir–Blodgett (LB) multilayers and have used this to control the permeability of K^+ ions[4a] and O_2/N_2 gases.[4b]

We have prepared a covalently-bonded dialkylsilane monolayer on a porous glass plate using the Langmuir–Blodgett technique and have used it to control the permeability of NaCl *via* the phase transition of the immobilized monolayer. Sagiv and coworkers have shown[5] that well-organized mono- and multi-layers can also be prepared on a flat glass plate by spontaneous adsorption of monoalkylsilane compounds.

Monolayer properties of the newly prepared γ-(*N*,*N*-dioctadecylsuccinylamino)propyltriethoxysilane ($2C_{18}$-Si)† or the commercial octadecyltrichlorosilane (C_{18}-Si, Tokyo Kasei, Co., Tokyo) were studied using a Lauda film balance. A chloroform solution (0.3 mg/ml) of amphiphiles was spread on the surface of doubly-distilled water at 10 °C. Pressure–area isotherms of $2C_{18}$-Si monolayers in the subphase at pH 5.8 or 2 are shown in Figure 1. When the subphase was at pH 5—7, the $2C_{18}$-Si monolayer showed two steep rises in the curve corresponding to the expanded liquid and condensed solid phases, respectively, in good agreement with other dialkyl surfactants.[4,6] The built-up multilayers (n = 30) when

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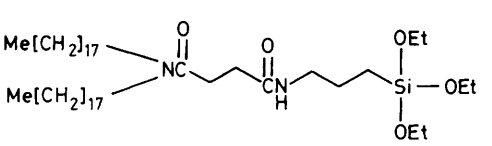
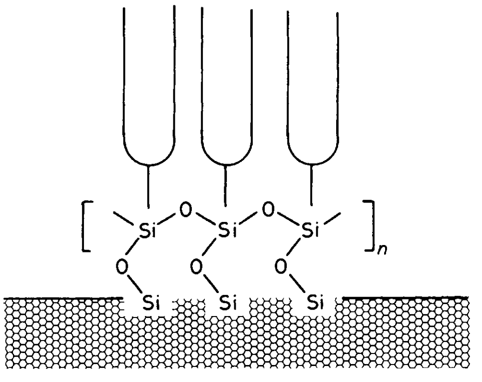
† The new compound $2C_{18}$-Si was prepared from *N*,*N*-dioctadecylsuccinyl chloride and γ-aminopropyltriethoxysilane in benzene at room temperature. A white waxy solid was obtained from ethanol, yield 46%, R_f 0.8 (diethyl ether). The structure was confirmed by n.m.r. spectra and elemental analyses.



$2C_{18}$-Si



transferred onto a CaF_2 plate at a surface pressure of 40 mN m^{-1} showed sharp absorptions in the Fourier transform i.r. spectra, corresponding to Si–O–C stretching,[7] at 1080 and 1103 cm^{-1}, which suggests that $2C_{18}$-Si amphiphiles exist in the monomeric triethoxysilyl form in the monolayer at neutral pH. The monomeric monolayer could not be transferred at a surface pressure of 20 mN m^{-1} (the expanded liquid phase).

In contrast, the $2C_{18}$-Si monolayer showed only a condensed solid phase at pH 2 in the pressure–area isotherms (Figure 1) and the built-up multilayers (n = 30) on a CaF_2 plate showed absorptions corresponding to Si–O–Si stretching at 1026 and 1095 cm^{-1} instead of Si–O–C absorptions.[7] The $2C_{18}$-Si monolayer at pH 2 could be transferred at a surface pressure of 20—40 mN m^{-1}. These results indicate that the $2C_{18}$-Si monolayer can be easily polymerized in the acidic subphase and transferred in the polymeric form. When the single chain, octadecyltrichlorosilane (C_{18}-Si) was spread on the neutral subphase, the monolayer showed only the polymerized, condensed phase because of the high reactivity of the trichlorosilyl groups.

The covalent binding of monolayers on a porous glass plate (0.9 × 10 × 10 mm, average pore diameter: 5 nm, average pore volume: 0.44 ml g^{-1}) was carried out as follows. The monolayer on the water surface was transferred onto a cleaned, activated porous glass plate, which had been immersed in the subphase before spreading the monolayer and was withdrawn at a surface pressure of 40 mN m^{-1}. The transfer ratio was found to be 0.95 ± 0.08. The silyl groups of the transferred monolayer were covalently bonded on the porous glass plate by heating at 80 °C for 20 min. The polymeric $2C_{18}$-Si monolayer on the glass plate showed a sharp endothermic peak at 44 °C in aqueous media from differential scanning calorimetry (d.s.c.) measurements, which may indicate a phase transition from solid to disordered liquid crystalline state of the immobilized monolayer. The monomeric $2C_{18}$-Si monolayer transferred from the neutral subphase showed a small, broad peak around 44 °C. The single chain C_{18}-Si monolayer transferred in the polymerized form showed no d.s.c. peaks. These d.s.c. data may suggest that the monomeric $2C_{18}$-Si and the polymeric C_{18}-Si monolayers do not have a well-oriented structure.

The porous glass plate with the immobilized monolayer was used to separate a 0.2 mol dm^{-3} aqueous solution of NaCl and distilled water, and permeation of NaCl was followed by increases in electrical conductance of the distilled water phase at various temperatures. Arrhenius plots of NaCl permeation are shown in Figure 2. The original, porous glass plate was semipermeable to NaCl and gave the usual straight Arrhenius plot. However, when the glass plate with the covalently bonded polymeric $2C_{18}$-Si monolayer was employed, the permeability of NaCl was decreased 2—5 times relative to that

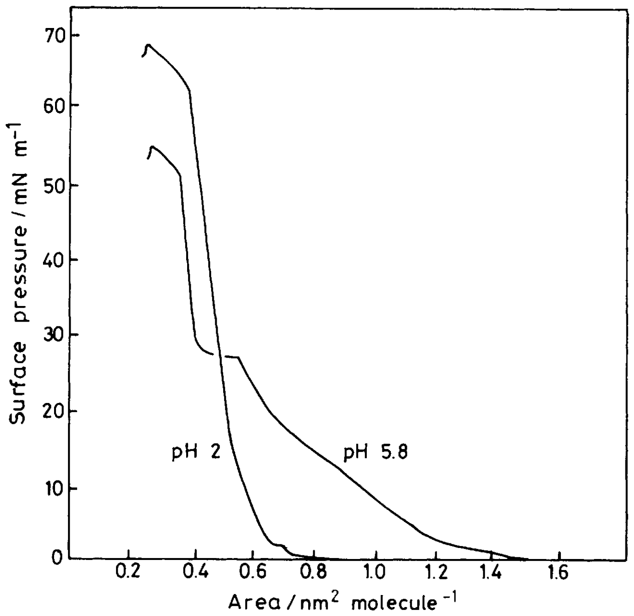


Figure 1. Surface pressure–area isotherms of $2C_{18}$-Si dialkyl amphiphiles on water (pH 5.8 and 2) at 10 °C.

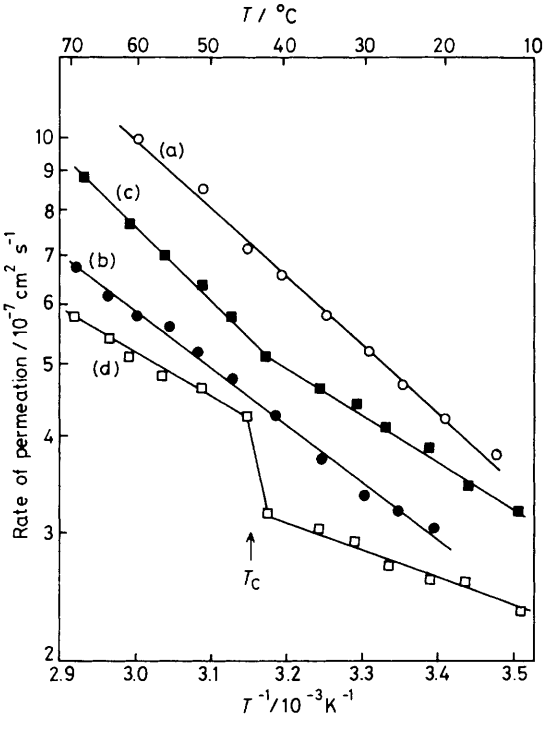


Figure 2. Arrhenius plots of NaCl permeation through the porous glass plate with the immobilized monolayer. (a) The original porous glass plate; (b) the polymeric, single chain C_{18}-Si immobilised monolayer; (c) the monomeric $2C_{18}$-Si immobilised monolayer; (d) the porous glass plate with the polymeric $2C_{18}$-Si immobilized monolayer.

of the original glass and the Arrhenius plot gave a discontinuity near 44 °C, consistent with the phase transition temperature (T_c) of the immobilized monolayer obtained from d.s.c. measurements. Thus, the immobilized $2C_{18}$-Si monolayer can control the permeability of substances such as NaCl by the phase transition from solid to liquid crystalline state. The glass plates with the immobilized monomeric $2C_{18}$-Si monolayer and the single chain, polymeric C_{18}-Si monolayer were relatively permeable to NaCl and gave slightly curved, and straight Arrhenius plots, respectively, because of the disordered structures of the monolayers.

In conclusion, a covalently bonded, polymeric dialkylsilane monolayer on a porous glass plate prepared using the LB techique can control the permeability by using the phase transition of the immobilized monolayer. This is the thinnest monolayer membrane to date which acts as a permeation valve. The glass plate with the immobilized monolayer can be used repeatedly without damaging the monolayer because the membrane is covalently bonded onto the glass.

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