Selective Storage and Permeation of NaOH and HCl across a Capsule Membrane Coated with Charged Synthetic Bilayers

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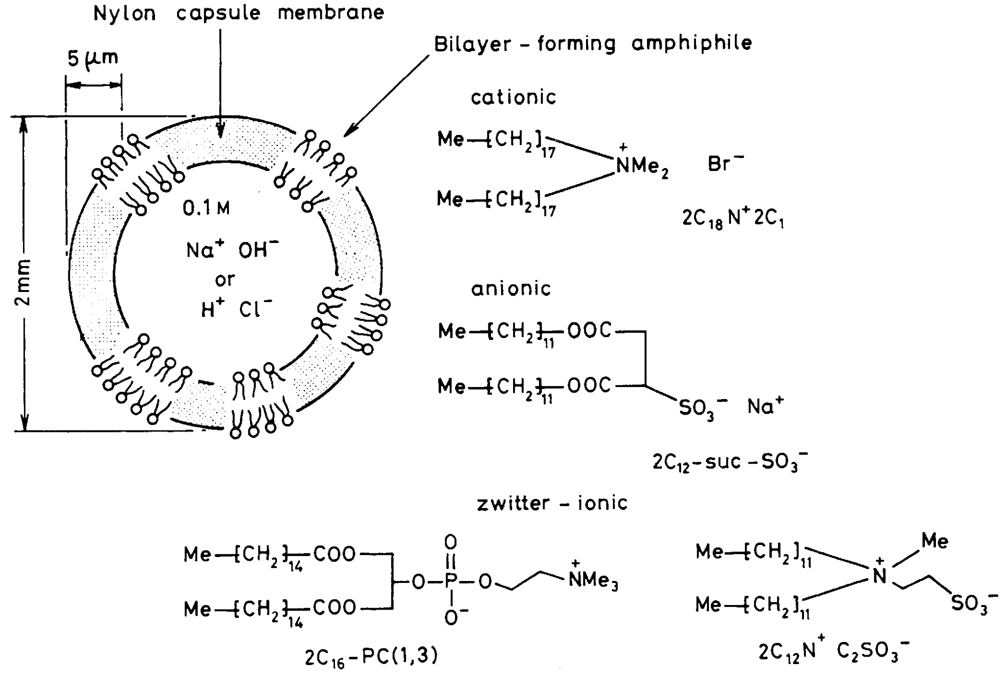
Nylon capsule membranes with positively or negatively charged bilayer coatings could selectively trap 0.1 M NaOH or HCl in the inner aqueous phase, respectively, and the permeation was reversibly controlled near the phase transition of the coating bilayer.

Numerous important membrane-related processes such as active transport or oxidative phosphorylation in mitochondria are connected with an electrochemical gradient of H^+ or OH^- across the membrane. The kinetics of passive transport and the storage of these ions, therefore, have been examined in various liposomes as models for biological membranes.[1–3] Phosphocholine-liposomes, however, do not seem to provide suitable systems for the storage of the H^+/OH^- electrochemical gradient. That is, they generally have a zwitterionic head group which is unfavourable for providing a selective permeability barrier for ions, they are chemically unstable under acidic and basic conditions, the inner aqueous phase is very small, and the bilayer wall is not necessarily sufficiently strong against osmotic pressure differences.

We report here that a chemically stable, bilayer-coated large nylon capsule membrane can selectively trap 0.1 M



Scheme 1

NaOH or HCl in the inner aqueous phase depending on the surface charge of the coating bilayer, and reversibly control the permeation of these ions from the inner aqueous phase near the phase transition temperature of the coating bilayer. We have already reported that such bilayer-coated capsules can combine the advantages of providing physically strong polymer capsules and physicochemically interesting bilayer properties.[4-7] A schematic illustration of the capsule is shown in Scheme 1.

Large nylon capsules (diameter: 2 mm; membrane thickness: 5 μm) were prepared by interfacial polymerization from ethylenediamine and 1,10-bis(chlorocarbonyl)decane (Nylon-2,12). The capsules obtained were dialysed against 0.1 M aqueous NaOH or HCl to provide capsules containing these ions in the inner aqueous phase. They were coated with dialkyl amphiphiles in dodecane according to previous methods.[4-7] Electron microscopy and differential scanning calorimetry (d.s.c.) confirmed[4-7] that the amphiphiles on the capsule (0.15 ± 0.03 mg/capsule) formed multi-bilayer structures and had a phase transition from gel to liquid crystal at a similar temperature to that for aqueous bilayer vesicles.

The permeability of these capsules to NaOH or HCl was measured by detecting increases in the electrical conductance of the outer water phase, after dropping one capsule into deionized water. The permeability of H^+ or OH^- was also followed directly by a pH meter. The permeability constants obtained from both methods gave the same values, indicating that H^+ or OH^- permeates together with the appropriate counter-ion (Cl^- or Na^+) across the membrane. The permeability constants, P, were obtained at various temperatures (20—80 °C) and Arrhenius plots are shown in Figure 1, with data for NaCl (neutral salt) permeation.[4-7]

In the case of the uncoated semipermeable capsule, all the three substances (NaOH, HCl, and NaCl) completely permeate within 20 min at the same rate, and plots of log P *vs.* $1/T$ were straight lines (shown by dotted lines in Figure 1). When the bilayer-coated capsule membrane was employed, the permeability of the neutral salt (NaCl) was reduced by factors of 20—100 relative to that of the uncoated capsule and Arrhenius plots showed distinct inflections for the three bilayers with different charges. The drastic change in NaCl release properties is associated with the phase transition of the coating bilayers from a rigid gel to a disordered liquid crystalline state.[4-7] Phase transition temperatures (T_C) obtained separately from d.s.c. measurements are shown by arrows in Figure 1.

The permeability of NaOH and HCl across the bilayer-coated capsule membrane was markedly affected by the surface charge of the coating bilayer. The positively charged capsule membrane coated with $2C_{18}N^+2C_1$ amphiphiles can retain 0.1 M NaOH and the permeation is regulated near T_C, as it is for NaCl, although the membrane is highly permeable to HCl. In contrast, the negatively charged capsule coated with the $2C_{12}$-suc-SO_3^- bilayer can trap 0.1 M HCl as well as NaCl, but not NaOH, in the inner core. When the zwitter-ionic $2C_{12}N^+C_2SO_3^-$ bilayer was employed, the permeation of both 0.1 M NaOH and HCl was relatively fast and was not regulated near T_C. Similar results were obtained from a phosphocholine-type $2C_{16}$-PC(1,3) bilayer-coated capsule (not shown in Figure 1).

Diffusion and permeation of H^+/OH^- through even hydrophobic bilayers are proposed to be exceptionally fast ($P = 10^{-3}$—10^{-5} cm/s), because water molecules present in bilayers are partly associated *via* hydrogen bonds. Proton and hydrogen ion-permeation, however, should proceed with a counter-ion in order to avoid forming a trans-membrane potential. Therefore, the permeation of NaOH or HCl across the membranes would be controlled by the rate-limiting flow of the counter ions (Na^+ or Cl^-). For the capsule membrane coated with positively charged bilayers, the negatively charged Cl^- may diffuse and permeate smoothly as compared with the positively charged Na^+ (see also schematic representations in Figure 1). Permeation of NaCl and NaOH, which have Na^+ as the counter-ion, is slow and regulated by the phase transition of the coating cationic bilayer. Cationic

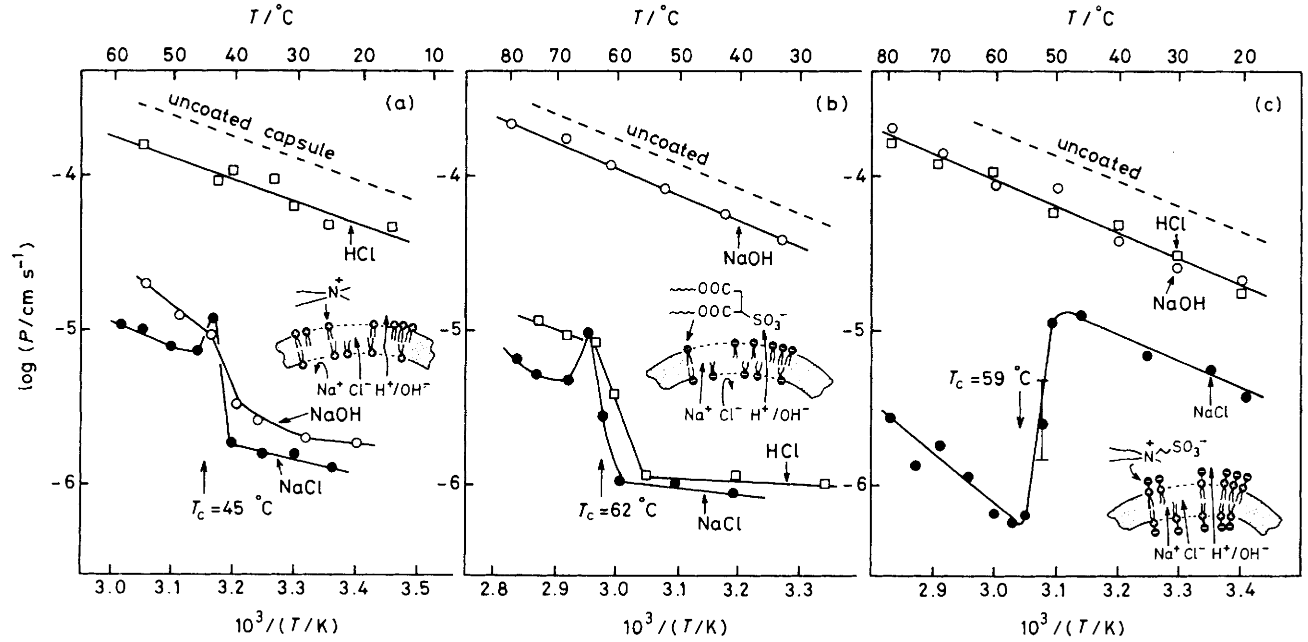


Figure 1. Arrhenius plots of selective permeation of NaOH, HCl, and NaCl across the capsule membrane coated with (a) cationic, (b) anionic, and (c) zwitter-ionic bilayers. The permeabilities of all three substances across the uncoated capsule are the same and the Arrhenius plots for this are shown as dotted lines.

bilayers do not provide a high barrier to HCl because the permeation of H^+ and the negatively charged Cl^- is fast. Opposite selectivity is observed for the negatively charged capsule; HCl, as well as NaCl, which have the negatively charged Cl^- as counter-ion, can be preserved in the inner aqueous phase. Neither NaOH nor HCl can be trapped in the zwitter-ionic capsule, since it provides a relatively low barrier for permeation of Na^+ and Cl^-. This is consistent with the fact that the pH difference across the membrane disappears in the time-scale of stopped-flow experiments in zwitter-ionic liposomes.[1–3]

In conclusion, capsule membranes coated with positively or negatively charged bilayers can selectively preserve NaOH or HCl, even at 0.1 M concentration, in the inner aqueous phase, respectively, and the permeation of these ions is reversibly controlled near the phase transition of coating bilayers. Liposomes cannot trap stably such a high concentration of H^+ or OH^- in the inner phase because of the zwitter-ionic surface charge and also because the bilayer walls are chemically and osmotically easily breakable.

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