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PERMEABILITY OF LARGE POLYAMIDE MICROCAPSULE COATED WITH SYNTHETIC BILAYER MEMBRANE

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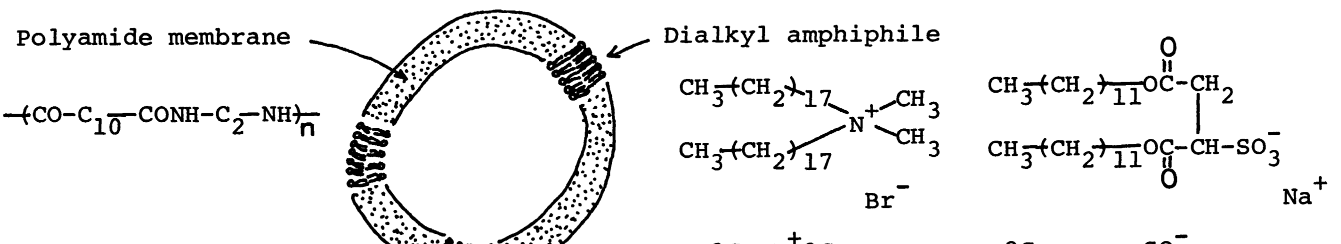
Polyamide ultrathin capsules coated with the bilayer membrane of dialkyl amphiphiles were prepared. Permeation of NaCl from the inner aqueous phase of the coated capsules was reduced 30-50 times relative to that of the uncoated semipermeable capsule, and drastically changed near the phase transition temperature of the coating bilayer membrane.

Since we reported the formation of the bilayer vesicle from the synthetic dialkyl amphiphiles,[1)] trapping of various water soluble substances in the inner water core has been examined by several groups.[2-5)] These synthetic vesicles, as well as liposomes from natural lipids, however, have some disadvantages with regard to compartmentalization. That is, these bilayer vesicles have very small inner water phases (0.5-1% of the outer aqueous phase) and the bilayer wall is easily broken when the difference in ionic strength or osmotic pressure exists between the inner and outer phases.

We describe in this letter preparation of the large and strong microcapsule with the bilayer characteristics by coating the semipermeable capsule membrane with dialkyl amphiphiles. The permeability of NaCl across the membrane is discussed. A schematic illustration of the capsule is shown below. Permeation of metal ions across the capsule membrane coated with egg lecithin is briefly reported.[6)]



$2C_{18}N^{+}2C_1$ $2C_{12}$-suc-SO_3^-

Large semipermeable capsules were prepared by interfacial polymerization using a drop technique[6)] from ethylenediamine and 1,10-decanedicarbonyl chloride. Polyamide capsules of ultrathin membrane (thickness; 5-6 μm) and large diameter (2.5 mm) were obtained, after removal of organic solvent and dialysis against water. Scanning electron micrographs of the inner, outer and sectional view of the capsule

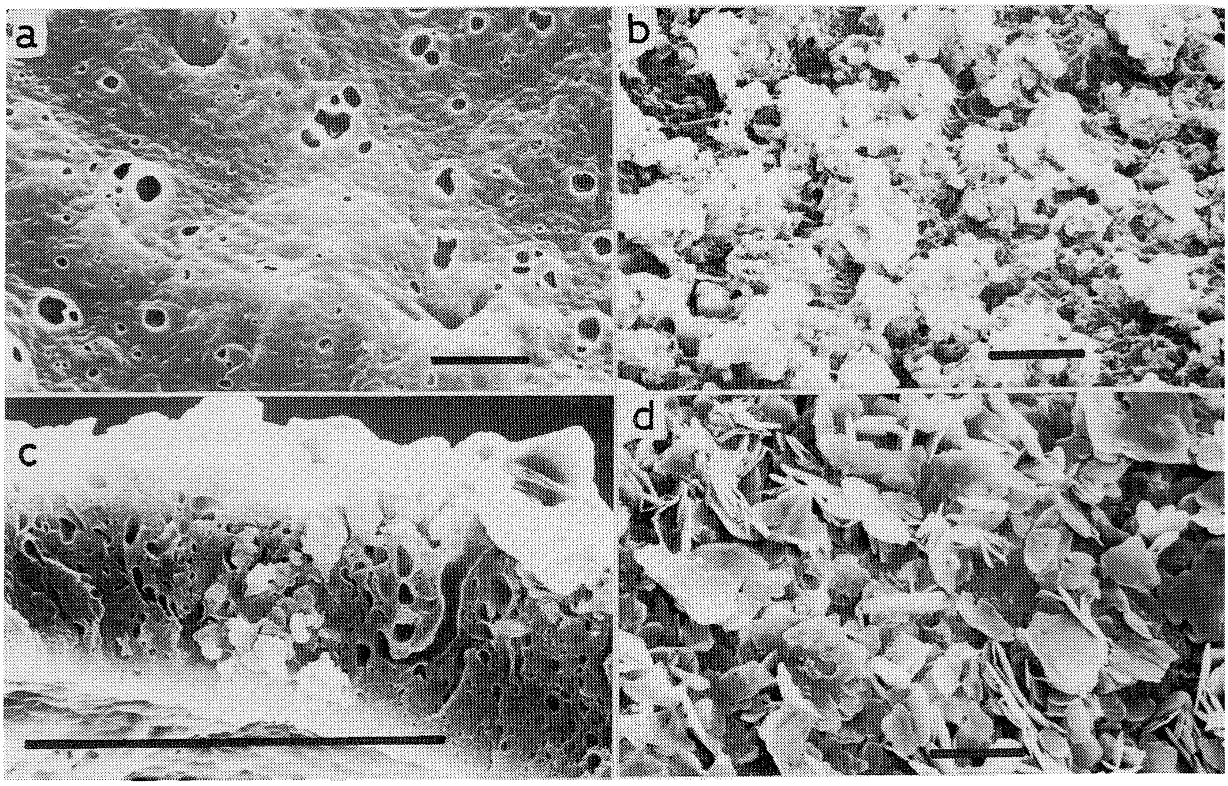


Fig. 1 Scanning electron microgaghs (scale= 10 μm)

a) Inner membrane surface of uncoated capsule, x2500

b) Outer membrane surface of uncoated capsule, x2500

c) Intersection of uncoated capsule membrane, x10000

d) Outer membrane surface of $2C_{18}N^{+}2C_{1}$-coated capsule, x2500

membrane are shown in Fig. 1a,b,c ,respectively. The polyamide capsule was proved to have an unsymmetrical and porous membrane structure whose inner and outer surface are flat and rough, respectively.

The bilayer membrane-coated capsules were prepared as follows. Dialyzed capsules were kept overnight in 0.2M NaCl aqueous solution to obtain capsules containing NaCl in the inner aqueous core. They were transferred to a dodecane solution (3 ml) of dialkyl amphiphiles(50 mg) and submerged at 60°C for 10 mim. Amphiphile-coated capsules were picked up and rolled on a filter paper to remove the excess dodecane solution. The amphiphile contents on the capsule were estimated to be 0.1-0.2 mg/capsule whose surface area was 0.27 cm^2. Scanning electron micrograph of the outer surface of $2C_{18}N^{+}2C_{1}$-coated capsule membrane is shown in Fig.1d. It was observed the amphiphile-coated capsule was entirely covered by plates of $2C_{18}N^{+}2C_{1}$ and clear pores were not seen in the intersection. Similar electron micrographs were obtained from the $2C_{12}$-suc-SO_3^- coated capsule.

The permeability of these capsules to NaCl was measured by detecting increases in the electrical conductance of the outer water phase, after dropping one capsule into distilled water. Fig.2 shows typical examples of the release of NaCl to the outer water phase with time. Complete release of NaCl was achieved within 40 mim when the uncoated capsule was employed. The dodecane-coated capsule showed the same tendency except for a short induction period. This indicates the polyamide capsule is made of semi-permeable membrane, in consistence with the observation of Fig.1a,b,c. A marked decrease in NaCl flux was observed with the $2C_{18}N^{+}2C_1$- or $2C_{12}$-suc-SO_3^--coated capsules. It was estimated from the change of specific conductance after destroying the capsule that the concentration of NaCl incorporated in the inner water phase was 0.18-0.19 M.

As Fick's law is applicable to the permeability of microcapsules,[7] the permeability constant P (cm/s) is calculated from eq.1.

$$P = S/\Delta C \cdot A \qquad (1)$$

where S is the efflux (slope of Fig.2), ΔC denotes the difference in electrolyte concentration between the outside and inside of capsules and A is the surface area of a capsule.

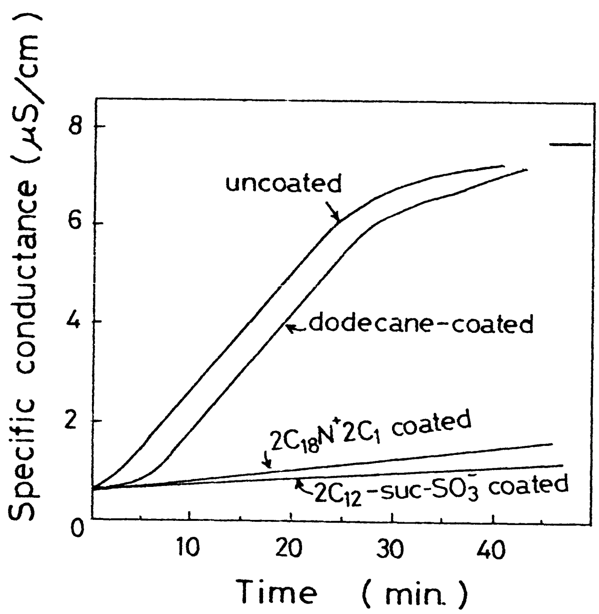


Fig. 2 NaCl release from polyamide capsule at 25°C

Permeability constants P obtained for uncoated, dodecane-coated, $2C_{18}N^{+}2C_1$-coated and $2C_{12}$-suc-SO_3^--coated capsules were 3.4×10^{-5}, 3.3×10^{-5}, 1.6×10^{-6} and 7.8×10^{-7} cm/s, respectively. Release of NaCl from the coated capsule was reduced 30-50 times compared to that of the uncoated and dodecane-coated ones.

Phase transition behavior between gel and liquid crystal states of the bilayer membrane of dialkyl amphiphiles is well known and probed by a variety of physical techniques such as differencial scanning calorimetry(DSC).[8] DSC measurement of dialkyl amphiphile-coated capsules are shown in Fig.3. The uncoated and dodecane-coated capsules had no peak in the range of 5-90°C. $2C_{18}N^{+}2C_1$- and $2C_{12}$-suc-SO_3^--coated capsules had a sharp endothermic peak at 42°C and 62°C, respectively. This clearly shows these amphiphiles incorporated in the capsule membrane exist as the bilayer assemblage similar to that in aqueous solution.

It is reported that the permeability of dialkyl amphiphile vesicles and dialkyl amphiphile-blended PVC polymer membrane is changed near the phase transition temperature (T_C) of bilayers.[9] Permeability constants (P) of coated capsules were obtained at various temperatures (20-80°C) to study the effect of the phase transition on NaCl release. Arrhenius plots are shown in Fig.4. In the case of the uncoated capsule, the plot of log P vs. 1/T gave a straight line. On the contrary, Arrhenius plots gave inflections with a maximum at 42°C and 65°C in the case of $2C_{18}N^{+}2C_1$- and $2C_{12}$-suc-SO_3^--coated capsules, respectively. These inflection and maximum points correspond exactly to T_c observed in Fig.3. The fast release of NaCl near and above T_c is associated with phase transition from a rigid gel to disordered liquid crystalline state of the bilayers on the capsule membrane.

It is very interesting the permeability is varied by a factor of 10 by changing temperature of less than 5°C near T_c.

The synthetic bilayer membrane-coated polyamide capsule has advantages of both polymer membrane and bilayer vesicle. Molecular-level-modified capsules of physically strong and ultrathin membrane should be useful the biological and industrial uses.

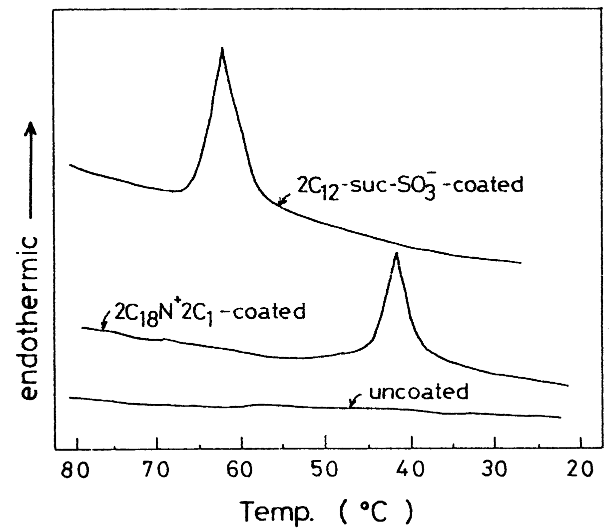


Fig. 3 DSC curve of dialkyl amphiphile-coated capsule in water
Heating rate; 2°C/mim

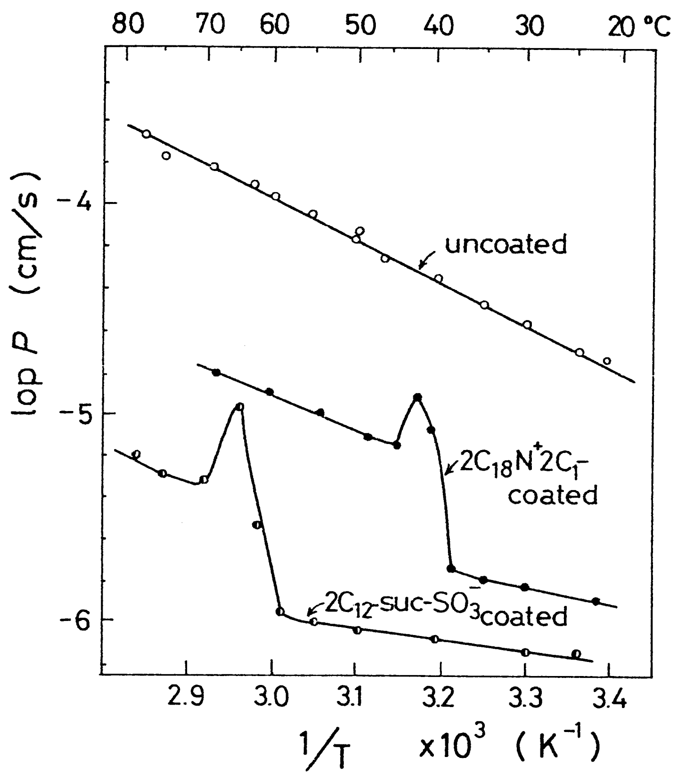


Fig. 4 Arrhenius plot of permeability constant P of uncoated and coated-polyamide capsule

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