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ULTRASOUND-RESPONSIVE PERMEABILITY CONTROL OF BILAYER-COATED CAPSULE MEMBRANES

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Permeation of NaCl from the inner aqueous phase of the bilayer-coated capsule membrane was reversibly regulated by ultrasonic waves. Activation energy data shows that the ultrasonic irradiation makes coating bilayers fluid like a liquid crystalline state and causes the increase of permeation of NaCl.

Recently we prepared functional nylon capsules whose porous membranes were coated with synthetic bilayer membranes.[1-4] The capsule is formed by physically strong nylon membranes and the coating shows characteristics of bilayer vesicles. Release of water-soluble substances trapped in the inner aqueous phase was reversibly controlled by stimuli from outside, such as temperature,[1-4] photoirradiation,[3] and metal ion interaction.[4] This controlled signal-receptive permeabilty is explained by the physical state change of coating bilayers which act as a kind of valve. Aqueous synthetic bilayer vesicles as well as liposomes could not achieve such a reversible permeability control because of their easily breakable bilayer walls.

In this communication, we describe that ultrasonic waves can act as a signal which causes the reversible permeability control of the bilayer-coated capsule membrane. A schematic illustration of the capsule and a diagram of apparatus for

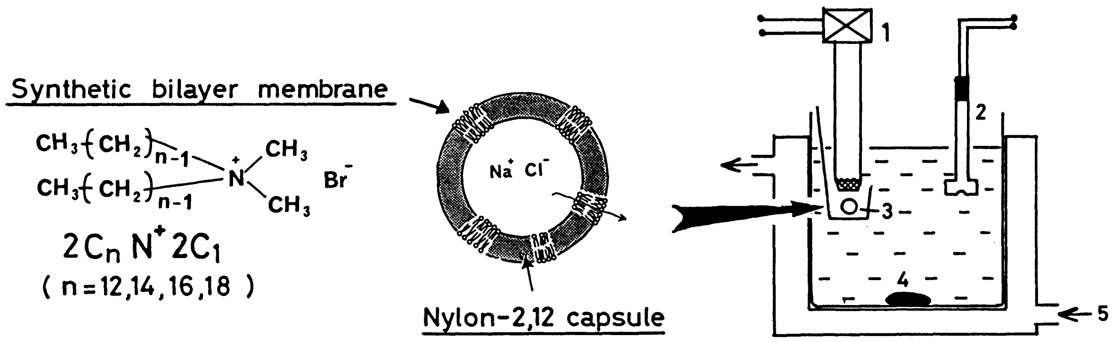

Fig. 1. Schematic illustrations of the bilayer-coated capsule and the apparatus for determination of NaCl release under ultrasonic waves. 1. sonicator(Model UR-200P, Tomy Seiko) 2. conductance cell 3. capsule membrane 4. stirring rod 5. thermostated circulating water.

the determination of permeability from the capsule under ultrasonic waves are shown in Fig. 1. Suzuki et al. reported that an activity of enzymes immobilized with phospholipids on a membrane could be regulated with ultrasonic irradiation.[5)]

The bilayer-coated capsules were prepared as follows.[1-4)] Large nylon-2,12 capsules were obtained from ethylenediamine and 1,10-bis(chlorocarbonyl)decane by an interfacial polymerization method. Capsules trapped 0.2 mol dm^{-3} NaCl in the inner core were coated with dialkyldimethylammonium amphiphiles ($2C_nN^+2C_1$, n = 12,14, 16, and 18) in dodecane solution at 60 °C. Pores of the capsule membrane were observed by scanning electron microscopy to be entirely covered with plates of amphiphiles.[1-3)] It was also confirmed by differential scanning calorimetry (DSC) that amphiphiles on the capsule exist as multiple-bilayers and have phase transition temperatures between gel and liquid crystal, as in the case of aqueous bilayer vesicles[6)] and bilayer-polymer blend.[7,8)] Amphiphile content on the capsule was estimated to be 0.15 ± 0.02 mg/capsule from elemental analysis.

Permeability of capsules toward NaCl was measured by detecting increases in the electrical conductance of the outer water phase, after dropping one capsule into the deionized water, as illustrated in the diagram. Figure 2 shows typical time courses of NaCl release under the intermittent ultrasonic irradiation (20 kHz, 10-15 W). Permeability P obtained from slopes were summarized in Table 1. In the case of the uncoated, semipermeable capsule, permeation rate was very fast and not affected with about this much ultrasonic power. When the $2C_{16}N^+2C_1$-coated capsule membrane was employed at 25 °C, NaCl release was reduced markedly because of the high barrier ability of the coating bilayer in the gel state (T_c = 35 °C).[2)] Permeation rate was enhanced 6.2 times under ultrasonic irradiation for 30 s, and permeability reduced to the original rate when ultrasonic irradiation ceased. This permeability control by ultrasonic power could be repeated more than 10 times without giving any damage to both coating bilayers and capsule membranes. Temperature of aqueous solution did not increase under such a relatively weak and short ultrasonic irradiation. Upon the irradiation of ultrasonic power above 20 W, release of NaCl even from the uncoated capsule was enhanced probably because of a vibration of capsule membranes, but coating bilayers were easily damaged. Below 7 W, however, ultrasonic irradiation gave no effect toward permeability.

The irradiation of ultrasonic waves may cause the physicochemical property change of coating bilayers, such as a phase transition. Figure 3 shows Arrhenius plots of permeability of uncoated- and $2C_{16}N^+2C_1$-coated capsules with or without ultrasonic irradiation, as a typical example. Underlined numbers in the figure indicate activation energies (kcal/mol, 1 cal = 4.184 J) obtained from slopes. The uncoated capsule gave the ordinary straight Arrhenius plot, however, the $2C_{16}N^+2C_1$-coated capsule gave the inflection with a maximum near T_c = 35 °C. The permeation mechanism below and above T_c has been explained as follows.[2)] At the temperature above T_c, NaCl may permeate through the fluid, though hydrophobic bilayer matrix with relatively high activation energy (E_a = 8.2 kcal/mol). When the bilayer is in the rigid gel state below T_c, permeation through the bilayer matrix becomes difficult, and NaCl permeates through defective pores in the coated capsule membrane, instead. The E_a value below T_c (E_a = 5.2 kcal/mol), then,

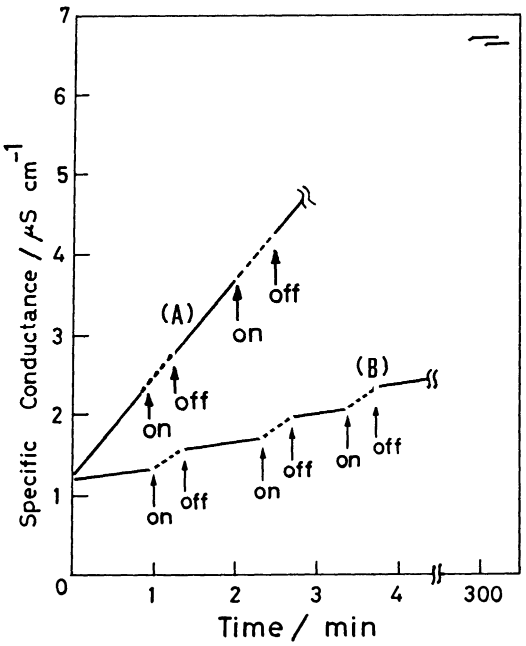

Fig. 2. Permeation control of NaCl across the uncoated capsule membrane (A) and the $2C_{16}N^{+}2C_{1}$-coated capsule membrane (B) at 25°C. Ultrasonic irradiation was started at on and stopped at off (20 kHz, 10-15 W).

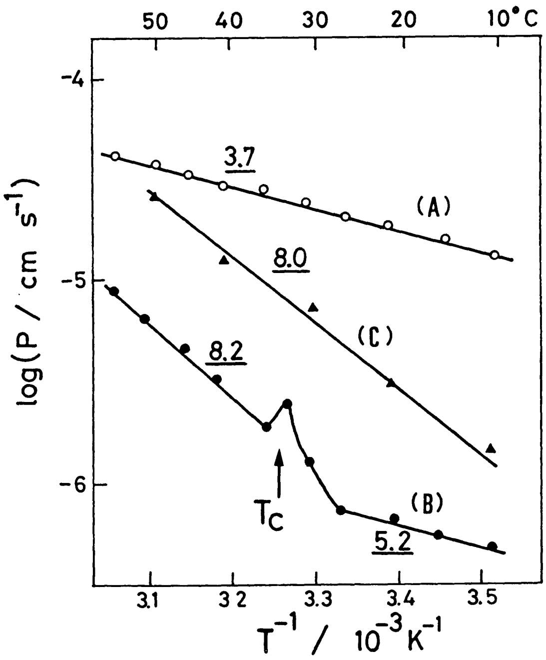

Fig. 3. Arrhenius plots of NaCl permeation from the uncoated capsule (A), the $2C_{16}N^{+}2C_{1}$-coated capsule (B), and the $2C_{16}N^{+}2C_{1}$-coated capsule under ultrasonic irradiation (C). The arrow shows T_c of the coating bilayers obtained from DSC measurements. Numbers underlined show activation energies (E_a, kcal/mol).

Table 1. Effect of ultrasonic power (20 kHz, 10-15 W) on permeability of NaCl across the capsule membranes at 25 °C

Capsule		T_c / °C	P / 10^{-6} cm s^{-1}		Ratio
			Control	Under ultrasonic irradiation	
Uncoated			50	51	1.0
Coated with	$2C_{12}N^{+}2C_{1}$	8	2.2	3.8	1.7
	$2C_{14}N^{+}2C_{1}$	25	1.2	4.8	4.0
	$2C_{16}N^{+}2C_{1}$	35	0.8	5.0	6.2
	$2C_{18}N^{+}2C_{1}$	42	0.7	1.5	2.1

becomes similar to that of the uncoated capsule (E_a = 3.7 kcal/mol), in which NaCl permeation mainly proceeds by the diffusion process.

Under ultrasonic irradiation, permeability was larger in the range of 5-7 than those without the irradiation and Arrhenius plot did not gave inflections, in the whole temperature range. Activation energy (E_a = 8.0 kcal/mol) of permeation under ultrasonic irradiation is nearly equal to that in the liquid crystalline state of $2C_{16}N^{+}2C_1$ bilayers. This indicates that when irradiated with ultrasound waves the coating bilayer in the gel state becomes fluid like the liquid crystalline state, and NaCl can permeate smoothly through the fluid bilayer matrix. In Table 1, the small affect of ultrasound waves toward $2C_{12}N^{+}2C_1$-coated capsule (T_c = 8 °C) is explained that the coating bilayer exists already as the fluid liquid crystalline state at the experimental condition (25 °C). In the case of the $2C_{18}N^{+}2C_1$-coated capsule, this extent of weak ultrasonic power (10-15 W) may be not enough to cause the phase transition because of the longer alkyl-chain of bilayers (high T_c).

In conclusion, permeability of the bilayer-coated capsule membrane can be controlled reversibly by the ultrasonic power, as well as temperature,[1-4] photo-irradiation,[3] and ion interaction from outside.[4] These signal-receptive capsule membranes are important for a model synaptic system in which a nerve impulse initiates the rapid release of a chemical intermediary such as acetylcholine.

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