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A Large Nylon Capsule Coated with a Synthetic Bilayer Membrane. Permeability Control of NaCl by Phase Transition of the Dialkylammonium Bilayer Coating[1]

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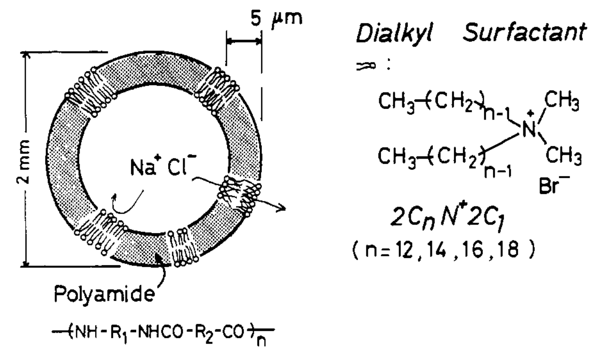
Abstract: Nylon ultrathin capsules coated with the bilayer membrane of dialkyldimethylammonium bromide ($2C_nN^+2C_1$, $n = 12-18$) were prepared. Permeation of NaCl from the inner aqueous phase was reduced by factors of 8–50 relative to that of the uncoated semipermeable capsule, and drastically changed near the phase transition temperature (T_c) of the coating bilayers. The permeability above T_c was enhanced with the decrease in the alkyl chain length of the bilayers. It is suggested from the activation energy data that NaCl permeates through the fluid bilayers above T_c and through small defective pores of the rigid bilayers and/or of the capsule membrane below T_c.

Since the first report in 1977 on the formation of stable bilayer vesicles from dialkyldimethylammonium bromides,[3,4] a large number of other long-chain amphiphiles were shown to form bilayer vesicles in dilute aqueous solution.[5-14] These synthetic bilayer vesicles, as well as liposomes from natural lipids, can trap water-soluble substances in the inner aqueous phase.[7,9,15,16] Bilayer vesicles, however, have some disadvantages with regard to compartmentalization. That is, they are mono- or multi-compartmented, the inner aqueous phases are small (0.2–2% of the outer aqueous phase), and the bilayer barrier is not necessarily strong. The bilayer wall may be easily broken when the osmotic pressure exists between the inner and outer phase. This weak point is being improved to some extent by polymerization of the bilayer wall.[17-22]

Scheme I



We describe in this paper the semipermeable nylon capsule membrane coated with dialkyldimethylammonium amphiphiles ($2C_nN^+2C_1$, n = 12, 14, 16, 18). These capsules can combine

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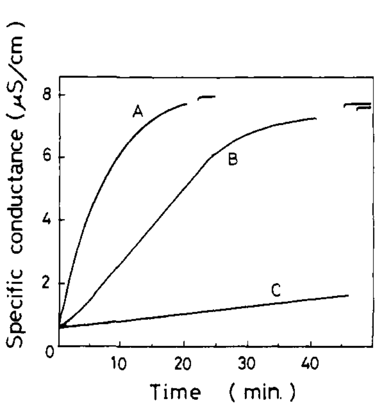

Figure 1. NaCl release from nylon capsule at 20 °C. One capsule that trapped ca. 0.19 M NaCl in the inner aqueous phase was placed in 50 mL of distilled water. (A) Uncoated Nylon-2,Ph capsule; (B) uncoated Nylon-2,12 capsule; (C) $2C_{18}N^+2C_1$-coated Nylon-2,12 capsule.

advantages of physically strong polymer capsules and physicochemically interesting bilayer properties. A schematic illustration of the capsule is shown in Scheme I. The permeation of sodium chloride across the capsule membrane is discussed in the relation with the phase transition of the bilayer membranes on the capsule.

Nylon capsules coated with egg lecithin have been reported by Chang et al. in connection with their studies on the artificial cell.[23,24]

Experimental Section

Preparation of Capsules. Large, semipermeable nylon capsules were prepared from ethylenediamine and terephthaloyl chloride or 1,10-decanedicarbonyl chloride by interfacial polymerization by using a drop technique, according to the literature.[23,25] We added, however, a small amount of a cross-linking agent (trimesoyl chloride, bp 180 °C (3 mmHg)) to obtain strong capsule membranes.[1]

Two milliliters of an aqueous solution of NaOH (0.8 M) and ethylenediamine (0.38 M) were added dropwise from a syringe to a mixture of chloroform (75 mL), cyclohexane (25 mL), acid chlorides (1 mmol), and trimesoyl chloride (0.03 mmol). Nylon capsules that have an ultrathin membrane thickness (5.0 ± 0.3 μm) and a large diameter (2.0 ± 0.2 mm) were obtained. After removal of the outer organic solvent, the capsules were dialyzed against 0.2 M aqueous NaCl for 2–3 days.

Bilayer membrane-coated capsules were prepared as follows. Ten pieces of capsule which had been kept in ca. 0.2 M aqueous NaCl were transferred to a dodecane solution (3 mL) of dialkyldimethylammonium bromides[26] ($2C_nN^+2C_1$, 50 mg) and maintained at 60 °C for 5–10 min. After being cooled, the amphiphile-coated capsules were picked up and rolled on filter paper to remove excess dodecane solution. The amphiphile content on the capsule was estimated to be 0.1–0.2 mg/capsule from the bromide analysis. The surface area of capsules was estimated to be 0.30 ± 0.03 cm².

Measurements. Permeation of NaCl from the inner aqueous phase was measured by detecting increases in the electrical conductance of the outer phase, after dropping one capsule into 50 mL of deionized water.

The amphiphile-coated and uncoated capsule membranes were observed by a Hitachi S-450 cryo-type scanning electron microscope, upon fracturing a frozen capsule at −100 °C under 10^{-4} torr in the cavity of the microscope.

Differential scanning calorimetry of the coating dialkylammonium amphiphile was carried out with a Daini-Seikosha Model SSC-560 instrument. Five crushed capsules were sealed with 50 μL of water in Ag sample pans and heated from 5 to 90 °C at a rate of 2 °C/min.

Results and Discussion

Large nylon capsules obtained from interfacial polymerization in the presence of 3–5 mol % of a cross-linking agent have a very strong capsule wall[27] and do not break even after expansion due to osmotic pressure between distilled water (outer phase) and 0.2–1.0 M NaCl (inner phase). When capsules were prepared without the cross-linking agent, they were easily split under the osmotic pressure.

Table I. Permeability Constant of NaCl across a Capsule Membrane (at 20 °C)

capsule	P (×10⁶ cm/s) Nylon-2,12	P (×10⁶ cm/s) Nylon-2,Ph
uncoated	80	200
dodecane coated	78	210
$2C_{18}N^+2C_1$ coated	1.5	180
$2C_{16}N^+2C_1$ coated	2.5	
$2C_{14}N^+2C_1$ coated	3.5	
$2C_{12}N^+2C_1$ coated	10	180

Permeation of Sodium Chloride. Permeation of NaCl from the inner phase was followed by detecting increases in electrical conductance in the outer water phase. Figure 1 shows typical time courses of release of NaCl to the outer phase. When a Nylon-2,Ph capsule prepared from ethylenediamine and terephthaloyl chloride was employed, NaCl was completely released within 15 min. A Nylon-2,12 capsule from ethylenediamine and 1,10-decanedicarbonyl chloride showed a relatively reduced rate of release, but NaCl permeated completely within 40 min. These nylon capsules were slightly expanded under these experiments and shrunk again slowly after complete release of NaCl. These results indicate that nylon capsules are made of a semipermeable membrane and water can permeate much faster than NaCl across the membrane.

Scanning electron micrographs (SEM) of the inner and outer surfaces and sectional views of Nylon-2,12 and Nylon-2,Ph capsule membranes are shown in Figure 2. The nylon capsules were proven to have unsymmetrical and porous membrane structures; the inner surface (water side in the interfacial polymerization) is smooth and the outer surface (organic side) is rough. This reflects the fact that the interfacial polymerization proceeds by diffusion of amine compounds from aqueous to organic phases. The SEM cross section of Nylon-2,Ph was more porous than that of Nylon-2,12. This is explained by faster permeation on NaCl across the Nylon-2,Ph capsule membrane than across the Nylon-2,12 counterpart.

A marked decrease in NaCl influx was observed when the capsule membrane of Nylon-2,12 was coated with $2C_{18}N^+2C_1$ amphiphile (Figure 1, curve C). The permeability constant P (cm/s) is calculated from the following equation:

$$P = kV/AC \tag{1}$$

where k, A, and V are efflux (slope of Figure 1), surface area of a capsule, and volume of the outer water phase, respectively. C denotes the concentration of NaCl trapped in the inner aqueous phase. It was estimated from the change of specific conductance after crushing the coated and uncoated capsules that the concentration of NaCl incorporated in the inner core was 0.19 ± 0.01 M which was nearly equal to the concentration of the dialysis solution (0.2 M).

The permeability constants of 20 °C obtained from eq 1 were summarized in Table I. Permeability of NaCl was reduced by factors of 8–50, when Nylon-2,12 capsules were coated with $2C_nN^+2C_1$ amphiphiles. The extent of the reduction depended on the alkyl chain length of the amphiphiles. Coating with dodecane produced no effect. The largest effect was observed for the $2C_{18}N^+2C_1$-coated capsule.

Figure 3 shows SEM of the outer surface and the sectional view of the $2C_{18}N^+2C_1$-coated Nylon-2,12 capsule membrane. The amphiphile-coated capsule membrane is entirely covered by plates of $2C_{18}N^+2C_1$ amphiphiles, and pores are not clearly seen in the intersection. The same result was obtained in the case of other $2C_nN^+2C_1$ (n = 12, 14, 16)-coated capsules. The marked decrease in NaCl efflux in the $2C_nN^+2C_1$-coated capsule is clearly due to

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(27) When the cross-linking agent (trimesoyl chloride) was used at more than 10 mol%, the capsule wall was very porous and breakable.

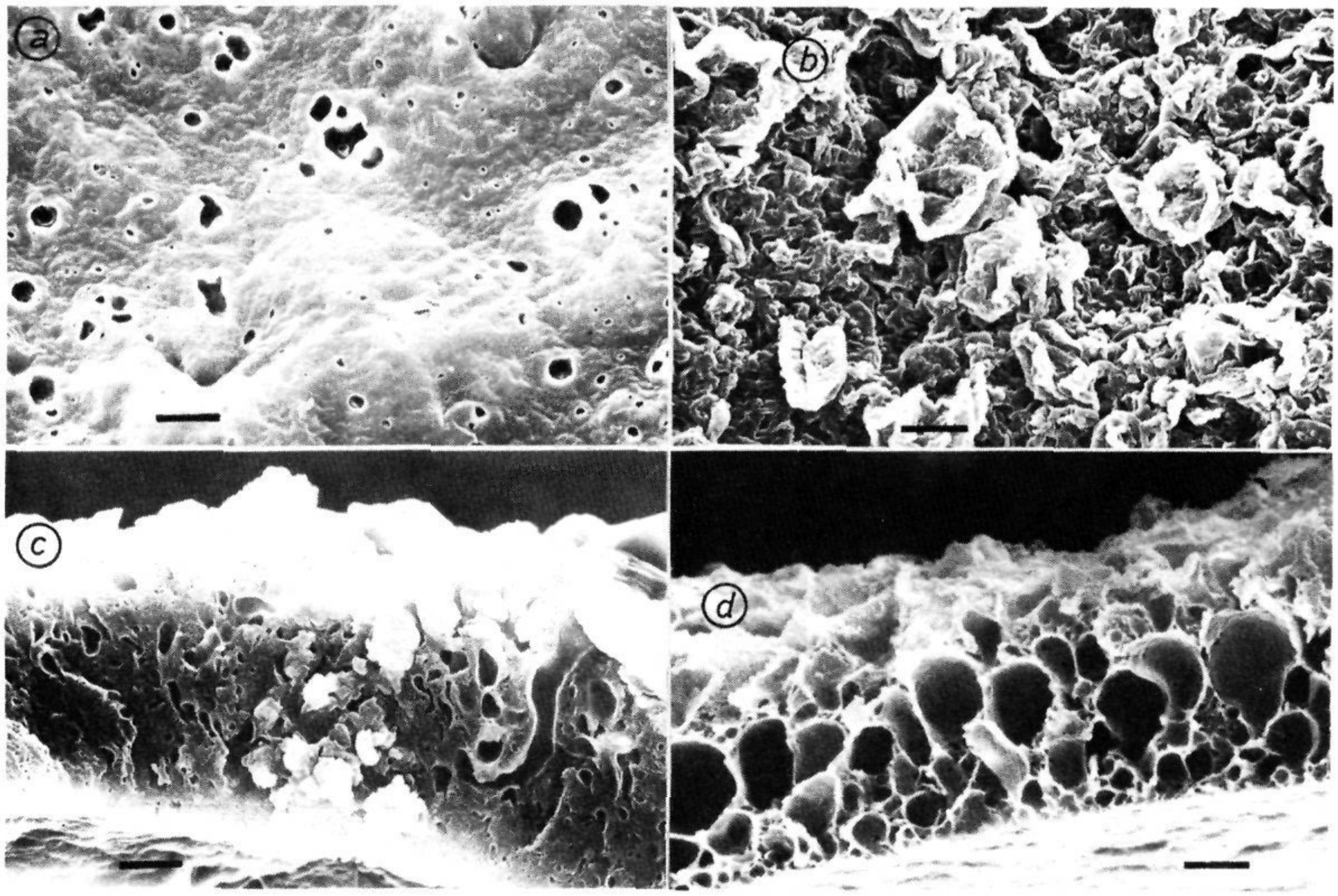

Figure 2. Scanning electron micrographs of capsule membrane (scale = 1 μm). Inner (a) and outer (b) membrane surface and intersection (c) of the Nylon-2,12 capsule; intersection (d) of the Nylon-2,Ph capsule.

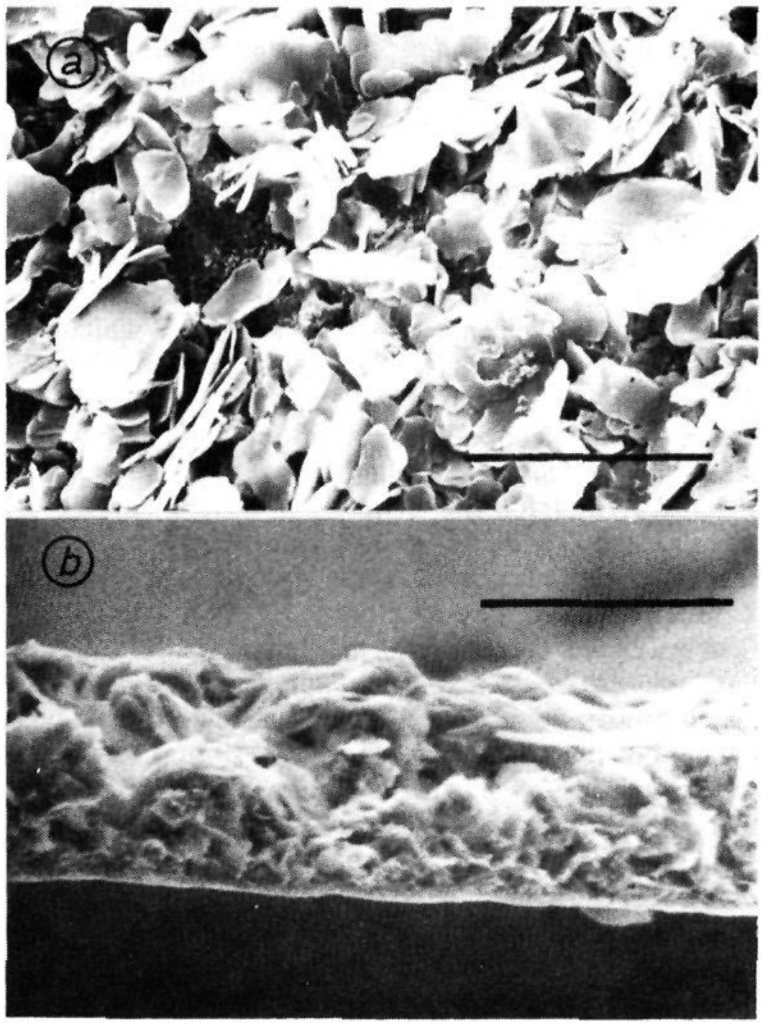

Figure 3. Scanning electron micrographs of amphiphile-coated capsule membrane (scale = 5 μm). Outer surface (a) and intersection (b) of the $2C_{18}N^{+}2C_{1}$-coated Nylon-2,12 capsule membrane.

the presence of the covering amphiphiles.

In the case of a very porous Nylon-2,Ph capsule membrane, detectable reductin of P was not observed (Table I). It seems that the amphiphiles cannot cover entirely the large intersectional pores of the Nylon-2,Ph membrane (Figure 2d).

Therefore, the Nylon-2,12 capsule was selected for the subsequent experiment.

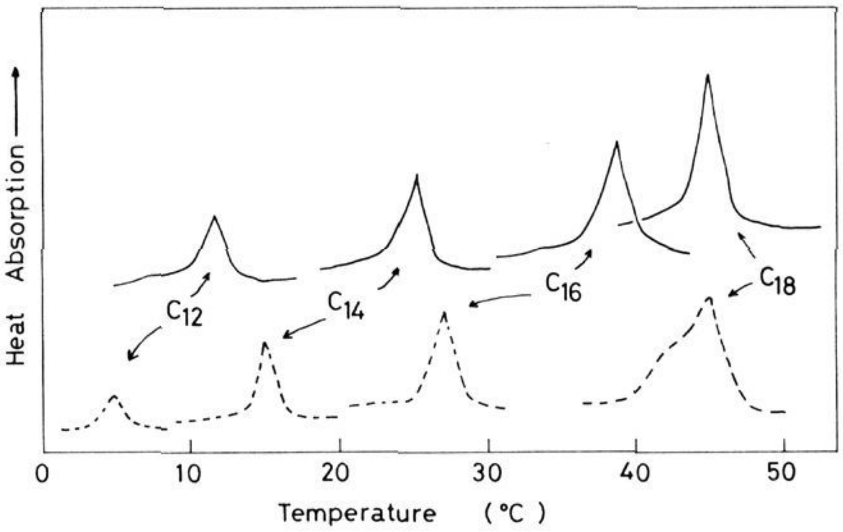

Figure 4. DSC curves of the bilayer of dialkyl amphiphiles ($2C_nN^{+}2C_1$, n = 12, 14, 16, 18): (—) coating bilayers on capsule membrane; (- - -) aqueous bilayer vesicles.[29]

Differential Scanning Calorimetry. It is important whether the coating amphiphile forms bilayer structures on the capsule membrane or not. The liquid-crystalline property is one of the fundamental physicochemical characteristics of the synthetic and biolipid bilayer membrane. The presence of the phase transition between the gel and the liquid crystal has been inferred or proven for dialkylammonium bilayers by a variety of physical techniques, such as differential scanning calorimetry (DSC),[28,29] NMR line broadening,[6,30] fluorescence depolarization,[30,31] turbidity measurement,[31] positron annihilation,[31] and reaction kinetics.[32-34]

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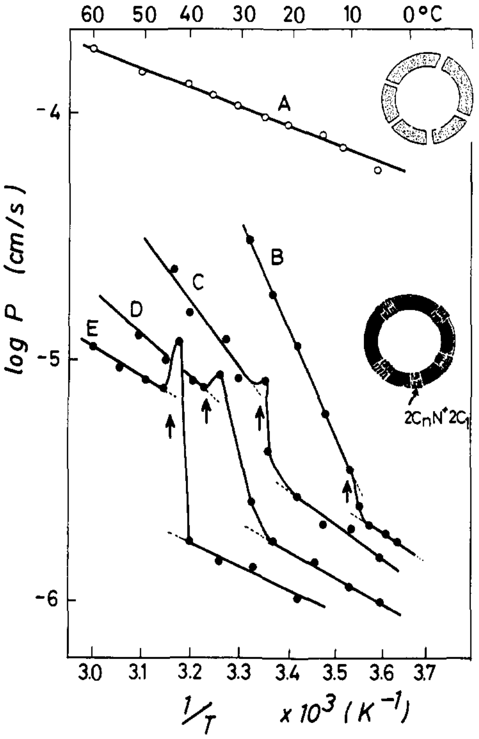

Figure 5. Arrhenius plot of NaCl permeation across capsule Membrane. Uncoated (A), $2C_{12}N^{+}2C_{1}$-coated (B), $2C_{14}N^{+}2C_{1}$-coated (C), $2C_{16}N^{+}2C_{1}$-coated (D), and $2C_{18}N^{+}2C_{1}$-coated (E) Nylon-2,12 capsule membrane. Arrows show T_c of the $2C_nN^{+}2C_1$ bilayers on the capsule membrane, obtained from DSC measurement (Figure 4).

Among these techniques, DSC is the most suitable and convenient one in order to prove the existence of bilayer characteristics on the coated capsule membrane.

DSC curves of $2C_nN^{+}2C_1$ amphiphile coated capsules are shown in Figure 4, together with those[29] of $2C_nN^{+}2C_1$ bilayer vesicles, represented by doted lines. $2C_nN^{+}2C_1$ (n = 12, 14, 16, 18)-coated capsules showed sharp endothermic peaks at 12, 26, 39, and 45 °C, respectively. The peak position was progressively enhanced with increasing alkyl chain lengths (C_{12} to C_{18}) and this trend was also found in the case of aqueous vesicles.[29] The dodecane-coated and uncoated capsules gave no peak in the range of 5–90 °C. This clearly shows that these coating amphiphiles exist as the bilayer assemblage, similar to those in aqueous solution. The peak position (phase transition temperature, T_c) was somewhat different between the corresponding bilayers on the capsule membrane and in aqueous vesicles. It is known that T_c is affected by the mode of dispersion of dialkylammonium bilayer assemblages. For example, T_c of $2C_{18}N^{+}2C_1$ bilayers appears at 45 °C on the capsule membrane as well as in the aqueous vesicle form,[29] at 51 °C in polymer blends,[31] and at 54 °C in the hydrated lamella form.[29]

Effect of Temperature, Arrhenius Plot. It has been reported that the permeability of liposomes as well as of synthetic vesicles and amphiphile-blended PVC polymer membranes changes near T_c.[31] Permeability constants, P, of amphiphile-coated and uncoated capsules were obtained at various temperatures (2–60 °C) to study the effect of the phase transition on the NaCl permeation. Arrhenius plots are shown in Figure 5. 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 or without maxima at 8, 25, 35, and 42 °C in the case of $2C_nN^{+}2C_1$ (n = 12–18)-coated capsules, respectively. These inflections and maximum points correspond well to T_c of the respective bilayer obtained from DSC measurements (shown by arrows in the figure). The drastic increase in NaCl release near and above T_c is associated with the phase transition of the bilayer coat from rigid gel to disordered liquid crystalline states. The capsule coated with the amphiphile of shorter alkyl chains showed smaller inflections with smaller maxima and steaper slopes above T_c.

Table II. Activation Energy and Permeation Gap above and below T_c

capsule	E_a[a] (kcal/mol) above T_c	E_a[a] (kcal/mol) below T_c	$\left(\frac{P_{\text{above } T_c}}{P_{\text{below } T_c}}\right)$
uncoated	3.7		
$2C_{18}N^{+}2C_1$	5.5	4.1	7.4
$2C_{16}N^{+}2C_1$	8.2	5.0	4.1
$2C_{14}N^{+}2C_1$	12	5.4	2.5
$2C_{12}N^{+}2C_1$	20	5.9	1.3

[a] 1 kcal = 4.184 kJ.

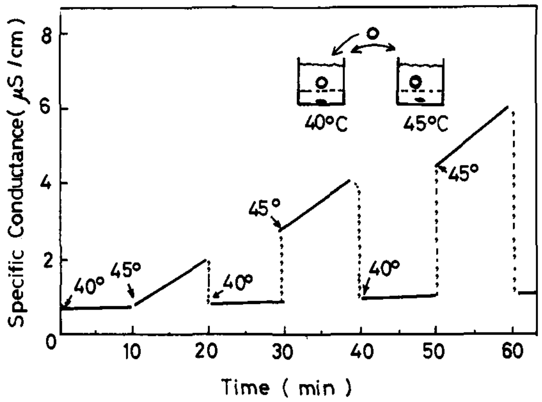

Figure 6. Reversible permeation control of the $2C_{18}N^{+}2C_1$-coated capsule membrane using phase transition phenomenon.

Activation energies E_a calculated from Arrhenius slopes above and below T_c are summarized in Table II together with the permeability gap ($P_{\text{above } T_c}/P_{\text{below } T_c}$) near inflections. Rather curious trends are found for the E_a variation. In the temperature range below T_c, E_a values of the amphiphile-coated capsules were almost constant in the range of 4.1-5.9 kcal/mol, which are independent of the alkyl chain length of $2C_nN^{+}2C_1$ amphiphiles and roughly equal to that of the uncoated one (E_a = 3.7 kcal/mol). At the temperature above T_c, E_a of amphiphile-coated capsules increases with decrease in the alkyl chain length of amphiphiles from 5.5 kcal/mol for the $2C_{18}N^{+}2C_1$-coated capsule to 20 kcal/mol for the $2C_{12}N^{+}2C_1$-coated capsule. These interesting trends may reflect the permeation mechanism of NaCl across the amphiphile-coated capsule membrane.

When the bilayer is in the regid gel state at temperatures below T_c, NaCl may permeate mainly through small defective pores in the coated capsule membrane. E_a values below T_c, then, become independent of the alkyl chain length and similar to that of the uncoated capsule (E_a = 3.7 kcal/mol), in which NaCl permeation mainly proceeds by the diffusion process (E_a = 3–6 kcal/mol[35-38]).

At the temperature above T_c, bilayers on the capsule become fluid and NaCl can penetrate through the liquid-crystalline bilayer. When a hydrated electrolyte permeates through the hydrophobic membrane, large E_a values will result. E_a values of permeation of Na^{+} or Cl^{-} through egg lecithin vesicles (liquid-crystalline state) have been reported to be 14–27 kcal/mol.[39,40] Incidentally, the corresponding E_a value for the gel state (below T_c) is not reported,

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because of the difficulty of the permeation experiment. The E_a values decrease with increasing alkyl chain lengths of the coating amphiphile in the temperature region above T_c. This suggests that NaCl permeates through the fluid, though hydrophobic, bilayer matrix if the alkyl chain is short. However, if the alkyl chain is long, the permeation through the hydrophobic matrix becomes difficult and NaCl permeates through defective pores (smaller E_a), instead.

The extent of permeability gap near T_c also depends on the alkyl chain length of the coating amphiphiles (Table II). The shorter $2C_nN^+2C_1$ bilayers gave smaller permeability gaps near T_c.

It is interesting that the permeability is varied by a factor of 7.4 by temperature change of less than 5 °C in the $2C_{18}N^+$-$2C_1$-coated capsules. The permeability change is reversibly controlled as shown in Figure 6. When a $2C_{18}N^+2C_1$-coated capsule was immersed alternatingly in distilled water at 40 and 45 °C, slow and fast leakage of NaCl was repeated at 40 °C (below T_c) and at 45 °C (above T_c), respectively. This indicates that the bilayer coat acts as a kind of thermo-valve.

Conclusion

Although nylon capsule membranes are simply semipermeable, the permeability of water-soluble substances such as NaCl can reversibly control the use of the phase transition of the coating bilayer in the case of dialkyl amphiphile-coated capsules. The bilayer-coated capsule membrane has advantages of both polymer membrane and bilayer vesicle: a large inner aqueous phase, a physically strong wall against osmotic pressure, and bilayer characteristics.

By choosing other synthetic amphiphiles, we can easily prepare new, signal-receptive capsule membranes that respond to stimuli from outside, such as pH change, photoirradiation,[41] metal ion interaction,[42] and so on. These capsules should be useful for biological and industrial uses.

Acknowledgment. The authors are grateful to Prof. T. Kunitake (Kyushu University) for his helpful comments, the gift of dialkylammonium amphiphiles, and the use of a DSC instrument. They also thank Prof. T. Iijima for his encouragement and Shiseido Co. for the use of a DSC and a cryo-type SEM instrument.

Registry No. NaCl, 7647-14-5; *N*-dodecyl-*N*,*N*-dimethyl-1-dodecanaminium bromide, 3282-73-3; *N*,*N*-dimethyl-*N*-tetradecyl-1-tetradecanaminium bromide, 68105-02-2; *N*-hexadecyl-*N*,*N*-dimethyl-1-hexadecanaminium bromide, 70755-47-4; *N*,*N*-dimethyl-*N*-octadecyl-1-octadecanaminium bromide, 3700-67-2.

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Theory of the Chemical Bond. 6. Accurate Relationship between Bond Energies and Electronegativity Differences

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Abstract: A new formula relating bond energies, D_{AB}, to bond polarities, f, is deduced. The formula has the form $D_{AB} = (1 - f)\bar{D}_{AB} + 252(f/R_e)$, where R_e is the equilibrium bond length and $\bar{D}_{AB} = (D_{AA} + D_{BB})/2$ is the arithmetic average of bond energies D_{AA} and D_{BB}. For a random sampling of bonds, predicted bond energies are found to vary from measured ones by an average of about 3%. The formula is used in conjunction with the observation $f/R_e \approx 2i/3$, where $i = 1 - \exp(-\Delta X^2/4)$ corresponds to Pauling's approximation to ionic character, to deduce the relationship $D_{AB} = \breve{D}_{AB} + K(1 - \exp(-30\Delta X^2/K))$, where $K = 103$, ΔX represents electronegativity differences $X_A - X_B$, and $\breve{D}_{AB}$ equals the geometric average $(D_{AA}D_{BB})^{1/2}$. This relationship is shown to yield accurate bond energy estimates for both ionic and covalent bonds. A comparison with Pauling's formula $D_{AB} = \breve{D}_{AB} + 30\Delta X^2$ is given. It is shown that for a representative sampling of bonds the new formula predicts bond energies with an average error of 2.6%. The corresponding error associated with Pauling's equation is 43.6%. Ramifications regarding a more accurate electronegativity scale are discussed.

I. Introduction

In the first paper[1] in this series,[1-4] a quantum mechanical technique called implicit perturbation theory was used to derive an accurate model relating bond dipole moment curves to three principal effects: charge transfer; charge polarization; and charge collision.[5] The leading term in this model is the charge-transfer term, fR, where f is the effective charge transferred in the curve-crossing region during bond formation and R is the internuclear spacing. This charge is approximately related to partial charges q_A and q_B by the equation

$$f = (q_A - q_B)/2 \tag{1}$$

For single bonds, f varies from one (ionic) to zero (covalent). The effective charge f is an accurate measure of asymmetry in bond charge distributions. To obtain f we utilize the equation (derived in paper 2)[2]

$$f = {}^5\!/_9\frac{\mu_e}{R_e} + {}^4\!/_9\mu_e' + {}^1\!/_{18}\mu_e'' \tag{2}$$

where μ_e^k is the kth derivative of the dipole moment curve, μ_e, evaluated at R_e.

Measurements of f indicate a highly regular and systematic variation throughout the periodic table. This is clearly illustrated in Figure 2 of ref 4. Since f is a direct measure of charge transfer occurring in bonds and since, by definition, charge transfer is directly related to electronegativity differences, f would seem to be a natural parameter on which to base an electronegativity scale.

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