Preparation and Application of Cholesteryl-Benzo-15-Crown-5/Cholesteryl Mixed Liquid Crystals

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Various mixed liquid crystals containing crown ether-cholesteryl liquid crystal, benzo-15-crown-5-COO-C₂₇H₄₅ (B15C5-COOCh), with various common cholesteric liquid crystals, e.g., cholesteryl chloride, cholesteryl benzoate and cholesteryl palmitate, were prepared and studied using polarizing microscopy and differential scanning calorimetry. Investigating the concentration effect of B15C5-COOCh in mixed liquid crystals revealed that the addition of B15C5-COOCh resulted in wider phase transition temperature ranges of these cholesteryl liquid crystals. The stability of these B15C5-COOCh/cholesteryl mixed liquid crystals was studied using comprehensive graphic molecular modeling computer programs (Insight II and Discover) to calculate their molecular energy and stability energy. The effect of salts, e.g. Na⁺, Co³⁺, Y³⁺ and La³⁺, on the transition temperature range of the mixed liquid crystals was also investigated. The crown ether cholesteric liquid crystal B15C5-COOCh was applied both as a surfactant and an ion transport carrier to transport metal ions through liquid membranes. Cholesteryl benzo-15-crown-5 exhibited distinctive characteristics of a surfactant and the critical micellar concentration (CMC) of the surfactant was investigated by the pyrene fluorescence probe method. Cholesteryl benzo-15-crown-5 was successfully applied as a good ion transport carrier (Ionophore) to transport various metal ions, e.g. Li⁺, Na⁺, La³⁺, Fe³⁺ and Co³⁺, through organic liquid membranes. The transport ability of the cholesteryl benzo-15-crown-5 surfactant for these metal ions was in the order: $Co^{3+} \ge Li^+ > Fe^{3+} > Na^+ > La^{3+}$.

Keywords: Liquid crystal; Crown ether liquid crystal; Surfactant; Ion transport carrier.

INTRODUCTION

Cholesteryl liquid crystals are very famous helical distortion liquid crystals¹⁻⁴ and can be applied as highly optical-sensitive ferro-liquid crystals (FLC)⁵⁻⁷ for optical display devices in microcomputers. The groups attaching to cholesteryl ($C_{27}H_{45}$), such as benzyl (C6H5), ester (RCOO) and chloride (Cl), can change the optical properties and the transition temperature of the cholesteryl liquid crystals. Crown ethers have a dual functionality, with a lipophilic segment on the outer surface of the ring and a polar segment on the inner surface that can form stable complexes with metal ions.⁸⁻¹³ Attaching a lipophilic long-chain alkyl group to a crown ether can convert it into a surfactant, which is capable of forming micelles in a manner analogous to classical non-ionic surfactants.¹⁴⁻¹⁵ In other words, cholesteryl-crown ether can be expected to show the characteristics of a surfactant. It is well known that some surfactants of certain concentrations can form liquid crystals. In addition, cholesteryl derivatives always exhibit characteristics of liquid crystals. Therefore, the crown ether cholesteryl liquid crystal can be expected to show the characteristics of a liquid crystal. Furthermore, a mixed liquid crystal composed of two different cholesteryl liquid crystals exhibits quite different optical sensitive properties and transition temperature ranges compared with the composed liquid crystals. In our previous study,¹⁶ a crown ether cholesteryl liquid crystal, cholesteryl benzo-15-crown-5 (B15C5-COOCh), was synthesized. However, its transition temperature range (approx. 120-165 °C) means it is not good enough to be used in optical display devices. Therefore, in this study, various mixed crystals containing a crown ether-cholesteryl liquid crystal with various common cholesteric liquid crystals, e.g., cholesteryl chloride, cholesteryl benzoate and cholesteryl palmitate, were prepared in order to obtain mixed liquid crystals with wider transition temperature ranges. The crown ether-choles-

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tery/cholestery mixed liquid crystals were studied using polarizing microscopy with comprehensive graphic molecular modeling computer programs (Insight II and Discover) to calculate their molecular energy and stability energy. As mentioned above, cholesteryl benzo-15-crown-5 can be expected to be a crown ether surfactant. Thus, in this study, the micellar formation of the crown ether surfactant was investigated using the pyrene fluorescence probe and surface tension methods. In addition, owing to their complexing ability with alkali metal ions, crown ethers are also expected to serve as ion transport carriers (Ionophores) through biomoimetric membranes.¹⁷⁻¹⁹ The transport of alkali metal ions across a membrane plays an important role in biology. Thus, in this study, the application of cholesteryl benzo-15-crown-5 as an ion transport carrier (Ionophore) to transport various metal ions was also studied and discussed.

EXPERIMENTAL

Synthesis of cholesteryl benzo-15-crown-5

Cholesteryl benzo-15-crown-5 (B15C5-COOC₂₇H₄₅) was prepared as shown in Fig. 1. The intermediate benzo-15crown-5 (B15C5) was prepared, as reported by Pederson,⁸ through the reaction between ortho-catechol (0.4 mol) and 1,11-dichloro-3,6,9-trioxaundecane (0.4 mol) in butanol (600 mL) mixed with NaOH (37.0 g) aqueous solution (40 mL) after being refluxed for 30 hr. The intermediates, namely 4'-acetyl-benzo-15-crown-5,4'-carboxyl-benzo-15-crown-5 and 4'-chloro-carbonyl benzo-15-crown-5 were synthesized as described by Stott,²⁰ Wada²¹ and Haines,²² respectively. The final solid product B15C5-COOC₂₇H₄₅ was obtained from the reaction between 4'-



Fig. 1. Scheme for the synthesis of cholesteryl benzo-15-crown-5 (B15C5COOC₂₇H₄₅).

chloro-carbonyl benzo-15-crown-5 (6.57 mol) and cholesterol (6.57 mol) with pyridine (13 mmol) in benzene after being refluxed for 24 h. The final product and the intermediates were identified by IR, NMR and mass spectra.

Liquid crystal study

The liquid crystal phases of various liquid crystals including cholesteryl benzo-15-crown-5 and various mixed crystals were observed using a polarizing microscope with a heating device and the transition temperatures of various liquid crystals were determined by differential scanning calorimetry. The mixed liquid crystal was prepared by dissolving the mixture of two liquid crystals in dichloromethane by stirring and heating to remove the organic solvent.

Computer simulation for molecular structure and energy calculation

A commercial graphic molecular modeling program Insight-II 2.10 was employed to draw the modeling structures of various liquid crystals including cholesteryl benzo-15-crown-5 and some mixed liquid crystals. An energy analytical program Discover 3.1 was also employed to calculate the molecular energy and stability energy for these pure liquid crystals and mixed liquid crystals.

Critical micellar concentration (CMC) measurements

In this study, cholesteryl benzo-15-crown-5 was found to exhibit distinctive characteristics of a surfactant. The pyrene fluorescence probe method was employed to measure the CMC of cholesteryl benzo-15-crown-5 in aqueous solutions. In the pyrene fluorescence method, an alteration intensity ratio (I₁/I₃) of pyrene fluorescence bands I (373 nm) and III (383 nm) occurs upon formation of micelles.²³⁻²⁶ The CMC of cholesteryl benzo-15-crown-5 surfactant was measured at various aqueous concentrations with 3×10^{-7} M pyrene added. The plot of I₁/I₃ against log [surfactant] shows a significant change in slope of the curve in which concentrations are denoted as CMC of cholesteryl benzo-15-crown-5.

Ion transport through liquid membranes

Fig. 2 shows the experimental setup of the ion transport of various metal ions through organic liquid membranes. Aqueous solution (0.1 M, 20 mL) containing metal salts (MX_n) and pure water (20 mL) were prepared as source solution and target solution, respectively, and cholesteryl benzo-15-crown-5 (10^{-3} M) in dichloromethane (30 mL) was prepared as the liquid membrane. Metal (M^{n+}) ions in the source solution were transported through the surfactant liquid membrane into the target solution and



Fig. 2. Ion transport apparatus with cholesteryl benzo- 15-crown-5 (B15C5COOC₂₇H₄₅) liquid membrane.

were then detected by a conductivity detector.

Apparatus

JASCO FTIR-5300 Fourier transform infra-red (FTIR) and JEOL EX400 Fourier transform NMR and JEOL JMS-DI300 mass spectrometers were employed to identify the final product, cholesteryl benzo-15-crown-5, and its intermediates. An OLYMPUS BH-2 polarizing microscope was also employed to observe the liquid crystal phases and a DSC-50I differential scanning calorimeter was utilized to determine the transition temperatures of various liquid crystals. A JASCO-FP 770 spectro-fluorometer and a KYOWA CBVP-A3 surface-tense meter were employed for determining the CMC of cholesteryl benzo-15-crown-5. A DCM-3 conductivity detector was employed to measure the amount of metal ions passing through the liquid membrane in the ion transport study.

Reagents

Cholesteryl chloride, cholesteryl benzoate and cholesteryl palmite were obtained from Janessen Co., while cholesterol was purchased from Fluka Co. All other chemicals used were of analytical grade.

RESULTS AND DISCUSSION

The liquid crystal characteristics and phase transition temperatures of various mixed crystals containing cholesteryl benzo-15-crown-5 (B15C5-COOC₂₇H₄₅, B15C5-COOCh) or crown ether B15C5-COOH with various common cholesteric liquid crystals, e.g., cholesteryl chloride ($C_{27}H_{45}Cl$, Ch-Cl), cholesteryl benzoate (Ch-Bz) and cholesteryl palmitate (Ch-PA), were investigated using differential scanning calorimetry (DSC) by cooling and heating processes. As shown in Fig. 3, these mixed crystals of B15C5-COOCh and common cholesteric liquid crystals, e.g., cholesteryl chloride (Ch-Cl), still show the characteristics of the liquid crystals and have transition temperatures of the liquid crystals by either cooling or heating processes. In addition, the transition temperature range (49.9-172.4 °C) of the B15C5-COOCh/Ch-Cl mixed liquid crystal seems to be greater than that of the single liquid crystal B15C5-COOCh (122-166 °C) or Ch-Cl (62-97 °C) as shown in Fig. 3. Similarly, other mixed liquid crystals, e.g., cholesteryl benzoate (Ch-Bz)/B15C5-COOCh, also showed liquid crystal characteristics (Fig. 4) and greater transition temperature ranges than single liquid crystals, e.g., Ch-Bz or B15C5-COOCh.

Furthermore, it was found that the transition temperature range of the mixed liquid crystal seemed to depend on the ratio (w/w) of the composed liquid crystals. For example, the transition temperature range of B15C5-COOCh/ Ch-Cl mixed liquid crystals can be significantly changed with different ratios (w/w) of B15C5-COOCh/Ch-Cl by cooling or heating processes as shown in Fig. 5. The opti-



Fig. 3. Thermal analysis curve of differential scanning calorimetry (DSC) for B15C5COOC₂₇H₄₅/ C₂₇H₄₅Cl mixed liquid crystal (LC).

mum ratio of B15C5-COOCh/Ch-Cl = 4 for obtaining the largest transition temperature range of the mixed liquid crystal was found. The plot of maximum and minimum transition temperature range against the ratio (w/w) of B15C5-COOCh/Ch-Cl reveals that the lowest minimum transition temperature at B15C5-COOCh/Ch-Cl = 4 is around 25 °C as shown in Fig. 6. In other words, the mixed liquid crystal with the ratio of B15C5-COOCh/Ch-Cl = 4.0 can be a liquid crystal at room temperature (25 °C) while B15C5-COOCh or Ch-Cl is a solid at room temperature. Even with the addition of common crown ether B15C5COOH which did not show the liquid crystal characteristics, the transition temperature range of cholesteryl liquid crystals, e.g., C27H45Cl (Ch-Cl) can be changed as shown in Fig. 7. B15C5COOH/Ch-Cl mixed crystal also showed liquid crystal characteristics and greater transition temperature ranges (40-170 °C) than those of the components, Ch-Cl (62-97 °C) and B15C5COOH (mp. 170 °C). Similarly, the transition temperature range of B15C5COOH/Ch-Cl mixed crystal also varied with the changes in weight ratio of B15C5COOH/Ch-Cl as shown in Fig. 7.

The greater transition temperature range of mixed cholesteryl liquid crystals than that of composed liquid crystals seems to indicate that mixed crystals are more stable than composed liquid crystals. In order to study the stability of mixed and composed mono-molecular cholesteryl liquid crystals, comprehensive graphic molecular model-



Fig. 4. DSC thermal analysis curve for B15C5COOC₂₇H₄₅/Ch-Ben mixed liquid crystal (Ch-Bz = Cholesteryl benzoate).

ing computer programs (Insight II and Discover) were employed to calculate their molecular energy and stability energy. The molecular modeling graphs of composed monomolecular liquid crystals (e.g. B15C5-COOCh) and mixed liquid crystals (e.g. B15C5-COOCh/Ch-Cl) in the lowest average molecular energy states can be obtained with the Insight II program as shown in Figs. 8 and 9, respectively. According to these molecular modeling graphs, two B15C5-COOCh molecules (Fig. 8) seem to overlap with each other while there is no overlap between B15C5-COOCh and Ch-Cl molecules (Fig. 9). This reveals that the B15C5-COOCh/Ch-Cl mixed liquid crystal is more stable than the



Fig. 5. Weight ratio effect of $B15C5COOC_{27}H_{45}/C_{27}H_{45}Cl$ on the transfer temperature range of the mixed liquid crystal by (a) cooling and (b) heating processes (Ch = $C_{27}H_{45}$).

mono-B15C5-COOCh molecular liquid crystal. Furthermore, the addition of Ch-Cl molecules may reduce the attraction between two B15C5-COOCh molecules, causing these molecules to be in array and increasing the stability of



Fig. 6. Cooling phase diagram of B15C5COOC₂₇H₄₅/ C₂₇H₄₅Cl mixed liquid crystal (A) Maximum temperature and (B) Minimum temperature for liquid crystal phase (Ch = C₂₇H₄₅).



Mole ratio (B15C5COOH/ Ch-Cl)

Fig. 7. Cooling phase diagram of B15C5COOH/ C₂₇H₄₅Cl mixed liquid crystal (A) Maximum temperature and (B) Minimum temperature for liquid crystal phase (Ch = C₂₇H₄₅).

the liquid crystal.

The stability of these liquid crystals can be estimated from their molecular energies. The average molecular energies of various cholestery mixed and mono-molecular liquid crystals were calculated using the Discover program and are shown in Table 1. As can be seen, the average molecular energy of the B15C5-COOCh/Ch-Cl mixed liquid crystal (170 Kcal/mole) is lower than that of the B15C5-COOCh mono-molecular liquid crystal (305 Kcal/mole), indicating that the B15C5-COOCh/Ch-Cl mixed liquid crystal is more stable than the B15C5-COOCh mono-molecular liquid crystal, which may result in a greater transition temperature range of B15C5-COOCh/Ch-Cl than of B15C5-COOCh. The stability energy (E_b) of a mixed liquid



Fig. 8. Computer simulating molecular modeling for mono-molecular B15C5COOC₂₇H₄₅/ B15C5COOC₂₇H₄₅ liquid crystal.

Liquid crystal (LC)	Compound ^a	Molecular energy (Kcal/mole)	Stability energy Eb (Kcal/mole) ^b
Homo-LC	B15C5Ch/B15C5Ch	305 (E ^o)	
Mixed-LC	ChCl/ChCl	96 (E ^o)	
	ChBZ/ChBz	170 (E ^o)	
	ChPA/ChPA	176 (E ^o)	
	B15C5COOH/B15C5COOH	136 (E ^o)	
	B15C5Ch/ChCl	170 (E _{AB})	31.0
	B15C5Ch/ChBz	224 (E _{AB})	16.5
	B15C5COOH/ChCl	86 (E _{AB})	47.0
	B15C5COOH/ChBz	161 (E _{AB})	12.0
	B15C5COOH/ChPA	147 (E _{AB})	6.0

Table 1. Molecular energy and stability energy of crown ether/cholesteryl mixed liquid crystals

^a B15C5Ch: Benzo-15-crown-5-COOC₂₇H₄₅; ChCl: Cholesteryl chloride; ChBz: Cholesteryl

benzoate; ChPA: Cholesteryl palmitate.

^b Stability energy (Eb) = $1/2 (E^{o}_{A} + E^{o}_{B}) - E_{AB}$



Fig. 9. Computer simulating molecular modeling for hetero-molecular B15C5COOC₂₇H₄₅/C₂₇H₄₅Cl mixed liquid crystal.

crystal AB can be estimated using the molecular energies of components A, B and the mixed crystal AB as follows:

Stability
$$(E_b) = 1/2 (E_A^o + E_B^o) - E_{AB}$$
 (1)

where E_A^o , E_B^o and E_{AB} are molecular energies of components A, B and the mixed liquid crystal AB, respectively. As shown in Table 1, mixed crown ether/cholesterol chloride (ChCl) liquid crystals, B15C5Ch/ChCl and B15C5COOH/ChCl, are more stable with much larger stability energies (31.0 and 47.0 Kcal/mole) than other mixed liquid crystals, e.g., B15C5Ch/ChBz and B15C5COOH /ChPA. This may be attributed to the greater steric effects of benzyl of ChBz and palmitate of ChPA than those of chloride of ChCl, which causes instability of B15C5Ch/ ChBz and B15C5COOH/ChPA mixed liquid crystals.

Since the crown ether B15C5 in the B15C5COOCh/ ChCl mixed liquid crystal can be expected to form stable complexes with various metal ions,⁸ the effect of metal ions on the stability and transfer temperature range of the B15C5COOCh/ChCl mixed liquid crystal was also investigated in this study. As shown in Fig. 10, the presence of La(NO₃)₃ with different mole ratios of La/LC (liquid crystal) in B15C5COOCh/ChCl mixed liquid crystal led to its loss of liquid crystal characteristics. This may be attributed to the formation of La(III)/B15C5COOCh complex, which results in large repulsion between two La(III)/ B15C5COOCh molecules, thus destroying the liquid crystal structure and causing the mixed liquid crystal to lose its liquid crystal characteristics. Similar effects of NaCl,



Fig. 10. Effect of La(NO₃)₃ added on the transfer temperature range of B15C5COOCh/C27H45Cl (mole ratio 1:1) mixed liquid crystal (LC) by cooling process. (Mole ratio: 1: La³⁺/ $La^{3+}/$ B15C5COOCh-ChCl 2: 0; La³⁺/ B15C5COOCh-ChCl 3: 1: B15C5COOCh-ChCl 2: 4: La³⁺/ B15C5COOCh-ChCl = 3).



Fig. 11. Effect of various salts on the transfer temperature range of B15C5COOC₂₇H₄₅/C₂₇H₄₅Cl mixed liquid crystal by cooling process. (1: No salt, 2: NaCl, 3: Co(NO₃)₃, 4: Y(NO₃)₃, 5: La(NO₃)₃; Mole ratio: Salt/B15C5COOC₂₇H₄₅/ C₂₇H₄₅Cl = 1:1:1).

 $Co(NO_3)_3$ and $Y(NO_3)_3$ on the loss of the liquid crystal characteristics of the B15C5COOCh/ChCl mixed liquid crystal were also found as shown in Fig. 11.

As mentioned above, cholesteryl-crown ether is expected to show the characteristics of a surfactant. In this study, the fluorescence probe of pyrene was applied as a sensitive tool to study the formation of micelles and determine the critical micellar concentration (CMC) of cholesteryl-crown ether B15C5COOCh. The CMC value of B15C5COOCh as a surfactant in aqueous solution was obtained by measuring pyrene fluorescence and plotting the I₁/I₃ intensity ratio against B15C5COOCh concentration where the slope of the curve changes dramatically, as shown in Fig. 12. The CMC value can be estimated as the B15C5COOCh concentration at the inflection point N in Fig. 12 and is approximately 8×10^{-4} M in H₂O as obtained by the pyrene fluorescence probe method. This seems to indicate that the cholesteryl-crown ether B15C5COOCh can be considered as a surfactant as expected.

The transport of metal ions, e.g. Na^+ and Fe^{3+} ions, across a membrane plays an important role in biology. The effect of the cholesteryl-crown ether B15C5COOCh as an ionophore to carry various metal ions through an organic (dichloromethane) liquid membrane was investigated in this study. A mechanism for the transport of metal ions, e.g. Na^+ , with B15C5COOCh was proposed as shown in Fig. 13. The Na^+ ion in the source aqueous layer first forms a complex with B15C5COOCh and is transported through the organic (CH₂Cl₂) liquid membrane into the target aqueous layer. The transport concentrations of Na^+ and Fe^{3+} ions in the target layer as a function of time were measured



Fig. 12. Determination of critical micellar concentration (CMC) of B15C5COOC₂₇H₄₅ in aqueous solutions using pyrene fluorescence probe method (Ch = $C_{27}H_{45}$).

using a conductivity detector. As shown in Fig. 14, the transport concentrations for both Na⁺ and Fe³⁺ ions appeared to reach equilibrium after 200 min. and the equilibrium transport concentration of Fe³⁺ ion was obviously greater than that of Na⁺ ion. The cavity of crown ether 15C5 of B15C5COOCh calculated using the Insight II graphic molecular modeling computer program was approximately 1.54 Å. However, the diameter of Na⁺ ion $(approx. 1.9 \text{ Å})^{27}$ is obviously too large for the cavity of B15C5COOCh (1.54 Å), which is relatively difficult to complex with B15C5COOCh. On the other hand, although the diameter of Fe³⁺ ion (approx. 1.25 Å) is slightly smaller than the cavity of B15C5COOCh (1.54 Å), the Fe^{3+} ion can still be inserted into the cavity of B15C5COOCh and forms Fe³⁺ B15C5COOCh complex, resulting in the transport of Fe³⁺ ions through the liquid membrane more easily than that of Na⁺ ions. The transport of other metal ions, e.g. Li⁺, Co³⁺ and La³⁺, through the liquid membrane was also investigated. As shown in Fig. 15, the transport concentration of these metal ions seems to be inversely proportional to the diameter of these metal ions. The diameter (approx. 1.5 Å) of Li⁺ ion obviously fits the cavity of B15C5COOCh (1.54 Å) quite well and Li⁺ ion can be expected to form stronger complex with B15C5COOCh than both Na⁺ and La^{3+} , which are too big for the cavity of B15C5COOCh. However, Co³⁺ ions show greater transport concentration



Source Solution

Liquid Membrane

(pure H₂O)

Fig. 13. Scheme for Na⁺ ion transport through the B15C5COOC₂₇H₄₅/dichloromethane liquid membrane.

than Li⁺ ions, which may be attributed to the larger charge/ size of Co³⁺ than that of Li⁺, resulting in stronger absorption of Co³⁺ ions into the cavity of B15C5COOCh and greater transport concentration of Co³⁺ ions through the liquid membrane. This result seems to indicate that both size and charge affect the association and dissociation of metal ions with liquid membranes.

CONCLUSION

In conclusion, the mixed liquid crystals composed of B15C5COOCh and common cholesteryl liquid crystals,



Fig. 14. Ion transport of (a) Na^+ and (b) Fe^{3+} through the B15C5COOC27H45/dichloromethane liquid membrane (C.E. = $B15C5COOC_{27}H_{45}$).

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Fransport Concentration / 10⁻⁴ M





Fig. 15. Effect of metal ion diameter on ion transports of various metal ions through the $B15C5COOC_{27}H_{45}/dichloromethane$ liquid membrane.

e.g. cholesteryl chloride and cholesteryl benzoate exhibited wider phase transition temperature ranges than those of common cholesteryl liquids. Some B15C5COOCh/ cholesteryl mixed liquid crystals showed the transition temperature at room temperature. The Insight II/Discover graphic molecular modeling computer programs were successfully employed to calculate the average molecular energy and explain the stability of mixed liquid crystals. Crown ether cholesteryl liquid crystal B15C5COOCh also showed the characteristics of a surfactant in forming micelles in water. Furthermore, B15C5COOCh also served as a good ion transport carrier to transport metal ions through the organic liquid membrane.

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Fransport Concentration / 10⁻⁴ M





Fig. 15. Effect of metal ion diameter on ion transports of various metal ions through the $B15C5COOC_{27}H_{45}/dichloromethane$ liquid membrane.

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