

Dependence of Ion Selectivity on Ordered Orientation of Neutral Carriers in Ion-Sensing Membranes Based on Thermotropic Liquid Crystals

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Thermotropic liquid-crystalline compounds were applied as membrane materials (membrane solvent and neutral carrier) for neutral carrier-type ion sensors to investigate how the ordered arrangement of neutral carriers affects the property of the resulting ion sensors. Nematic, smectic, and cholesteric liquid-crystalline compounds were used as the membrane solvents and crown ether derivatives with a molecular structure similar to the liquid-crystalline solvent as the K⁺ neutral carriers. Polarized IR spectroscopy and X-ray diffraction experiments confirmed that the highly ordered arrangement of membrane components was retained in the liquid-crystal-based ion-sensing membranes containing a neutral carrier and a lipophilic salt. The ordered arrangement of neutral carriers in the liquid-crystalline membranes enhanced the ion selectivity significantly, probably due to the efficient cooperation of two adjacent crown ether moieties in the highly ordered and aggregated state.

Potentiometric ion sensors such as the ion-selective electrode (ISE) and ion-sensitive field-effect transistor (ISFET), especially the neutral carrier types, are very useful.¹ An ion sensory property such as ion selectivity is generally determined by ion-exchange equilibrium at the interface between the membrane and aqueous sample phases, which is in turn the metal ion extraction equilibrium between the two immiscible phases.² The ion selectivity for liquid-membrane ion sensors based on neutral carriers is often governed by the ion selectivity of the neutral carriers in the membrane. However, the whole ion selectivity for the neutral carrier-type ion sensors is also affected considerably by other membrane conditions such as the kind of membrane solvent or plasticizer. For instance, the polarity of water-immiscible solvent modified the selectivity in metal ion extraction with neutral carriers and thereby in ion sensors. We came up with the idea that the orientation of neutral carrier and solvent molecules might affect their ion-exchange equilibria in the membrane interface. The ion

sensor property might be therefore controlled by the orientation of the membrane components.

Liquid-crystalline compounds possess ordered molecular orientation, which is able to affect molecular orientation of other organic components existing in small quantities in the liquid-crystal phase. For instance, in ion-conducting composites containing liquid-crystalline crown ethers, their ion conductivity can be altered by the phase transition induced by external stimuli such as heat and light.^{3–6} Liquid-crystalline compounds are also candidates for functional membrane solvents for ISEs, as far as they keep fluidity that guarantees the mobility of a neutral carrier enough for quick ion exchange in the membrane.⁷ In that case, it may be possible to know how the ordered orientation of neutral carriers modifies the ion sensor property. The ordered orientation of neutral carriers by thermotropic liquid crystals might improve ion sensor properties such as selectivity, which might be switched by the measurement temperatures. Liquid-crystalline compounds can be incorporated into poly(vinyl chloride) (PVC)-based ion-sensing membranes,⁷ but the liquid-crystal effect in that case does not seem to be very significant due to their compatibility with the polymer support. We have therefore attempted to use pure liquid membranes consisting of a liquid-crystalline membrane solvent and a neutral carrier for ion sensors, without using any polymer support. We already communicated that ion selectivity for neutral carrier-type ISEs based on liquid crystal membranes is enhanced in their nematic state as compared with in their isotropic liquid state.⁸ Here we report in detail the ion sensor properties for the neutral carrier-type liquid-membrane ion sensors (ISEs and ISFETs) using nematic, smectic, and cholesteric liquid-crystalline compounds.

EXPERIMENTAL SECTION

Materials. The liquid-crystalline compounds, 4-cyano-4'-hexylbiphenyl (**1**) (K18, Merck) 4-cyano-4'-octylbiphenyl (**2**) (K24,

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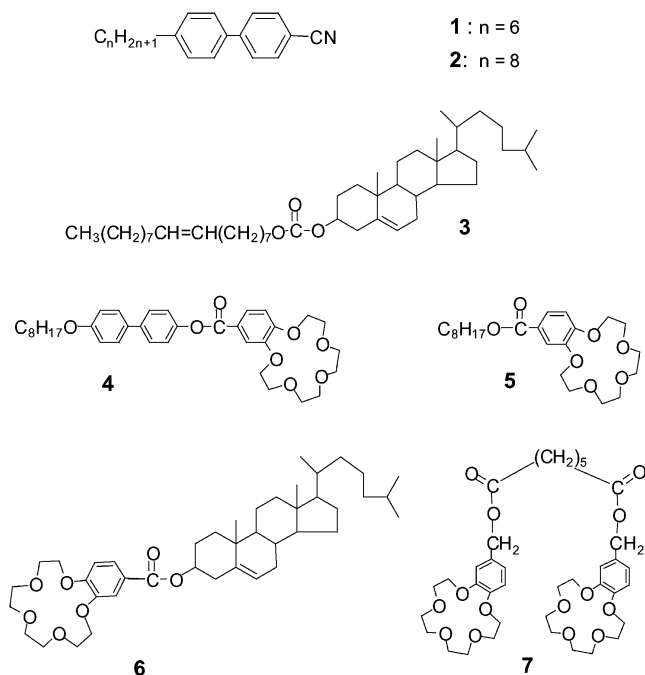
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Merck), and cholesteryl oleyl carbonate (**3**) (Acros Organics) were purchased and used as received. The conventional PVC plasticizer, *o*-nitrophenyl octyl ether (NPOE), and potassium tetrakis(*p*-chlorophenyl)borate (KTPClPB) were obtained from Dojindo Lab.

The neutral carriers, 4'-[(4''-octyloxy)biphenyloxycarbonyl]-benzo-15-crown-5 (**4**),⁹ 4'-octyloxycarbonylbenzo-15-crown-5 (**5**),¹⁰ and cholesteryloxycarbonylbenzo-15-crown-5 (**6**)⁶ were prepared in following synthetic procedures in the literature. The bis(15-crown-5) neutral carrier **7** is commercially available from Dojindo Lab. Alkali metal chlorides were of analytical reagent grade. Tetrahydrofuran (THF) was distilled and water was deionized.

Preparation of Sensing Membrane. The general procedure for preparing the ion-sensing liquid membranes is as follows. For uniform mixing of the membrane components, a liquid-crystalline compound (**1**, **2**, or **3**) or NPOE (93.7 wt %), a neutral carrier (5 wt %), and KTPClPB (1.3 wt %) were dissolved in THF, which was then evaporated off. For capillary-type electrodes, a plastic tip with an inner diameter of 0.5 mm for a micropipet (Quality Science Plastics, Q-110) was used as the container for the liquid membrane. To the fine point of the plastic tip was injected 10 μL of 1×10^{-3} M KCl aqueous solution (an internal filling solution) and then 5 μL of a liquid membrane mixture. A Ag–AgCl internal electrode was then set inside the capillary. For the application of a cholesteric liquid-crystal membrane to ISFET, an aliquot (1 μL) of a mixture (40 mg, **3** in 93.7 wt %, neutral carrier **6** in 5 wt %, and KTPClPB in 1.3 wt %) dissolved in 100 μL of THF was cast on its gate surface and the THF was evaporated off. Both types of ion sensors were generally conditioned by soaking in a mixture of an aqueous solution of 1×10^{-1} M KCl and 1×10^{-1} M NaCl overnight.

EMF Measurements. EMF measurements by the capillary electrodes and ISFETs were made at an appropriate temperature

using a pH/mV meter (Toko, TP-1000) or an ISFET meter (Shindengen Electric Inc.), respectively. The measurement temperature was controlled using a circulating thermostated bath. The external reference electrode was a double-junction-type Ag–AgCl electrode with a 3 M KCl internal solution and a 1 M $\text{CH}_3\text{CO}_2\text{Li}$ external solution. The electrochemical cell for the EMF measurement by the capillary electrodes was Ag | AgCl | 1×10^{-3} M KCl | membrane | sample solution || 1 M $\text{CH}_3\text{CO}_2\text{Li}$ || 3 M KCl | AgCl | Ag. The source-drain voltage (V_{ds}) and current (I_{ds}) for the ISFET measurements were adjusted to 1 V and 100 μA , respectively. The metal ion activities were changed by injection of high-concentration solutions to the sample solutions, while stirring with a magnetic stir bar. The EMF readings were made after the potential reached a constant value. The activity coefficients (γ) were calculated according to the Davies equation,¹¹ $\log \gamma = -0.51z^2I^{1/2}/(1 + 0.33\alpha I^{1/2}) + 0.1z^2I$, where z , α , and I stand for electric charge, ionic parameter (3 for K^+ and 4 for Na^+), and ionic strength, respectively. Selectivity coefficients for K^+ with respect to Na^+ were determined by the fixed interference method.¹² In other words, the EMF was measured with solutions of a constant level of Na^+ , a_{Na} , and varying activity of K^+ . The EMF values were plotted against the K^+ activity, and the intersection of the extrapolation of the linear portions of the resulted curve indicated a_{K} . The selectivity coefficient values were then computed from the equation: $k_{\text{K,Na}}^{\text{Pot}} = a_{\text{K}}/a_{\text{Na}}$. The background Na^+ concentration was generally 3×10^{-1} M, but it was 1×10^{-2} M for the control membrane not containing any neutral carrier and 1×10^{-1} M for the cholesteric liquid-crystal membrane at 45 $^\circ\text{C}$. Response times (t_{90}) were determined on changing the ion activity of sample solution from 1×10^{-3} to 3×10^{-3} M.

Characterization. Differential scanning calorimetry (DSC) was performed using a calorimeter (Seiko Instruments Inc., DSC6200) and an aluminum pan (Seiko Instruments Inc., SSC000E030) with a temperature-increasing rate of 5 $^\circ\text{C min}^{-1}$. Phase transition temperatures were determined at the top peak of endothermic peaks.

Polarized IR spectrometry was carried out using a FT-IR spectrometer (Perkin-Elmer, Spectrum One) equipped with a polarizer kit (KRS-5, Specac). A plastic capillary (Sunplatec 13121), the fine point of which was flattened at an area of 3 mm \times 0.5 mm, contained a liquid-crystal membrane and the sample was set into the cell compartment of the spectrometer.

X-ray diffraction was measured in a quartz glass capillary (an inner diameter of 1 mm) containing a liquid-crystal membrane, using an X-ray diffractometer (Rint/Rapid, Rigaku) with imaging plates.

RESULTS AND DISCUSSION

Liquid-Crystalline Property of Ion-Sensing Membranes.

Three types of liquid-crystalline compounds, **1**–**3**, which show nematic, smectic, and cholesteric phases, respectively, at room temperature or a little higher temperature, were selected as the membrane solvents for ion sensors, because EMF measurements for liquid-crystal-based ion sensors are experimentally difficult at temperatures much higher than room temperature. Crown ethers **4** and **6** were applied as the neutral carrier for nematic (or

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Table 1. Phase Transition Temperatures for Liquid-Crystal Membranes Based on **1**

membrane	T_{K-N} (°C) ^a	T_{N-I} (°C) ^b
1 only	15.3	29.2
1 -KTPCIPB	14.3	22.6
1 - 4 -KTPCIPB	15.3	32.5
1 - 5 -KTPCIPB	15.2	21.6
1 - 7 -KTPCIPB	15.7	31.1

^a K-N: phase transition from crystal to nematic. ^b N-I: phase transition from nematic to isotropic liquid.

Table 2. Phase Transition Temperatures for Liquid-crystal Membranes Based on **2**

membrane	T_{K-S} (°C) ^a	T_{S-N} (°C) ^b	T_{N-I} (°C) ^c
2 only	22.1	33.0	40.2
2 -KTPCIPB	20.5	25.7	32.9
2 - 4 -KTPCIPB	20.0	36.8	43.6
2 - 5 -KTPCIPB	20.0	28.4	36.8
2 - 7 -KTPCIPB	24.4	27.6	35.2

^a K-S: phase transition from crystal to smectic. ^b S-N: phase transition from smectic to nematic. ^c N-I: phase transition from nematic to isotropic liquid.

Table 3. Phase Transition Temperatures for Liquid-Crystal Membranes Based on **3**

membrane	T_{S-Ch} (°C) ^a	T_{Ch-I} (°C) ^b
3 only	18.9	33.2
3 - 6 -KTPCIPB	11.7	25.3

^a S-Ch: phase transition from smectic to cholesteric. ^b Ch-I: phase transition from cholesteric to isotropic liquid.

smectic) and cholesteric liquid-crystalline ion-sensing membranes based on **1** (or **2**) and **3** due to their structural similarity. Crown ether **5** and bis(crown ether) **7** were also employed as the neutral carrier for liquid-crystal-based ion-sensing membranes for comparison. A small quantity of KTPCIPB was added to the liquid-crystal membranes as an anion excluder.

DSC measurements were carried out as to verify that the ion-sensing membranes are in their corresponding liquid-crystal phases even if they include active components such as a neutral carrier (5 wt %) and an anion excluder (1.3 wt %). The DSC data for **1**-**3**-based liquid-crystal membranes are summarized in Tables 1-3, respectively. The addition of the active components to a liquid-crystalline compound generally modified its original phase transition temperatures slightly, but the phase transition behavior similar to the corresponding pure liquid-crystalline compounds was retained even in the mixture membranes. It was thus found that the ion-sensing membranes containing **1**-**3** are in nematic, smectic, and cholesteric liquid-crystal phases, respectively, at room temperature or a little higher.

Polarized IR spectroscopy also supported that liquid-crystalline **1** and **2** are highly oriented in their corresponding ion-sensing membranes. For instance, Figure 1 shows how the transmittance (% *T*) depends on the incident angle of polarized light in the capillary membrane consisting of **2**, **4**, and KTPCIPB at room temperature, for comparison with the systems of NPOE-**4**-

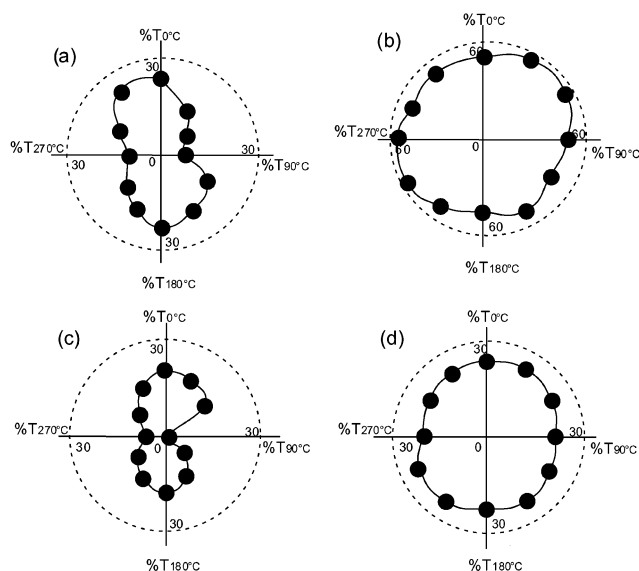


Figure 1. Dependence of transmittance on incident light angle on polarized IR spectroscopy for capillary membrane systems consisting of **2**-**4**-KTPCIPB (a), NPOE-**4**-KTPCIPB (b), only **2** (c), and only NPOE (d). Wavenumber: 2227 cm⁻¹ for (a) and (c) and 1523 cm⁻¹ for (b) and (d).

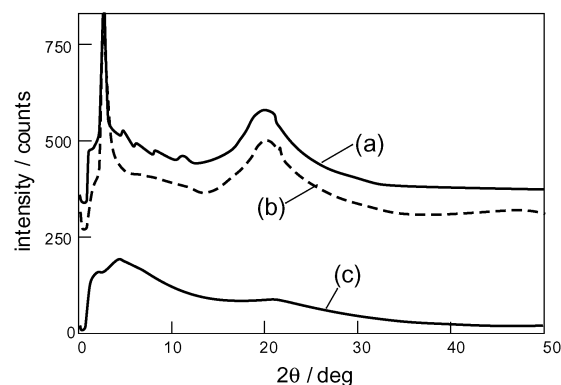


Figure 2. X-ray diffraction 2θ profiles for **2**-**4**-KTPCIPB (a) and (b) membranes in capillary and blank capillary (c).

KTPCIPB, **2** itself, and NPOE itself. There is a drastic dependence of the transmittance for ν_{CN} of **2** on the incident angle in the **2**-**4**-KTPCIPB system that is in smectic liquid-crystalline state at room temperature in a way similar to the membrane of **2** itself. To the contrary, any significant incident angle dependence of the transmittance for ν_{CO} of NPOE was not found in the NPOE-**4**-KTPCIPB system, as anticipated from the dependence for the membrane of NPOE itself. This indicates that the liquid-crystalline molecule **2** (or **1**) for the **2** (or **1**)-**4**-KTPCIPB system is highly oriented even in the capillary membranes.

Figure 2 demonstrates the X-ray diffraction 2θ-intensity profile for the **2**-**4**-KTPCIPB membrane system, suggesting the structure for the liquid-crystalline phase in capillary. Two strong peaks were observed at 2θ values of 2.8° and 20°, which corresponds to the spacing of 32 and 4 Å. The long spacing is the molecular length for the neutral carrier **4** and the short one the distance between two neighboring molecules of liquid-crystalline compound **2**.

Ion Sensors Based on Nematic Liquid Crystal. Typical potential responses for K⁺-selective capillary electrodes based on

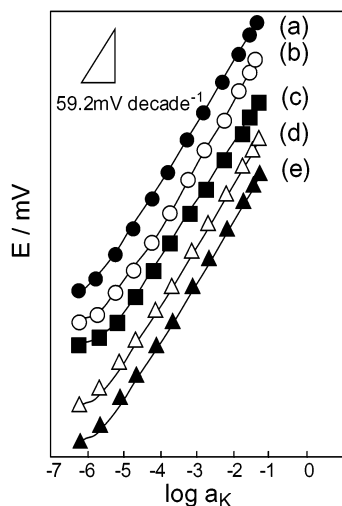


Figure 3. EMF response to K^+ activity changes in capillary ISEs based on liquid crystal **1**: (a) **1-4-KTpCIPB** system at 25 °C; (b) **1-4-KTpCIPB** system at 35 °C; (c) **1-5-KTpCIPB** system at 25 °C; (d) **1-7-KTpCIPB** system at 25 °C; (e) **NPOE-4-KTpCIPB** system at 25 °C.

1-4-KTpCIPB membrane at 25 °C, which is in nematic liquid-crystal state, are shown in Figure 3, together with those for the other neutral carrier systems containing **5** and bis(15-crown-5) **7** and for the **NPOE-4-KTpCIPB** system. The figure also includes a calibration graph for the **1-4-KTpCIPB** membrane system at 35 °C that is in isotropic liquid state, for comparison with the corresponding nematic state at 25 °C. The K^+ -selective capillary electrodes based on **1-4-KTpCIPB** membrane respond to K^+ activity changes with a Nernstian slope (59.1 mV decade $^{-1}$) in a wide activity range of 3×10^{-6} – 1×10^{-1} M at 25 °C, as is the case with the other neutral carrier system. Also, in the EMF response profile, the **1-4-KTpCIPB** membrane system resembles the corresponding membrane system of **NPOE** that is a conventional solvent for ion-sensing PVC membranes. A similar highly sensitive EMF response was found at 35 °C with a Nernstian slope of 61.1 mV decade $^{-1}$ in the **1-4-KTpCIPB** membrane electrode. The EMF response for the ion-selective capillary electrodes based on the liquid-crystal membrane was quite rapid, the response time being ~ 5 s at either of the measurement temperatures.

Comparison of K^+ selectivity against Na^+ among the capillary electrodes based on the liquid-crystal membranes is of much interest, especially in the temperature dependence of selectivity (Figure 4). An important factor for K^+ -selective electrodes based on neutral carrier is K^+ selectivity against Na^+ . The selectivity coefficient for K^+ with respect to Na^+ ($\log k_{K,Na}^{Pot}$) is -3.16 for **1-4-KTpCIPB** system at 25 °C, where the membrane is in nematic liquid-crystal state, being very similar to the value (-3.13) for the bis(crown ether) (**1-7-KTpCIPB**) system. Of course, the corresponding membrane system without any neutral carrier (**1-KTpCIPB**) afforded only a poor K^+ selectivity over Na^+ , as anticipated. It is well known that the high K^+ selectivity against Na^+ in ion-selective electrodes based on bis(15-crown-5) **7** is attributed to the efficient formation of sandwich-type K^+ complexes

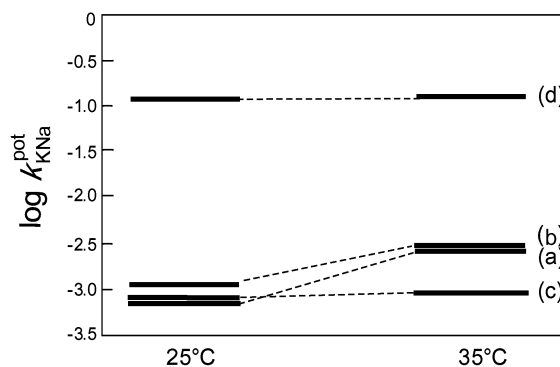


Figure 4. Temperature dependence of selectivity coefficients for K^+ with respect to Na^+ in capillary ISEs based on liquid crystal **1**: (a) **1-4-KTpCIPB** system; (b) **1-5-KTpCIPB** system; (c) **1-7-KTpCIPB**; (d) **1-KTpCIPB** system without neutral carrier at 25 and 35 °C.

by the cooperate action of two adjacent 15-crown-5 rings.^{13,14} Since molecules of neutral carrier **4** are aggregated and oriented in the nematic liquid-crystal state, the neutral carrier might behave as if two neighboring molecules of **4** were a bis(crown ether) molecule [bis(crown ether) effect]. It should be noted that the high K^+ selectivity against Na^+ for the ion-selective electrodes of **1-4-KTpCIPB** membrane is diminished significantly at 35 °C, the $\log k_{K,Na}^{Pot}$ value being -2.61 . For the membrane based on bis(15-crown-5) **7**, on the other hand, the selectivity remained unchanged at the higher temperature. This implies that the situation for the monocyclic crown ether in isotropic liquid at the membrane interface is very different from that in nematic liquid crystal. A temperature dependence of ion selectivity similar to the **1-4-KTpCIPB** membrane system was observed in another membrane system containing monocyclic crown ether **5** (**1-5-KTpCIPB**). Thus, even monocyclic crown ethers can realize such high ion selectivities as seen for the bis(crown ether) in the nematic liquid-crystal state, which aggregates and orients the neutral carrier molecules.

Ion Sensors Based on Smectic Liquid Crystal. What happens in the EMF response and selectivity of liquid-crystal membrane electrodes based on neutral carrier **4** if liquid-crystalline **1** for the membrane solvent is replaced with **2**, which exhibits a smectic liquid-crystal phase as well as a nematic one around room temperature? Figure 5 depicts the EMF responses for K^+ -selective capillary electrodes based on **2-4-KTpCIPB** membrane at three different temperatures, 25, 35, and 45 °C, where the neutral carrier was already confirmed to be in smectic and nematic liquid crystals and in isotropic liquid, respectively, by DSC measurements. The EMF response profiles are almost the same at the three temperatures, being Nernstian. A difference between the liquid-crystal membrane systems of **1** and **2** is that the K^+ activity ranges for linear Nernstian response are narrower in the **2** membrane system than the **1** system. Also, the **2** membrane system possesses longer response times (~ 10 s) as compared with those for the **1** membrane system. The differences in response time between the two liquid-crystal systems might

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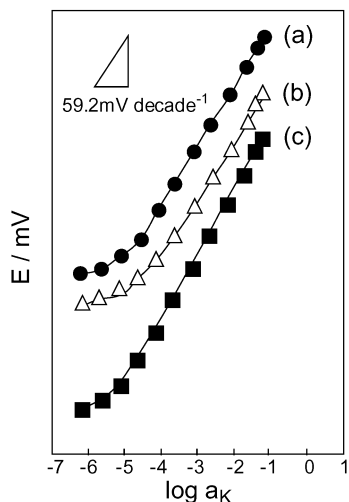


Figure 5. EMF response to K^+ activity changes in capillary ISEs based on **2-4-KTpCIPB** membrane system at (a) 25, (b) 35, and (c) 45 °C.

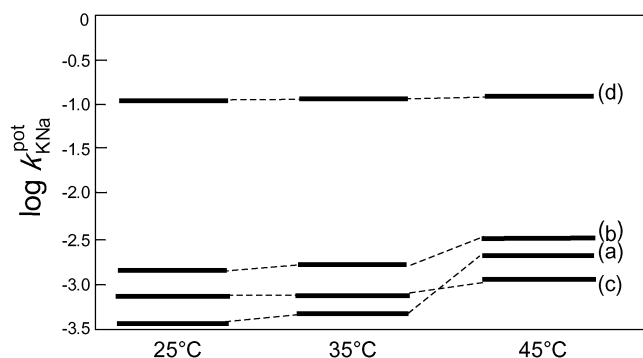


Figure 6. Temperature dependence of selectivity coefficients for K^+ with respect to Na^+ in capillary ISEs based on liquid crystal **2**: (a) **2-4-KTpCIPB** system; (b) **2-5-KTpCIPB** system; (c) **2-7-KTpCIPB**; (d) **2-KTpCIPB** system without neutral carrier at 25, 35, and 45 °C.

be due to the slow cation exchange, which is in turn derived from the lower mobility of neutral carrier **4** in liquid-crystalline **2**, showing a highly ordered state, smectic phase. Anyway, in the **2-4-KTpCIPB** systems, the sensitivity for the K^+ -selective capillary electrodes does not seem very different among the three states of smectic and nematic liquid crystals and of isotropic liquid.

The K^+ selectivity for the electrodes of **2-4-KTpCIPB** membranes can be compared with the three states in Figure 6. The K^+ selectivity against Na^+ in the capillary electrodes based on the **2-4-KTpCIPB** system is much higher in smectic and nematic liquid-crystal states of the membrane than in its isotropic liquid state. The smectic membrane of **2-4-KTpCIPB** system at 25 °C is slightly higher in the K^+ selectivity than the corresponding nematic membrane at 35 °C (The $\log K_{K,Na}^{Pot}$ value is -3.47 and -3.27 at 25 and 35 °C, respectively). The smectic state, which aggregates and orients the neutral carrier more orderly than the nematic one, might promote the above-mentioned bis(crown ether) effect, in turn providing monocyclic crown ether **4** with enhanced K^+ selectivity over Na^+ . The **2-4-KTpCIPB** membrane system exhibits the much lower K^+ selectivity in the isotropic liquid state ($\log K_{K,Na}^{Pot}$ value of -2.72 at 45 °C) than in the corresponding liquid-crystal states, as is the case with the **1**

Table 4. Temperature Dependence of Selectivity Coefficients for K^+ with Respect to Na^+ in Capillary ISEs Based on NPOE

membrane	$\log K_{K,Na}^{Pot}$		
	25 °C	35 °C	45 °C
NPOE- 4 -KTpCIPB	-3.18	-3.06	-3.03
NPOE- 5 -KTpCIPB	-3.20	-3.11	-3.05
NPOE- 7 -KTpCIPB	-3.21	-3.14	-3.02

membrane systems. Also, there are only slight differences in the selectivity for the **2**-based membrane containing bis(15-crown-5) **7** among its three different states (values are -3.18 , -3.18 , and -3.04 at 25, 35, and 45 °C, respectively). It is worth noting that the selectivity coefficient ($\log K_{K,Na}^{Pot}$ value of -3.47) for the **2-4-KTpCIPB** membrane system in smectic liquid-crystal state is even smaller than that ($\log K_{K,Na}^{Pot}$ value of -3.18) for the corresponding bis(15-crown-5) membrane system (**2-7-KTpCIPB**).

For comparison, a conventional membrane solvent for neutral carrier-type ISEs, NPOE, was employed instead of liquid-crystalline solvents **1** and **2**. The $\log K_{K,Na}^{Pot}$ values for the NPOE membranes containing neutral carriers **4**, **5**, and **7** were determined at the three different temperatures and are summarized in Table 4. In any of the NPOE systems, the $\log K_{K,Na}^{Pot}$ value was somewhat increased with increasing temperature, but the temperature dependence of the $\log K_{K,Na}^{Pot}$ value is definitely smaller than that for the liquid-crystalline membrane systems of **4**. Thus, the highly oriented smectic liquid-crystal state of the **2-4-KTpCIPB** membrane as well as the nematic liquid-crystal state of the **1-4-KTpCIPB** and **2-4-KTpCIPB** membranes enhances the K^+ selectivity against Na^+ in the electrodes based on the monocyclic 15-crown-5 derivative, which even surpasses that in the bis(crown ether)-based electrodes (**2-7-KTpCIPB**).

Ion Sensors Based on Cholesteric Liquid Crystal. As a membrane solvent for neutral carrier-based liquid-crystal membranes, **3** was also employed, showing a cholesteric liquid-crystal state in which the molecules are sophisticatedly oriented. A benzo-15-crown-5 derivative carrying a cholesteryl group **6** was adopted as the neutral carrier, taking advantage of its compatibility with the cholesteric liquid-crystalline compound. It was however found that capillary electrodes containing the membrane mixture were difficult to fabricate owing to the poor fluidity of the membrane. Instead, ISFETs, the gate surfaces of which were coated with the membranes containing **3** and **6**, were used to investigate the ion sensor property. Figure 7 demonstrates typical EMF responses to K^+ activity changes in an ISFET based on the **3-6-KTpCIPB** membrane. The K^+ ISFET showed only a sub-Nernstian response in the cholesteric liquid-crystal state at 25 °C, partly due to the extremely low mobility of the neutral carrier in the membrane. In the isotropic liquid state at 45 °C, on the other hand, the ion sensor responds to the K^+ activity changes with a near-Nernstian slope in the activity range of 1×10^{-4} – 1×10^{-1} M. The EMF responses for the K^+ ISFET of **3-6-KTpCIPB** membrane, especially in its cholesteric liquid-crystal state at 25 °C, were sluggish as compared with those for the ISEs based on the other liquid-crystalline compounds, **1** and **2**. The response times are 110 and 35 s in the cholesteric liquid-crystal and isotropic liquid states of the **3-6-KTpCIPB** membrane, respectively.

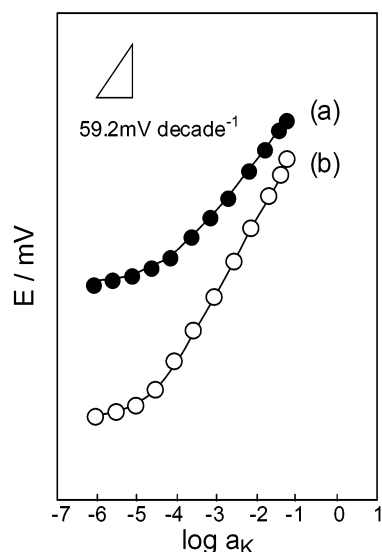


Figure 7. EMF response to K^+ activity changes in ISFETs based on **3-6**-KTpCIPB membrane at (a) 25 and (b) 45 °C.

A most striking thing for the ISFET of the **3-6**-KTpCIPB membrane is the great difference in ion selectivity between in its cholesteric liquid-crystal and isotropic liquid states (Figure 8). The K^+ selectivity over Na^+ is very high in the cholesteric liquid-crystal state of the membrane at 25 °C, the $\log k_{K,Na}^{Pot}$ value being -3.45 . The K^+ selectivity was decreased by 2 orders of magnitude in the isotropic liquid state at 45 °C, the $\log k_{K,Na}^{Pot}$ value turning out to be -1.40 . The corresponding smectic liquid-crystal system (**2-6**-KTpCIPB) is not as drastic as the cholesteric liquid-crystal system in the temperature change of the ion selectivity. The dramatic difference in ion selectivity for the ion sensors of the **3-6**-KTpCIPB membrane between the two states might be

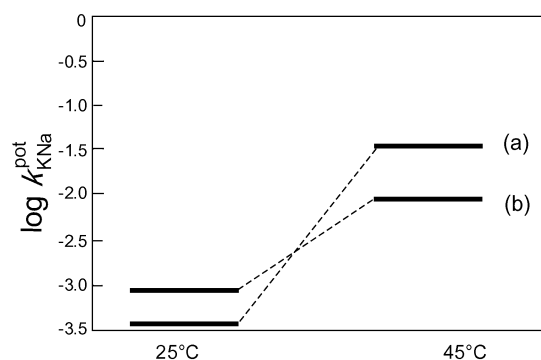


Figure 8. Temperature dependence of selectivity coefficients for K^+ with respect to Na^+ in ISFETs based on **3-6**-KTpCIPB system (a) and **2-6**-KTpCIPB system (b) at 25 and 45 °C.

reflected in the ordered orientation in the cholesteric liquid-crystal state of the membrane system.

CONCLUSION

Liquid-crystalline compounds are candidates for functional membrane solvents of neutral carrier-type ion sensors. The ordered orientation of neutral carrier affects significantly the sensor property, especially the ion selectivity. Thus, the modification and thermal control of ion sensor properties of neutral carrier-type ion sensors is feasible by adopting liquid-crystalline compounds as the membrane solvents. The present work demonstrated that even neutral carriers with a simple structure exhibit a capability of realizing extremely high ion selectivities.

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