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Liquid crystal effect on neutral-carrier-type ion-sensing membranes

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Liquid crystallinity of membrane solvent and neutral carriers for potentiometric ion sensors affects the orientation of neutral carrier molecules in the ion-sensing membranes, thus bringing about significant changes in the ion selectivity for the membrane electrodes.

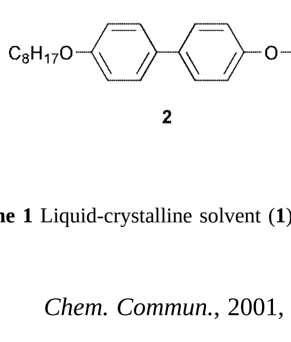
Neutral-carrier-type ion-sensing membranes are very attractive for potentiometric ion sensors such as ion-selective electrodes (ISEs) and ion-sensitive field-effect transistors.[1] The ion selectivities are governed not only by the original selectivity of neutral carriers themselves but also by the kind of plasticizers, because their ion-exchange equilibrium resembles that for liquid–liquid extraction.[2,3] We became very much interested in how the orientation of neutral carrier and solvent molecules affects their ion exchange in the membrane interface. The ion sensor property might be controlled by the orientation of the membrane components. Since liquid crystals possess some molecular orientation as well as mobility, they may be a useful material for PVC-based ion-sensing membranes.[4] We have therefore attempted to use a liquid-crystalline membrane solvent and a neutral carrier as the membrane components for ISEs, expecting some improvement of ion sensor property. Here we report a remarkable liquid crystal effect of membrane solvent and neutral carrier on the resulting membrane electrodes.

In order to elucidate the ‘pure’ liquid crystal effect on the ion sensor property, we decided to use bulk liquid-crystalline membranes, not PVC-dispersed liquid-crystalline membranes. Bulk membranes consisting of 5.0 wt% neutral carrier, 1.3 wt% potassium tetrakis(*p*-chlorophenylborate) (KTpClPB), and 93.7 wt% solvent were incorporated into the plastic tip of an adjustable pipette (Quality Science Plastics, Q-110) for the neutral carrier-type ion-sensors. For the membrane solvent we employed liquid-crystalline compound, 4-cyano-4′-hexylbiphenyl **1** (K-18, Merck) (Scheme 1), as well as 2-nitrophenyl octyl ether (NPOE) for comparison. The neutral carriers were a liquid-crystalline neutral carrier **2**[5] and [bis(benzo-15-crown-5)-4-methyl] pimelate [bis(benzo-15-crown-5)]. The electrochemical cell for the emf measurements was Ag | AgCl | 1 × 10^{-3} mol dm^{-3} KCl | ion-sensing membrane | sample solution || 1 mol dm^{-3} CH_3CO_2Li || 3 mol dm^{-3} KCl | AgCl | Ag. The selectivity coefficients of K^+ with respect to Na^+ were determined by a mixed solution method, that is, the fixed interference method (FIM) at the Na^+ background concentration of 1 × 10^{-2} or 3 × 10^{-1} mol dm^{-3}.

Potassium ion-selective electrodes based on the liquid-crystalline membrane containing liquid-crystalline neutral carrier **2** as well as KTpClPB responded to K^+ activity changes with a Nernstian or near-Nernstian slope in the activity range of 3 × 10^{-6} to 1 × 10^{-1} mol dm^{-3} at 25 °C. This was the case for the corresponding liquid membrane systems containing NPOE instead of **1**. There was not any significant difference in the sensitivity at the three measuring temperatures of 19, 25, and 35 °C. The potential response was as fast as that for conventional plasticized-PVC membrane electrodes with t_{90} of several seconds.

The selectivity for K^+ over Na^+ (selectivity coefficient of K^+ with respect to Na^+, $k^{\text{Pot}}_{\text{K,Na}}$) was measured in the liquid-crystalline membrane systems at the three different temperatures (Fig. 1). It should be noted that the selectivity coefficients depend significantly on the measuring temperatures in the membrane systems containing neutral carrier **2**. On the other hand, little significant change in the selectivity with temperature was observed in the membrane system with bis(benzo-15-crown-5) and without any neutral carrier. The selectivity coefficients of K^+ with respect to Na^+ measured at temperatures of 19 and 25 °C are much smaller than those at 35 °C in the membrane systems containing **2**.

The phase transition temperatures for the above-mentioned membrane systems were followed by differential scanning calorimeter, and are summarized in Table 1. The liquid-crystalline compound **1**, by itself, has a transition from crystal to nematic phase (K–N) at 15.3 °C and from nematic to isotropic phase (N–I) at 29.2 °C. The addition of a small amount of neutral carrier and/or KTpClPB altered the transition temperature to some extent, as anticipated. The drastic temperature dependence of the ion selectivities as shown in Fig. 1 indicates that the higher selectivity for K^+ over Na^+ is attained in the nematic state in the neutral-carrier-type liquid-crystalline membranes of **2**. This means that the highly oriented nematic phase enhances the K^+ selectivity of the 15-crown-5 derivatives over Na^+, as compared with the corresponding isotropic liquid phase. The selectivity coefficients for the membrane system of



Scheme 1 Liquid-crystalline solvent (**1**) and neutral carrier (**2**) employed here.

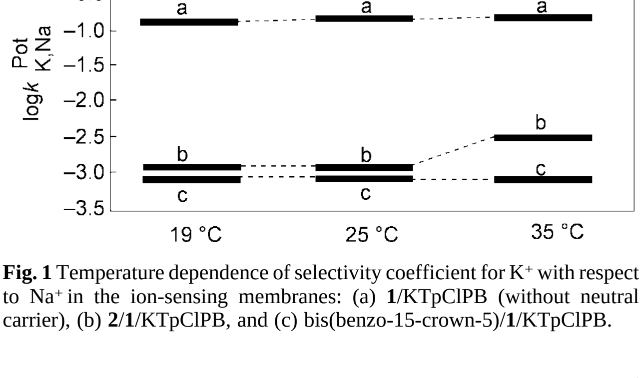


Fig. 1 Temperature dependence of selectivity coefficient for K^+ with respect to Na^+ in the ion-sensing membranes: (a) **1**/KTpClPB (without neutral carrier), (b) **2**/**1**/KTpClPB, and (c) bis(benzo-15-crown-5)/**1**/KTpClPB.

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Table 1 Phase transition temperatures measured by differential scanning calorimetry (°C)

Membrane system	K–N (Crystal-nematic)	N–I (Nematic-isotropic)
1	15.3	29.2
1/KTpClPB	15.2	23.3
2/**1**/KTpClPB	15.3	32.5
Bis(b15C5)[a]/**1**/KTpClPB	15.7	31.1

[a] Bis(b15C5): bis(benzo-15-crown-5) or [bis(benzo-15-crown-5)-4-methyl] pimelate

2/**1**/KTpClPB at 19 and 25 °C are quite comparable to those for the corresponding membrane system containing a bis(benzo-15-crown-5) derivative, bis[(benzo-15-crown-5)-4-methyl] pimelate, instead of **2**. It is well-known that bis(benzo-15-crown-5) derivatives display excellent K^+ selectivity over Na^+ by cooperative action of two adjacent crown ether rings.[6,7] This implies that the highly oriented phase in the membrane urges the monocyclic neutral carriers to aggregate to each other, which in turn allows the neutral carriers to behave as if they were bis(crown ether) neutral carriers.

Even when the bis(benzo-15-crown-5) derivative was employed for the neutral carrier of the liquid-crystalline membrane (**1**/KTpClPB), the K^+ selectivity over Na^+ hardly depended on the temperature over the range from 19 to 35 °C. Also, no significant temperature dependence on the K^+ selectivity over Na^+ was found when NPOE, a well-known plasticizer for PVC-based ion-sensing membranes, was applied as the membrane solvent instead of the liquid- crystalline solvent **1**. This confirms that the enhanced K^+ selectivity over Na^+ for the liquid-crystalline membrane system is quite specific to the highly oriented state of neutral carrier in the membrane.

Thus, the present results suggest that the ordered orientation of neutral carrier molecules in ion-sensing membranes modifies their ion-sensor selectivities to a great extent. The orientation control of neutral carriers not only by temperature but also other external stimuli, such as electric field and light, would switch their membrane ion selectivity. Further study is now under way.

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