Photocontrol of ion-sensor performances in neutral-carrier-type ion sensors based on liquid-crystalline membranes

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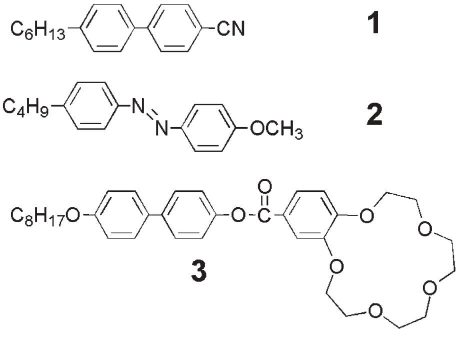
Neutral-carrier-type ion-selective electrodes based on liquid-crystalline ion-sensing membranes containing an azobenzene derivative as the photosensitive chromophore show remarkable changes in their ion selectivity on photoirradiation, which is induced by the phase transition of the membranes.

Neutral-carrier-type ion-selective electrodes (ISEs) are excellent ion-sensors.[1] The ion selectivity for liquid-membrane ion-sensors based on neutral carriers is often governed by the ion selectivity of the neutral carriers themselves in the membrane. However, the ion selectivity for the neutral-carrier-type ion sensors is also considerably affected by other membrane conditions, such as the property of the other membrane materials. We have previously reported that thermotropic liquid-crystalline compounds are very promising as functional membrane solvents for ISEs.[2–4] The ion selectivity could be controlled by the orientation of the membrane components, which is in turn derived from the thermoinduced phase transition of the liquid-crystalline membranes. In other words, the liquid-crystalline compounds can induce an ordered molecular orientation of the other membrane components in the liquid crystal state.

It is known that phase transition of liquid crystals containing an azobenzene derivative as the photosensitive chromophore is triggered by photoirradiation.[5,6] The photoinduced phase transition is based on a significant change in the molecular shape of azobenzene derivatives, which are isomerized from their *trans* form to the *cis* one by UV irradiation and *vice versa* by visible-light irradiation or heating. We have applied the photochromic molecule to the photoinduced phase transition of liquid crystal in order to control the ion-sensor performance of ISEs based on liquid-crystalline membranes containing an azobenzene derivative not only by heating but also by photoirradiation. Here we report the photocontrol of ion-sensor performances in neutral-carrier-type ISEs based on liquid-crystalline membranes containing a small quantity of an azobenzene derivative.

The ion-sensing membranes consisted of 4-cyano-4′-hexylbiphenyl (**1**) (K-18, Merck) as the liquid-crystalline membrane solvent, 4-butyl-4′-methoxyazobenzene (**2**) as the azobenzene derivative, 4′-[(4″-octyloxy)biphenyloxycarbonyl]-benzo-15-crown-5 (**3**) as a liquid-crystalline neutral carrier (see Scheme 1) and potassium tetrakis(*p*-chlorophenyl)borate (**4**) (KT*p*ClPB, Dojindo Lab.) as an anion excluder.[7] The pure liquid membrane was incorporated into a plastic tip of an adjustable pipette (Q-110, Quality Science Plastics) for the neutral carrier-type ion selective electrode. The electrochemical cell for the potential (emf) difference measurements was a Ag | AgCl | 3 M KCl ‖ 1 M CH_3COOLi ‖ sample solution | membrane | 1 × 10^{-3} M KCl | AgCl | Ag. The selectivity coefficients for K^+ with respect to Na^+ were determined by a fixed interference method (FIM),[8] using a Na^+ background concentration of 0.3 M. All potential difference measurements were carried out without any stray light. Under dark conditions, the measurement temperature was controlled at 25 and 45 °C by using a circulating thermostated bath. Under photoirradiation conditions, UV and visible lights from a Xe lamp were irradiated through a UV-D36 (ASAHI TECHNOGLASS) and a Y-50 (ASAHI TECHNOGLASS) color filter, respectively. In the case of the photoirradiation conditions, the measurements were carried out at ambient temperature, because the irradiating light might be obstructed by the circulating thermostatted bath. A digital microscope (DMBA300, SHIMADZU) equipped with a hot stage (10021, JAPAN HIGH TECH) and polarizers was used to observe the states of the membranes under the same conditions as the potential difference measurements.

Under the conditions corresponding to the potential difference measurements, the ion-sensing membranes containing the azobenzene derivative **2** were observed by polarization microscopy. The probe light was hardly transmitted with increasing temperature from 25 to 45 °C. This means that the phase transition of the membranes is induced by heating. This was also the case with UV irradiation. The photoinduced phase transition is due to the isomerization of the azobenzene derivative. Thus, the phase transition of the membranes containing the azobenzene derivative **2** from its liquid crystal state to the isotropic liquid one, can be induced by heating and photoirradiation. The potassium ISEs



Scheme 1 Liquid-crystalline membrane solvent (**1**), azobenzene derivative (**2**), and liquid-crystalline neutral carrier (**3**) employed here.

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based on the liquid-crystalline membranes containing the azobenzene derivative **2** responded to potassium ion activity changes with a Nernstian or near-Nernstian slope in the activity range of 1×10^{-4} to 3×10^{-1} M under any of the conditions. The membranes without the azobenzene derivative **2** also exhibited as good a response for the potassium ion as observed in the membranes with **2**. These results reveal that the azobenzene derivative in the membranes does not interfere with the potential difference responses for the potassium ISEs.

The selectivity coefficients for K^+ with respect to Na^+ ($k^{\mathrm{pot}}_{\mathrm{K,Na}}$) are determined under different membrane conditions. In the case of the membranes containing the azobenzene derivative **2**, the $\log k^{\mathrm{pot}}_{\mathrm{K,Na}}$ values are −3.02 (±0.06) and −2.76 (±0.03) at 25 and 45 °C, respectively. The selectivity coefficient was significantly larger at 45 °C than that at 25 °C. Similarly, the replacement of visible light by UV one increased the values of the selectivity coefficient. The values were −2.98 (±0.03) and −2.76 (±0.03) under visible- and UV-light irradiation conditions, respectively. The membranes without azobenzene derivative **2** also showed a marked temperature dependence of the selectivity coefficients, the $\log k^{\mathrm{pot}}_{\mathrm{K,Na}}$ values being −3.13 (±0.07) and −2.75 (±0.02) at 25 and 45 °C, respectively. However, the selectivity coefficients under photoirradiation conditions hardly changed in the membranes without **2**. The $\log k^{\mathrm{pot}}_{\mathrm{K,Na}}$ values were −3.21 (±0.08) and −3.16 (±0.11) under visible- and UV-light irradiation conditions, respectively. The results under photoirradiation conditions arise from the difference in the phase transition behavior in between the presence and absence of the azobenzene derivative in the membranes: the presence of **2** leads to a clear phase transition of the membranes from nematic liquid crystal to isotropic liquid, while the absence of **2** does not bring about such a significant phase transition. On the other hand, the selectivity coefficients for K^+ with respect to Cs^+ in ISEs based on the membranes containing the azobenzene derivative **2** did not change significantly by the phase transition of the liquid-crystalline ion-sensing membranes. We have already reported that the two neighboring neutral carriers might behave like a bis(15-crown-5) molecule by the cooperative action of two adjacent 15-crown-5 rings [bis(crown ether) effect] to efficiently form sandwich-type K^+ complexes with a 1 : 2 stoichiometry of metal ion and crown ether ring.[2,3] The changes in the selectivity coefficients may reflect the phenomenon that neutral carrier **3** molecules are aggregated and oriented in the liquid crystal state, while being dispersed randomly in the isotropic liquid state. Therefore, the different results between two interfering ions, Na^+ and Cs^+, in the photo- and thermoinduced changes of the $\log k^{\mathrm{pot}}_{\mathrm{K,M}}$ values may support the above consideration. The remarkable changes in the selectivity coefficients for K^+ with respect to Na^+ by the phase transition result considerably from the formation of 1 : 1 complexes of Na^+ and the neutral carrier **3**. In contrast, the selectivity coefficients for K^+ with respect to Cs^+ did not show any significant change, since Cs^+ also forms 1 : 2 complexes with the neutral carrier **3** in a similar way to the corresponding K^+ complexes.

The external stimuli, photoirradiation or heating of the membranes, might deteriorate the membrane components. However, this sensor system does not seem to be deteriorated by repeated photoirradiation, the photoinduced switching of the ion selectivity being reproducible. This was also the case with the repeated temperature changes. In other words, the external stimuli on the ion-sensing membranes hardly affect the sensor properties of the liquid-crystalline membranes containing azobenzene derivative **2**. These results indicate that the ion-sensor performance of ISEs based on the liquid-crystalline membranes containing the azobenzene derivative **2** can be controlled by photoirradiation as well as by temperature changes. The reproducible changes in the selectivity coefficients for K^+ with respect to Na^+ suggest that the membranes employed here are stable under the present measurements conditions.

The tunable selectivity by photoirradiation is interesting from the viewpoint of photocontrollable analysis and application.[9,10] In addition, we had reported that the ISEs based on the similar liquid-crystalline membranes without any azobenzene derivative were applied successfully to K^+ assays in blood sera.[4] Therefore, the ISEs based on the liquid-crystalline membranes containing azobenzene derivative **2** are also useful for K^+ assays in real biological samples, because the sensitivity and selectivity for K^+ are comparable to or higher than those for K^+-ISEs reported previously. This type of photochromic ion-sensing membranes based on liquid-crystalline compounds, the ion selectivity of which can be switched both thermo- and photochemically, may be extended to other neutral-carrier-type ion sensors.

Notes and references

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