Lithium-Selective Coloration of Spirobenzopyran Derivative Incorporating Monoaza-12-Crown-4 in Micellar Solution

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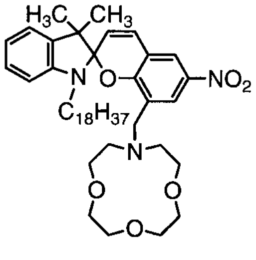
A spirobenzopyran derivative bearing a monoaza-12-crown-4 moiety and an octadecyl group as a lipophilic chain was synthesized and was used as a chromogenic reagent for alkali metal ion in micellar solutions. The crowned spirobenzopyran derivative exhibited highly Li^+-selective spectral changes under high pH conditions.

Crowned spirobenzopyran derivatives have been used as photochromic compounds, and studied on metal-ion selective potential photoresponse and photoresponsive metal ion transport.[1–7] On the other hand, crowned spirobenzopyran exhibited metal-ion selective spectral changes by complexation of crown ether moiety and metal ion in organic solvents.[8] Especially for spirobenzopyran derivative incorporating monoaza-12-crown-4 moiety, high Li^+-selective spectral change in the organic phase was observed in the liquid–liquid extraction system using 1,2-dichloroethane as an organic solvent.[9] In these systems, the spiropyran form is isomerized to the corresponding merocyanine one by complexation of its crown ether unit with metal ion to result in a drastic spectral change. Here we describe metal-ion recognition behavior of spirobenzopyran derivative bearing monoaza-12-crown-4 moiety and octadecyl group **1** in aqueous micellar solutions containing dodecylsulfate ion as an anionic surface-activate agent. Effective extraction of metal ion and thereby efficient coloration of spirobenzopyran derivative can be expected in specific environment such as micellar solution.

Compound **1** was synthesized in the same manner as described in the previous work.[5] For comparison, spirobenzopyran derivative **2** incorporating a piperidine moiety instead of the monoaza-12-crown-4 moiety was also synthesized in a similar way to **1**.[10]



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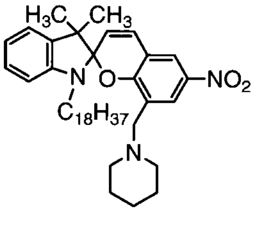

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In a 50-mL stoppered centrifuge tube was placed an aqueous solution (10 mL) containing 1.5×10^{-5} mol dm^{-3} spirobenzopyran derivative and 9.5×10^{-3} mol dm^{-3} tetramethylammonium dodecylsulfate (TMADS).[11] Spirobenzopyran derivatives **1** and **2** were hardly dissolved in pure water. They were, however, soluble in the aqueous micellar solution to exhibit absorption spectra having maximum absorption wavelengths (λ_{max}) at 521 nm for **1** and 525 nm for **2** under the dark conditions. The visible absorption is attributable to their merocyanine forms bearing a protonated nitrogen atom on the azacrown ether or the piperidine units, respectively, under neutral pH conditions.

On addition of aqueous tetramethylammonium hydroxide (TMAOH) solution, the maximum absorption wavelengths of the solutions containing **1** and **2** shifted to a longer wavelength with an increase of the TMAOH concentration (Figure 1). The values of λ_{max} for both solutions of **1** and **2** moved to 549 nm at 9.1×10^{-2} mol dm^{-3} of TMAOH. Obviously, the spectral changes are caused by the dissociation of a proton on the nitrogen atom of azacrown ether or piperidine units, since the red shift was enhanced by the decrease of the proton concentration. The value of λ_{max} is based on the merocyanine forms of the compounds **1** and **2**, of which phenoxide ion should slightly interact with TMA^+ ion because TMA^+ ion is in a large excess (about 0.1 mol dm^{-3}) to the other cations in the micellar solution. The reason for the decrease of absorbance at the maximum absorption wavelength is not clear at the moment.

On the other hand, addition of an HCl solution into the aqueous micellar solutions containing compounds **1** and **2** brought about drastic decreases of the absorbance at 521 nm and 525 nm, respectively, together with increases of the absorbance at 405 nm. These spectral changes demonstrate that the protonation of the phenoxide ion in the merocyanine forms of **1** and **2** was promoted by an increase of the proton concentration.

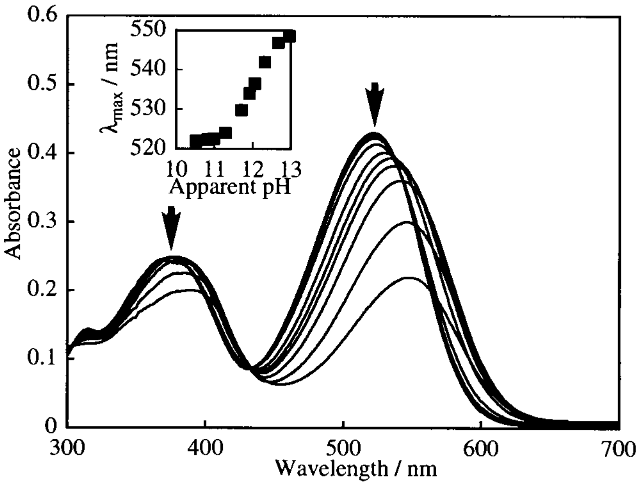

Figure 1. Absorption spectral change of aqueous micellar solution of **1** with apparent pH. Inset: Plots of maximum absorption wavelength of the solution *vs.* apparent pH. [**1**] = 1.5×10^{-3} mol dm^{-3}; [TMADS] = 9.5×10^{-3} mol dm^{-3}; Apparent pH = 10.5, 10.8, 11.0, 11.3, 11.7, 11.9, 12.1, 12.3, 12.7, 13.0

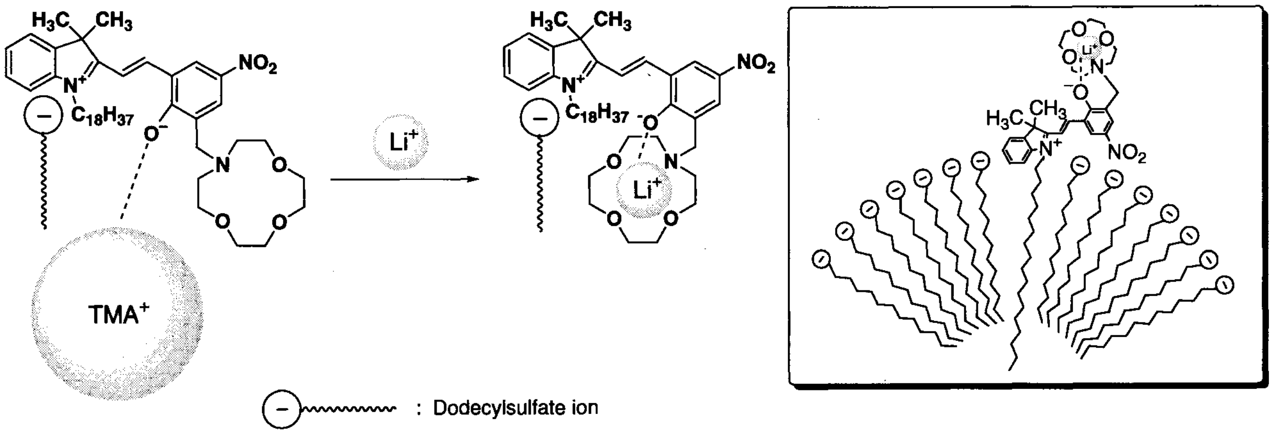

Figure 3. Postulated scheme for formation of complexes of **1** and Li^+ in aqueous micellar alkaline solution

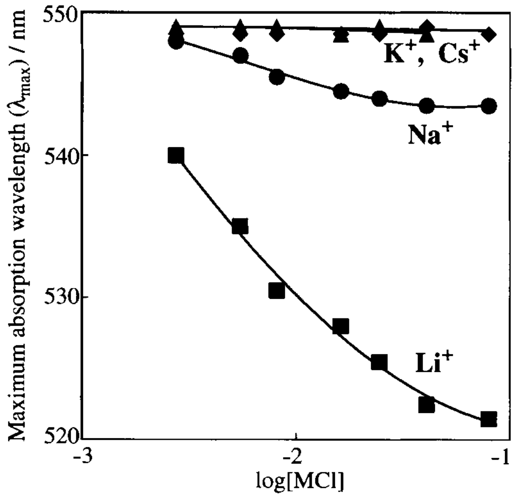

Figure 2. Plots of maximum absorption wavelength of aqueous micellar alkaline solution of **1** *vs.* log[metal chloride]
$[\mathbf{1}] = 1.4 \times 10^{-5}$ mol dm^{-3}; [TMADS] $= 8.6 \times 10^{-3}$ mol dm^{-3}
[TMAOH] $= 0.1$ mol dm^{-3}

An alkali metal chloride solution was added after addition (1.0 mL) of 1.1 mol dm^{-3} TMAOH solution to the micellar solution. The mixed solution was then shaken vigorously for about 30 s at room temperature under dark conditions. The absorption spectra were measured immediately after the shaking. The aqueous alkaline solution containing **1** without any metal ion gave an absorption spectrum with a maximum absorption wavelength (λ_{max}) at 549 nm. On addition of LiCl, the maximum absorption wavelength shifted to a shorter wavelength with the Li^+ concentration selectively and shifted to 523 nm at 8.0×10^{-2} mol dm^{-3} LiCl (Figure 2). The wavelength is close to that of the protonated merocyanine form as mentioned above (521nm). It is also found in Figure 2 that the addition of NaCl gave rise to a slight shift of the maximum absorption wavelength, while the addition of KCl and CsCl hardly changed the original wavelength. To the contrary, no shift of the maximum absorption wavelength of the solution containing **2** was observed by addition of any alkali metal chloride. These results demonstrate that, in the micellar surface, the monoaza-12-crown-4 moiety of **1** complexes Li^+ selectively and that the bound Li^+ interacts strongly with phenoxide anion of the merocyanine form to make a stable six-membered complex (Figure 3).

Thus, in the anionic mecellar solution, spirobenzopyran derivatives bearing monoaza-12-crown-4 or piperidine moieties were isomerized into the merocyanine forms, and the derivative incorporating 12-crown-4 moiety exhibited the high Li^+ recognition ability.

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References and Notes

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10 Elemental analysis and spectroscopic data of the compound **2** are as follows: ^{1}H-NMR ($CDCl_3$, 300 MHz) $\delta = 0.87$ (3H, t, $J = 7$ Hz, CH_2CH_3), 1.2–1.5 [44H, m, $(CH_2)_{16}CH_3$, CCH_3 and 3''-, 4''- and 5''-H of piperidine], 2.18–2.22 (4H, m, NCH_2 of piperidine), 3.09–3.23 [4H, m, $NCH_2(CH_2)_{16}$ and $PhCH_2$], 5.85 (1H, d, $J = 10$ Hz, CH=CHPh), 6.54 (1H, d, $J = 8$ Hz, 7-H of indoline), 6.7–7.2 (4H, m, CH=CHPh and 4-, 5- and 6-H of indoline), 7.88 (1H, d, $J = 3$ Hz, 5-H of benzopyran), 8,10 (1H, d, $J = 3$ Hz, 7-H of benzopyran); MS(ESI, in acetone) $m/z = 658$ $(M + H)^+$; Anal. Found: C, 76.71; H, 9.70; N, 5.91. Calcd for $C_{42}H_{63}N_3O_3$: C, 76.67; H, 9.65; N, 6.39.
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