Selective Colorimetry of Sodium Ion in Anionic Micellar Solution Containing Dibenzo-16-crown-5 Chromoionophore

Toshiharu Kuboyama, Shigeo Nakamura, Makoto Takagi,* Jong Chan Lee,† and Takashi Hayashita*††
Department of Chemical Systems and Engineering, Graduate School of Engineering, Kyushu University, Higashi-ku, Fukuoka 812-81
†Department of Chemistry, Chung-Ang University, Seoul 156-756, Korea
††Department of Chemistry, Graduate School of Science, Tohoku University, Aoba-ku, Sendai 980-77

(Received February 2, 1998; CL-980073)

Colorimetric response of a lipophilic dibenzo-16-crown-5 chromoionophore **1** in aqueous micellar solution has been examined. A selective color change was obtained for Na^+ ion in the anionic micellar solution of **1**.

The extraction photometry by a crown ether chromoionophore requires toxic and volatile organic solvents and an inconvenient phase separation process in the analysis.[1,2] If alkali metal cation photometry could be performed in homogeneous aqueous media, a wide variety of applications would be feasible.[3-5] In this study, a selective colorimetry of alkali metal cations in aqueous micellar solution containing dibenzo-16-crown-5 (DB16C5) chromoionophore **1**[5] has been examined. DB16C5 skeleton possesses an appropriate ring cavity to match the ionic diameter of Na^+.[6] The micellar solution is expected to provide a hydrophobic circumstance which solubilizes the lipophilic crown ether chromoionophores in aqueous solution and enhances the ionophore-metal interaction.[7] We report herein the first evidence that an anionic micelle containing **1** showed a selective colorimetric response for Na^+ in aqueous solution (Figure 1).

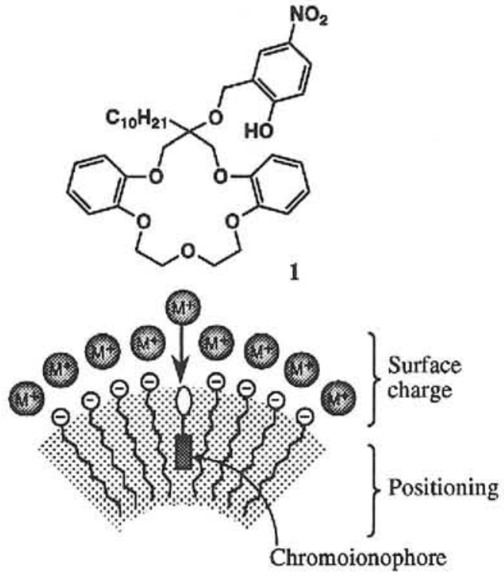

Figure 1. Structure of Chromoionophore **1** and concept of metal ion sensing in aquoues micellar solution.

The colorimetric behavior of **1** for alkali metal cations was evaluated spectrophotometrically in aqueous micellar solution. The aqueous solution (50 cm^3) contained 5.6×10^{-5} M (1 M= 1 mol dm^{-3}) chromoionophore, 1×10^{-3} M HCl, 5×10^{-4} M 2-morphorinoethanesulfonic acid (MES), 10.0 mM surfactant, and 0.10 M alkali metal chlorides or tetramethylammonium chloride (TMACl) was stirred in 80 cm^3 jacket cell at 30℃ under N_2 atomosphere. The surfactants used in this study are cetyltrimethylammonium bromide (CTAB, Kishida Chemical Co.,Ltd.), Triton X-100 (Wako Pure Chemical Ind. Ltd.), and tetramethylammonium dodecylsulfate (TMADS, prepared by modifying the reported procedure[8]). Titration was made with 7.5 wt% TMAOH aqueous solution using APB-410 auto piston buret (Kyoto Electronic Ltd.) to adjust the pH, and then the electronic spectrum was measured at each pH. The pH of the aqueous solution was calibrated from Gran's plot.[9]

The resultant spectral characteristics of chromoionophore **1** in 10.0 mM micellar solution of (a) CTAB, (b) Triton X-100, and (c) TMADS are shown in Figure 2. Increasing the pH promotes proton dissociation of the phenolic chromophore and absorptions based on the dissociated species (L^-) appeared at 405-408 nm. The apparent pK_a (pK_a^{app}) values calculated from these data are summarized in Table 1. In both CTAB and Triton X-100, no significant differences in the pK_a^{app} values was noted. The low pK_a^{app} values observed for CTAB reveals that the cationic charge of the micellar surface accelerates proton dissociation of the phenolic chromophore. For Triton X-100, the pK_a^{app} values are apparently higher than that of *p*-nitrophenol in aqueous solution ($pK_a = 7.1$).[10] This is attributable to a hydrogen bonding between the chromophore proton and polyoxyethylene unit in

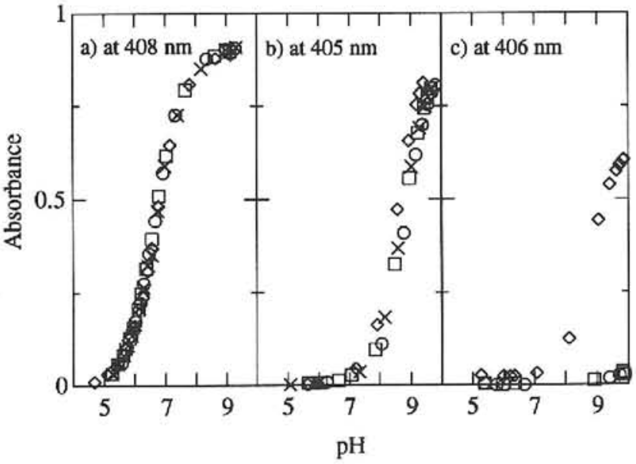

Figure 2. UV-spectra of **1** as a function of pH in aqueous (a) CTAB, (b) Triton X-100, and (c) TMADS solution. Salts concentration: 0.10 M of (○) TMACl, (□) LiCl, (◇) NaCl, and (×) KCl.

Triton X-100. In contrast, a selective coloration of chromoionophore **1** was observed for TMADS solution. Thus the absorbance at 406.0 nm raises only in the presence of Na^+ ion. This is a first instance that crown ether chromoionophore exhibited a highly selective colorimetric response for alkali metal cations in micellar solution. It should be noted that the spectral characteristics of **1** for K^+ was not recorded in Figure 2 due to a precipitation of potassium dodecylsulfate (PDS) in the presence of 0.1 M K^+.[11]

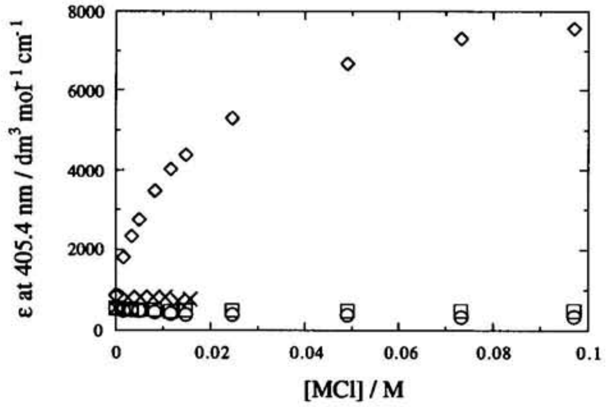

Figure 3. Molar absorptivity at 405.4 nm as a function of metal ion concentration. Chromoionophore: 2.8×10^{-5} M; Buffer: 1.0×10^{-2} M; Salts: LiCl (□), NaCl (◇), KCl (×), and TMACl (○).

Since distribution of the lipophilic chromoionophore **1** from a micellar phase into a bulk aqueous phase is negligible, the following ion-exchange equilibrium may be derived,

$$HL_m + M^+_a \overset{K_{ex}}{\leftrightarrows} ML_m + H^+_a \tag{1}$$

where K_{ex}, subscripts "m" and "a" are the ion-exchange constant, micellar and aqueous phase, respectively. The apparent molar absorptivity (ε) of the chromoionophore is expressed as,

$$\varepsilon = \frac{\varepsilon_{HL} + \varepsilon_{ML} K_{ex} [M^+]_a/[H^+]_a}{1 + K_{ex} [M^+]_a/[H^+]_a} \tag{2}$$

where ε_{HL} and ε_{ML} denote molar absorptivity of HL and ML species, respectively. Plots of the apparent molar absorptivity vs. metal ion concentration at pH 9.40 are shown in Figure 3. The K_{ex} values for each metal cations are determined from a non-linear least-squares program. The obtained pK_{ex} value was 7.67 for Na^+ (The changes in absorbance for Li^+, K^+, and TMA^+ were too small to evaluate). On the assumption that L^- species in the micellar phase is negligible, the apparent acidity constant K_a^{app} is mostly equal to $K_{ex}[M^+]_a$. Thus the pK_a^{app} value is estimated to be 8.67, which is in consistent with the pK_a^{app} value of 8.73 obtained in Table 1.

Table 1. Apparent acidity constant of chromoionophore **1**[a]

Surfactant	pK_a^{app}			
	Li^+	Na^+	K^+	TMA^+
CTAB	6.62	6.69	6.69	6.65
Triton X-100	8.73	8.57	8.75	8.85
TMADS	-	8.73	-	-

[a] Calculated from the data in Figure 2.

Although further investigation is required to elucidate the detailed mechanism of this system, it is probable that the anionic charge of the micellar surface inhibits the formation of a loose ion-pair metal-chromoionophore complex because of an electric repulsion of the surface charge with phenolate anion of the chromophore. Thus the complex formation would be restricted to cations which can form a tight ion-pair in the binding site of the chromoionophore.

In summary, the anionic micellar solution is shown to be a quite effective medium for alkali metal ion sensing. This result demonstrates that a highly selective colorimetry for metal cations would be feasible through a proper combination of anionic micelle or vesicle systems with molecular designed lipophilic chromoionophores.

This work was supported by a Grant-in-Aid for Scientific Research (No. 09650893) from the Ministry of Education, Science, Sports and Culture, Japan.

References and Notes

1 M. Takagi, In "Cation Binding by Macrocycles", ed by Y. Inoue, G. W. Gokel, Marcel Dekker: New York (1990), p.465.

2 T. Hayashita and M. Takagi, In "Comprehensive Supra-molecular Chemistry. Molecular Recognition: Receptors for Cationic Guests", ed by G. W. Gokel, Pergamon: New York (1996), Vol. 1, p. 635.

3 D. J. Cram, R. A. Carmack, and R. C. Helgeson, *J. Am. Chem. Soc.*, **110**, 571 (1988); R. C. Helgeson, B. P. Czech, E. Chapoteau, C. R. Gebaver, A. Kumar, D. J. Cram, *J. Am. Chem. Soc.*, **111**, 6339 (1989).

4 B. P. Czech, E. Chapoteau, W. Zazulak, C. R. Gebaver, and A. Kumar, *Anal. Chim. Acta*, **241**, 127 (1990); B. P. Czech, E. Chapoteau, M. Z. Chimenti, W. Zazulak, C. R. Gebaver, and A. Kumar, *Anal. Chim. Acta*, **263**, 159 (1992); E. Chapoteau, M. S. Chowdhary, B. P. Czech, A. Kumar, and W. Zazulak, *J. Org. Chem.*, **27**, 2804 (1992).

5 T. Hayashita, K. Kunogi, M. Takagi, J. C. Lee, and R. A. Bartsch, *Chem. Lett.*, **1995**, 597; T. Hayashita, K. Kunogi, M. Takagi, J. C. Lee, and R. A. Bartsch, *Anal. Sci. Techn.*, **8**, 793 (1995).

6 T. Hayashita, M. -J. Goo, J. C. Lee, J. S. Kim, and R. A. Bartsch, *Anal. Chem.*, **62**, 2283 (1990); R. A. Bartsch, T. Hayashita, J. H. Lee, J. S. Kim, and M. G. Hankins, *Supramol. Chem.*, **1**, 305 (1993).

7 C. Tanford, In "The Hydrophobic Effect", John Wiley & Sons: New York (1979).

8 K. Meguro and T. Kondo, *Nihon Kagakukaishi*, **80**, 823 (1959); ^{1}H-NMR (D_2O, 250 MHz): δ 0.70 (t, 3H), 1.0-1.3 (m, 18H), 1.48 (m, 2H), 3.01 (s, 12H), 3.81 (t, 2H). Anal. Calcd for $C_{16}H_{37}NO_4S$: C, 56.60 %; H, 10.98 %; N, 4.13 %. Found: C, 56.57 %; H, 11.03 %; N, 4.12 %.

9 G. Gran, Analyst, 77, 661 (1952); T. Miyajima, K. Yoshida, and E. Hogfeldt, *J. Coll. Int. Sci.*, **156**, 383 (1993).

10 H. Hoshino, T. Saitoh, H. Taketomi, and T. Yotsuyanagi, *Anal. Chim. Acta*, **147**, 339 (1983).

11 Kraft point of PDS is relatively high (ca. 40℃).[8]