

Effect of Solvent on the Cation-Sensitive Fluorescence of Polyanions Bearing 4'-Acryloylbenzo-18-crown-6 Units

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Changes in the fluorescence intensity of polyanions bearing 4'-acryloylbenzo-18-crown-6 units on the addition of cations were studied in a mixed solvent of methanol and water at 30°C. The sensitivity of the change in fluorescence intensities of the polymers toward cations was strongly enhanced compared to that of the corresponding model compound. When alkali metal cations were added, the fluorescence intensity of the polymers decreased in the orders $\text{Li}^+ > \text{Na}^+ > \text{Cs}^+ > \text{Rb}^+ > \text{K}^+$ in a methanol-water (1:9) mixture and $\text{Li}^+ > \text{Na}^+ > \text{Rb}^+ > \text{K}^+ \approx \text{Cs}^+$ in a methanol-water (9:1) mixture. Alkaline earth metal cations and alkylamine hydrochlorides decreased the fluorescence intensity of the polymers in a methanol-water (1:9) mixture. The cation-dependent decrease in the fluorescence intensity of the polymers was affected by the water fraction in a mixed solvent of methanol and water.

KEY WORDS: Cation sensing; fluoroionophore; poly(crown ether); solvent effect.

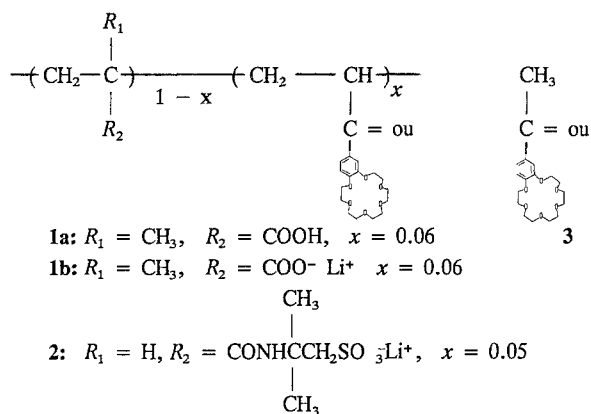
INTRODUCTION

It is well-known that crown ethers bind alkali and alkaline earth metal cations in their cavities. Crown ethers can be used for the spectrophotometric detection of cations by means of ion-pair extractions of complexes between crown ether and a cation with a counter-anion such as picrate [1] and by means of chromogenic crown ether reagents [2,3]. The absorption spectrum of the chromogenic reagents, which have both chromophoric and crown ether moieties in a molecule, changes remarkably in response to alkali and alkaline earth metal cations. Fluorimetry can, in principle, be more sensitive than absorption photometry. The effects of alkali cation complexation on the emission properties of crown ethers [4-8], cryptands [9,10], and podands [7,11] have been

investigated by several workers. Recently we reported the effect of cations on the fluorescence of crowned acetophenones [12] and polyanions bearing crowned acetophenone moieties as a fluorophore [13,14]. Although the cation binding ability of crown ethers is low in aqueous media, the sensitivity of the change in the fluorescence intensities toward cations has been enhanced by anchoring the fluorescent crown ether moieties into the backbone of polyanions, because the anionic group such as $-\text{COO}^-$ or $-\text{SO}_3^-$ in the polymer chain increases the concentration of cations close to the polymer-bound fluorescent crown ether groups. The concentration of cations close to the polyanions is very dependent on solvent. In this paper we report the effect of solvent on the cation-sensitive fluorescence of polyanions 1a-b and 2, which have 4'-acryloylbenzo-18-crown-6 units. The cation-sensitive fluorescence of the polymers was compared with that of 4'-acetylbenzo-18-crown-6 (3).

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EXPERIMENTAL

Materials. **1a** was prepared by the radical copolymerization of methacrylic acid and 4'-acryloylbenzo-18-crown-6 (**4**). The preparation of **4** has been reported elsewhere [14]. A tube with a stopcock was charged with methacrylic acid (758 mg, 8.8 mmol), **4** (170 mg, 0.46 mmol), azobisisobutyronitrile (5 mg), 1-dodecanethiol (1.9 mg, 9.4×10^{-6} mol), and *N,N*-dimethylformamide (0.8 ml) and degassed under vacuum by repeated freeze-thaw cycles. Polymerization was carried out at 55°C for 6 h. The polymer was isolated by pouring the reaction mixture into excess diethyl ether. The polymer was purified by dissolving in methanol and precipitating with diethyl ether. Yield, 0.79 g (85%). The molecular weight determined using a molecular weight-viscosity relationship [15] for poly(methacrylic acid) ($[\eta]/(\text{ml g}^{-1}) = 0.242 M^{0.51}$) was 3.73×10^4 . **1b** was prepared by neutralization of **1a** with LiOH. **2** was prepared by the radical copolymerization of the lithium salt of 2-acrylamido-2-methyl-1-propanesulfonic acid and **4** by a method similar to that described for **1a** without 1-dodecanethiol. The polymer was purified by dialysis against water for 3 days. Yield, 73%, $\eta_{sp}/C = 0.16$ ($[C = 5.1 \times 10^{-4}$ g/ml in 0.5 *N* NaOH at 25°C). The contents of **4** units in the polymers were determined by measuring absorbance at 277 nm in a methanol-water (1:1) mixture. The molar extinction coefficient (11400 L/mol-cm) was assumed to be equal to that of 4'-acetylbenzo-18-crown-6 (**3**). The contents of **4** units for **1a**, **1b**, and **2** were 0.06, 0.06, and 0.05, respectively. The preparation of **3** has been reported [16]. Alkali and alkaline earth metal chlorides were of reagent grade and used without further purification.

Measurements. The fluorescence spectra were measured in a methanol-water mixture at 30°C using a Shimadzu RF-500 spectrofluorophotometer. The methanol-water ratio of the mixed solvent shown in the text is the

volume ratio. The slit widths of excitation and emission were 3 and 10 nm, respectively. The wavelength of the excitation light was 330 nm. The absorbance of samples at 330 nm were kept below 0.1. The quantum yields of fluorescence were determined by comparison of the intensities of the fluorescence of the polymers with the fluorescence of quinine sulfate [17].

RESULTS AND DISCUSSION

Polymers **1a-b** and **2** showed an absorption maximum at 229 nm and shoulder peaks at 276 and 305 nm in a methanol-water (1:9) mixture. On the addition of alkali metal chlorides, the absorption peaks of the polymers slightly shifted to a shorter wavelength (2–3 nm). The magnitude of the peak shifts was roughly consistent with the order of the cation binding ability of benzo-18-crown-6. The absorption peaks of benzocrown ethers have been known to shift to shorter wavelengths when alkali metal cations are bound to the crown ether cavities [18]. However, the shift of the absorption peak is too small to use as a means for detecting cations.

On excitation with 330-nm light, **1a-b** and **2** showed fluorescence at 410 nm in a methanol-water (1:9) mixture at 30°C. When the fluorescence intensity at 410 nm was monitored, the λ_{max} of the excitation spectrum was observed at 330 nm for **1a-b** and **2**. When the water fraction in a methanol-water mixture increased, the λ_{max} of the excitation spectrum shifted to a shorter wavelength, suggesting that the fluorescence at 410 nm arose from an $n-\pi^*$ excitation of the chromophore. Figure 1 shows the change in fluorescence spectrum of **1b** on the addition of KCl. The fluorescence intensity of the polymers decreased with increasing KCl added. The decrease in the fluorescence intensity of **4** units of the polymers is due to the increase in the intersystem crossing efficiency from the $n-\pi^*$ singlet state to the $\pi-\pi^*$ triplet state by decreasing the electron-donating ability of the crown ether groups as a substituent of the phenyl ring by the binding of cations to the crown ether cavity. Similar findings have been described for acetophenone derivatives having substituents on the phenyl ring [19].

Figure 2 shows the effect of water fraction in a methanol-water mixture on the fluorescence quantum yields (Φ_0) of **1a-b**, **2**, and **3**. **1a** and **3** were insoluble in the solvents at water fractions above 90%. **1b** and **2** were insoluble in the solvents at water fractions below 10%. Although the Φ_0 values increased with water fraction in the mixed solvent, the Φ_0 value for **2** was not as sensitive to the water fraction in the solvent as those for **1a-b** and **3**. The Φ_0 values of **1b**, **2**, and **3** were

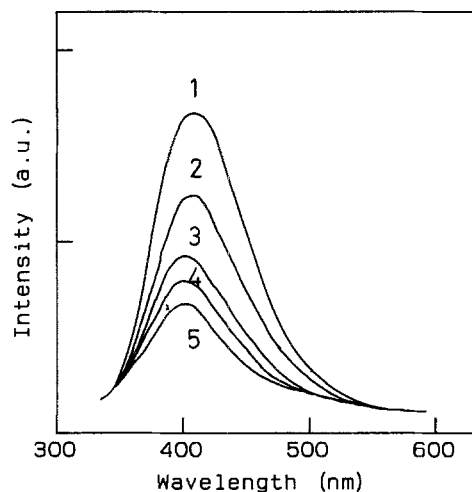


Fig. 1. Changes in the fluorescence spectrum of **1b** on the addition of KCl in a methanol-water (1:9) mixture at 30°C. [Crown units] = 1×10^{-4} mol/L. KCl concentration (mol/L): (1) 0; (2) 5×10^{-5} ; (3) 1×10^{-4} ; (4) 1×10^{-3} ; (5) 2×10^{-3} .

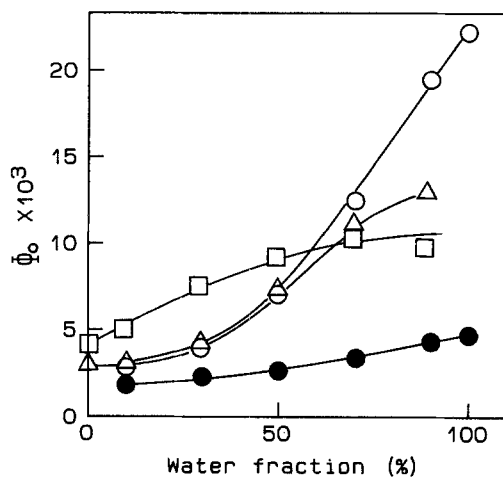


Fig. 2. Effect of the water fraction in a methanol-water mixture on the fluorescence quantum yields (Φ_0) of **1a** (Δ), **1b** (\circ), **2** (\bullet), and **3** (\square) at 30°C. [Crown units] = 1×10^{-4} mol/L.

1.9×10^{-2} , 3.4×10^{-3} , and 8.8×10^{-3} , respectively, in methanol-water (1:9) mixture.

Figure 3 shows the Φ/Φ_0 ratios of **1a**–**b**, **2**, and **3** on the addition of alkali metal chlorides in a methanol-water (1:9) mixture at 30°C, where Φ and Φ_0 are the observed fluorescence quantum yields in the presence and absence of alkali metal chlorides, respectively. The Φ/Φ_0 values for **1b** and **2** decreased in the order $\text{Li}^+ > \text{Na}^+ > \text{Cs}^+ > \text{Rb}^+ > \text{K}^+$. This order was roughly

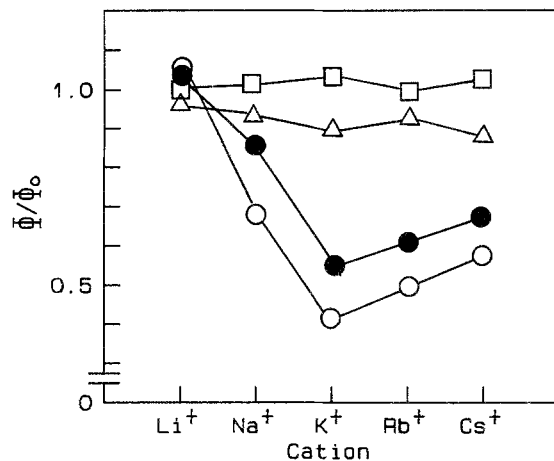


Fig. 3. Effect of alkali metal chlorides on the Φ/Φ_0 ratios of **1a** (Δ), **1b** (\circ), **2** (\bullet), and **3** (\square) in a methanol-water (1:9) mixture at 30°C. [Crown units] = 1×10^{-4} mol/L; [alkali metal chlorides] = 2×10^{-3} mol/L.

consistent with the reverse order of the cation binding ability of benzo-18-crown-6. **1a** and **3** did not show a significant change in Φ/Φ_0 values on the addition of alkali metal chlorides. The Φ/Φ_0 values were employed as a means for evaluating the total number of cation-crown complexes formed in this system. The degree of complex formation depends on both the cation concentration in the neighborhood of the polymer-bound crown ether units and the cation binding ability of the crown ether units. The association constants between crown ethers and cations are quite low in aqueous solutions because of the strong hydration of cations. However, in this system, the neighboring $-\text{COO}^-$ or $-\text{SO}_3^-$ groups in the polymer chain play an important role in increasing concentrations of cations close to the polymer chain by the electrostatic binding. The higher Φ/Φ_0 values for **1a** and **3** than for **1b** and **2** are due to the absence of the concentration effect for cations.

Figure 4 shows the Φ/Φ_0 ratios of **1a**–**b**, **2**, and **3** on the addition of alkali metal chlorides in a methanol-water (9:1) mixture at 30°C. The Φ/Φ_0 values for **1a**–**b** and **2** decreased in the order $\text{Li}^+ > \text{Na}^+ > \text{Rb}^+ > \text{K}^+ \approx \text{Cs}^+$. However, the Φ/Φ_0 values for **3** decreased in the order $\text{Li}^+ > \text{Cs}^+ > \text{Na}^+ > \text{Rb}^+ > \text{K}^+$. The cation binding ability of **3** in a methanol-water (9:1) mixture was much higher than that in methanol-water (1:9) mixture. The Φ/Φ_0 values for both $\text{Cs}^+/\mathbf{1a-b}$ and $\text{Cs}^+/\mathbf{2}$ systems in a methanol-water (9:1) mixture were lower than those in a methanol-water (1:9) mixture. This suggests that Cs^+ can form 1:2 complexes with crown ether moieties of the polymer chain in the methanol-water

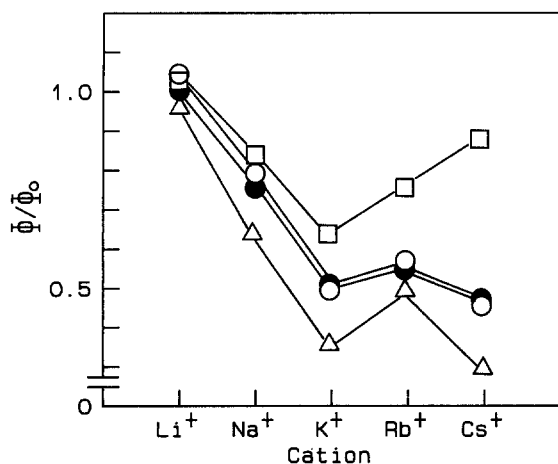


Fig. 4. Effect of alkali metal chlorides on the Φ/Φ_0 ratios of **1a** (Δ), **1b** (\circ), **2** (\bullet), and **3** (\square) in a methanol-water (9:1) mixture at 30°C. [Crown units] = 1×10^{-4} mol/L; [alkali metal chlorides] = 2×10^{-2} mol/L.

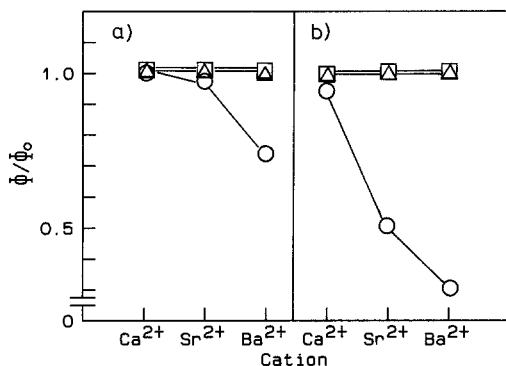


Fig. 5. Effect of alkaline earth metal chlorides on the Φ/Φ_0 ratios of **1a** (Δ), **1b** (\circ), and **3** (\square) in methanol-water (a) 9:1 and (b) 1:9 mixtures at 30°C. [Crown units] = 1×10^{-4} mol/L; [alkaline earth metal chlorides] = 1×10^{-4} mol/L.

(9:1) mixture in which the polymer coils contracted. Alkali metal cations that are too large to fit into the cavities of crown ethers are known to form cation-crown ether (1:2) complexes [1]. It has been reported that poly(vinylbenzo-18-crown-6) strongly binds Cs⁺ because of the formation of stable complexes between Cs⁺ and neighboring two-crown ether moieties [16].

Figure 5 shows the Φ/Φ_0 ratios of **1a**–**b** and **3** on the addition of alkaline earth metal chlorides in methanol-water 9:1 and 1:9 mixtures. Although in a methanol-water (1:9) mixture the Φ/Φ_0 values for **1b** decreased in the order Ca²⁺ > Sr²⁺ > Ba²⁺, in a methanol-water

(9:1) mixture the Φ/Φ_0 values for only, the **1b**/Ba²⁺ system slightly decreased. No significant decrease in the Φ/Φ_0 values for **1a** and **3** was observed on the addition of alkaline earth metal chlorides in both solvents, because **1a** and **3** have no anionic groups. Although the binding ability of 18-crown-6 for alkaline earth metal cations is lower than that for K⁺, Rb⁺, or Cs⁺, the decrease in Φ/Φ_0 values was observed in the methanol-water (1:9) mixture because concentration effect of polyanions for bivalent cations is superior to that for univalent ones.

The binding ability of 18-crown-6 for alkylamine hydrochlorides is very low in aqueous media. However, it was found that in the methanol-water (1:9) mixture, the Φ/Φ_0 values for **1b** and **2** decreased on the addition of alkylamine hydrochlorides such as C₂H₅NH₃Cl, *n*-C₄H₉NH₃Cl, and C₆H₅CH₂NH₃Cl. The concentration effect for the alkylamine hydrochlorides in the neighborhood of the polymer-bound crown ether units by the electrostatic and/or hydrophobic binding induced significant complex formation between alkylamine hydrochlorides and crown ether units, resulting in the decrease in fluorescence intensity.

CONCLUSIONS

The effect of cations on the fluorescence intensity of polymers bearing both anionic groups such as —COO[−] or —SO₃[−] and fluorescent crown ether units was studied in a mixed solvent of methanol and water at 30°C. The enhanced sensitivity of the change in fluorescence intensities toward cations was due to the increased concentration of cations close to the polymer-bound fluorescence crown ethers because of the electrostatic binding of cations by anionic groups of the polymers. The cation binding ability and cation selectivity of the polymers were strongly dependent on the water fraction of a mixed solvent of methanol and water.

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