

# 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

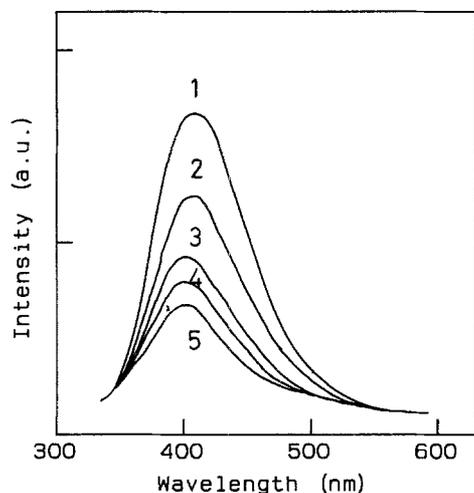
It is well-known that crown ethers bind alkali and alkaline earth metal cations in their cavities. Crown ethers can be used for the spectrophotometric detection of cations by means of ion-pair extractions of complexes between crown ether and a cation with a counter-anion such as picrate [1] and by means 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).

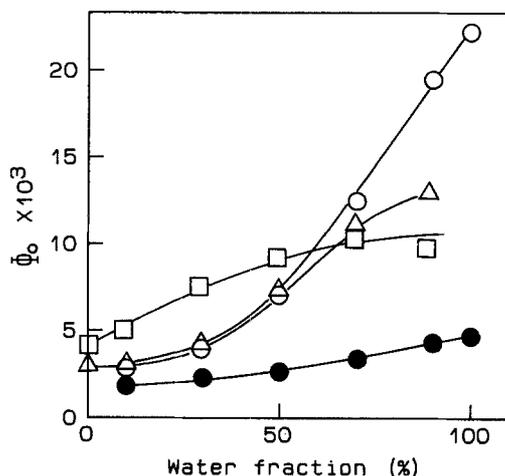
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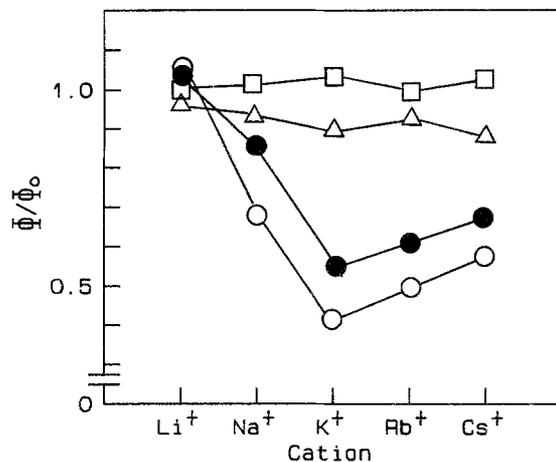
**Fig. 1.** Changes in the fluorescence spectrum of **1b** on the addition of KCl in a methanol-water (1:9) mixture at 30°C. [Crown units] =  $1 \times 10^{-4}$  mol/L. KCl concentration (mol/L): (1) 0; (2)  $5 \times 10^{-5}$ ; (3)  $1 \times 10^{-4}$ ; (4)  $1 \times 10^{-3}$ ; (5)  $2 \times 10^{-3}$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



**Fig. 2.** Effect of the water fraction in a methanol-water mixture on the fluorescence quantum yields ( $\Phi_0$ ) of **1a** ( $\Delta$ ), **1b** ( $\circ$ ), **2** ( $\bullet$ ), and **3** ( $\square$ ) at 30°C. [Crown units] =  $1 \times 10^{-4}$  mol/L.

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

Figure 3 shows the  $\Phi/\Phi_0$  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  $\Phi$  and  $\Phi_0$  are the observed fluorescence quantum yields in the presence and absence of alkali metal chlorides, respectively. The  $\Phi/\Phi_0$  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  $\Phi/\Phi_0$  ratios of **1a** ( $\Delta$ ), **1b** ( $\circ$ ), **2** ( $\bullet$ ), and **3** ( $\square$ ) in a methanol-water (1:9) mixture at 30°C. [Crown units] =  $1 \times 10^{-4}$  mol/L; [alkali metal chlorides] =  $2 \times 10^{-3}$  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  $\Phi/\Phi_0$  values on the addition of alkali metal chlorides. The  $\Phi/\Phi_0$  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  $\Phi/\Phi_0$  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  $\Phi/\Phi_0$  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  $\Phi/\Phi_0$  values for **1a**–**b** and **2** decreased in the order  $\text{Li}^+ > \text{Na}^+ > \text{Rb}^+ > \text{K}^+ \approx \text{Cs}^+$ . However, the  $\Phi/\Phi_0$  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  $\Phi/\Phi_0$  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  $\text{Cs}^+$  can form 1:2 complexes with crown ether moieties of the polymer chain in the methanol-water

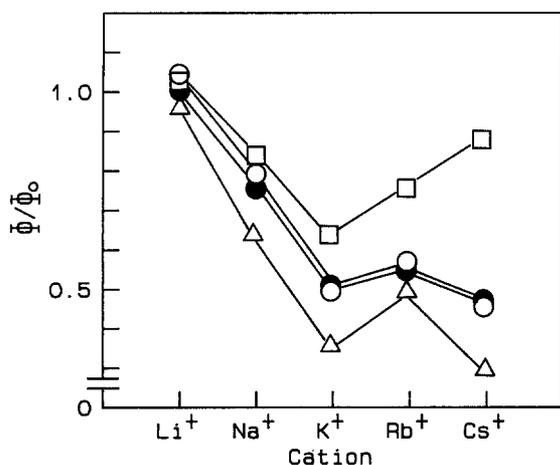


Fig. 4. Effect of alkali metal chlorides on the  $\Phi/\Phi_0$  ratios of **1a** ( $\Delta$ ), **1b** ( $\circ$ ), **2** ( $\bullet$ ), and **3** ( $\square$ ) in a methanol-water (9:1) mixture at 30°C. [Crown units] =  $1 \times 10^{-4}$  mol/L; [alkali metal chlorides] =  $2 \times 10^{-2}$  mol/L.

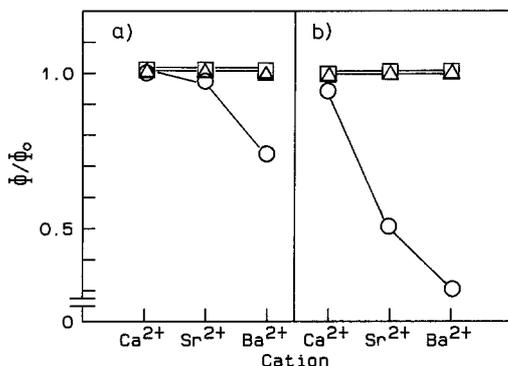


Fig. 5. Effect of alkaline earth metal chlorides on the  $\Phi/\Phi_0$  ratios of **1a** ( $\Delta$ ), **1b** ( $\circ$ ), and **3** ( $\square$ ) in methanol-water (a) 9:1 and (b) 1:9 mixtures at 30°C. [Crown units] =  $1 \times 10^{-4}$  mol/L; [alkaline earth metal chlorides] =  $1 \times 10^{-4}$  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  $\text{Cs}^+$  because of the formation of stable complexes between  $\text{Cs}^+$  and neighboring two-crown ether moieties [16].

Figure 5 shows the  $\Phi/\Phi_0$  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  $\Phi/\Phi_0$  values for **1b** decreased in the order  $\text{Ca}^{2+} > \text{Sr}^{2+} > \text{Ba}^{2+}$ , in a methanol-water

(9:1) mixture the  $\Phi/\Phi_0$  values for only, the **1b**/ $\text{Ba}^{2+}$  system slightly decreased. No significant decrease in the  $\Phi/\Phi_0$  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  $\text{K}^+$ ,  $\text{Rb}^+$ , or  $\text{Cs}^+$ , the decrease in  $\Phi/\Phi_0$  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  $\Phi/\Phi_0$  values for **1b** and **2** decreased on the addition of alkylamine hydrochlorides such as  $\text{C}_2\text{H}_5\text{NH}_3\text{Cl}$ ,  $n\text{-C}_4\text{H}_9\text{NH}_3\text{Cl}$ , and  $\text{C}_6\text{H}_5\text{CH}_2\text{NH}_3\text{Cl}$ . 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  $\text{—COO}^-$  or  $\text{—SO}_3^-$  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.

## REFERENCES

1. F. Vögtle and E. Weber (1984) *Host-Guest Complex Chemistry III*, Springer Verlag, Berlin.
2. K. Nakashima, S. Nakatsuji, S. Akiyama, I. Tanigawa, T. Kameda, and S. Misumi (1984) *Talanta* **31**, 749–751.
3. H. G. Lohr and F. Vögtle (1985) *Acc. Chem. Res.* **18**, 65–72.
4. L. R. Sousa and J. M. Larson (1977) *J. Am. Chem. Soc.* **99**, 307–310.
5. J. M. Larson and L. R. Sousa (1978) *J. Am. Chem. Soc.* **100**, 1943–1944.
6. H. Shizuka, T. Takada, and T. Morita (1980) *J. Phys. Chem.* **84**, 994–999.

7. O. S. Wolfbeis and H. Offenbacher (1984) *Monatsh. Chem.* **115**, 647–654.
8. A. P. Silva and S. A. Silva (1986) *J. Chem. Soc. Chem. Commun.* 1709–1710.
9. J. P. Konopelski, F. Kotzba-Hibert, J. M. Lehn, J. P. Desvergne, F. Fages, A. Castettan, and H. Bouas-Laurent (1985) *J. Chem. Soc. Chem. Commun.* 433–436.
10. B. Alpha, J. M. Lehn, and G. Mathis (1987) *Angew. Chem. Int. Ed. Engl.* **26**, 266–267.
11. K. Hirata (1987) *J. Chem. Soc. Chem. Commun.* 960–961.
12. M. Shirai, S. Morimoto, and M. Tanaka (1990) *J. Chem. Soc. Perkin Trans. 2*, 1187–1190.
13. M. Shirai, S. Ishimaru, and M. Tsunooka (1991) *Macromolecules* **24**, 1690–1691.
14. M. Shirai, S. Ishimaru, and M. Tsunooka (1991) *Makromol. Chem.* **192**, 3063–3069.
15. J. Brandrup and E. H. Immergut (1975) *Polymer Handbook*, 3rd ed., John Wiley and Sons, New York, p. VII-10.
16. S. Kopolow, T. E. Hogen-Esch, and J. Smid (1973) *Macromolecules* **6**, 133–142.
17. J. N. Demas and G. A. Crosby (1971) *J. Phys. Chem.* **75**, 991–1024.
18. C. J. Pedersen (1967) *J. Am. Chem. Soc.* **89**, 7017–7036.
19. N. J. Turro (1978) *Modern Molecular Photochemistry*, Benjamin/Cummings, Menlo Park, CA, pp. 362–412.