

Cation-Sensitive Fluorescence of Anionic Polymers Bearing Naphtho-18-Crown-6 Units

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Changes in the fluorescence intensity of anionic polymers bearing naphtho-18-crown-6 moieties on addition of cations were studied in water at 30 °C. On addition of alkali metal cations, the fluorescence intensity of the polymers decreased sharply for Tl⁺, less for Cs⁺ and little for Li⁺, K⁺ and Rb⁺. On addition of alkaline earth metal cations, Ba²⁺ caused the strongest decrease of the fluorescence intensity of the polymers. The decrease of the fluorescence intensity of the polymers was suggested to be caused by the external heavy-atom effect of the cations bound to the cavity of the crowned naphthalene moiety. The content of the crowned naphthalene units in the polymers affected the cation-dependent fluorescence change. The fluorescence change of the polymers based on the cation complexation competition was also studied.

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

INTRODUCTION

Crown ethers are known to bind cations in their cavities.⁽¹⁾ They 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⁽²⁾ and by means of chromogenic crown ethers.^(3,4) The absorption spectrum of the chromogenic reagents, which have both chromophoric and crown ether moieties in a molecule, can change remarkably in response to cations. Fluorimetry can, in principle, be more sensitive than absorption photometry. Crown ethers,⁽⁵⁻⁹⁾ cryptands^(10,11) and podands⁽¹²⁾ which have fluorescent moieties were synthesized, and the effect of the binding of alkali metal and alkaline earth metal cations on the fluorescence and/or phosphorescence properties of the ionophores was studied. In a recent communication,⁽¹³⁾ we have reported the preliminary results concerning the cation-sensitive fluorescence of the anionic polymers bearing crowned naphthalene

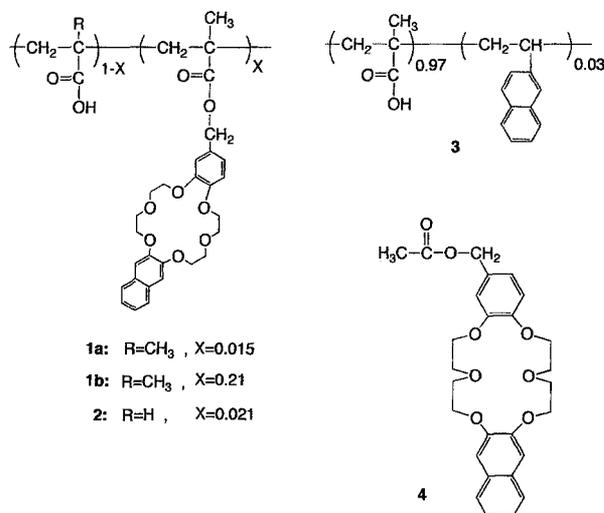
moieties. In this paper we fully report the fluorescence properties of the polymers, effect of cations on the emission properties, and cation sensing using cation complexation competition. The polymers are interesting as fluorescent chemosensors for ion recognition. Although the cation binding ability of crown ethers is very low in aqueous media, it can be largely enhanced by anchoring the crown ether units into the backbone of anionic polymers, because the anionic group -COO⁻ in the polymer chain increases the concentration of cations close to the polymer-bound crown ethers.^(14,15)

EXPERIMENTAL

Materials

Syntheses of the monomer 2,3-(4'-methacryloyloxymethylbenzo)-11,12-naphtho-1,4,7,10,13,16-hexaoxacyclooctadeca-2,11-diene and 2,3-(4'-acetoxymethylbenzo)-11,12-naphtho-1,4,7,10,13,16-hexaoxacyclooctadeca-2,11-diene (4) were reported elsewhere.⁽¹³⁾

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Methacrylic acid and acrylic acid were of reagent grade and used after distillation. Alkali metal chlorides, alkaline earth metal chlorides and alkylamine hydrochlorides were used as purchased. TiCl₃ was converted to TiClO₄ by recrystallizing several times in HClO₄ aqueous solution (60%) and then in water until there were no indications of acid or Cl⁻ impurity. Polymers **1a-b**, **2**, and **3** were prepared by the radical copolymerization of corresponding monomers in *N,N*-dimethylformamide using azobis(isobutyronitrile) at 55 °C. Detailed polymerization conditions were reported in a previous paper.⁽¹³⁾ Polymers were purified by dissolving in a methanol-1,4-dioxane mixture and precipitating with diethyl ether. The content of crowned naphthalene units in the polymers was determined by measuring the absorbance at 322 nm in methanol-1,4-dioxane (1:1, v/v) mixture. The molar extinction coefficient of the crowned naphthalene units in the polymers was estimated to be equal to that of the model compound **4**, ϵ being 3.77×10^3 L mol⁻¹·cm⁻¹ at 322 nm. The contents of crowned naphthalene units in **1a**, **1b** and **2** were found to be 0.015, 0.21, and 0.021, respectively. The content of naphthalene units in the polymer **3** was found to be 0.03, which was determined by measuring absorbance at 320 nm. The molar extinction coefficient of naphthalene was used to calculate the naphthalene content in **3**.

Measurements

The polymers were neutralized with LiOH and used for the measurements of the fluorescence spectrum. The fluorescence spectrum was measured in water at 30 °C in air with a Shimadzu RF-500 spectrofluorophotometer. The excitation and emission slit widths were 10 and 5

nm, respectively. The wavelength of the excitation light was 285 nm. The quantum yields of fluorescence were determined by comparison of the intensities of the fluorescence of the polymers with that of quinine sulfate.⁽¹⁶⁾

RESULTS AND DISCUSSION

Fluorescence spectra of the free ligands

The polymers **1a**, **1b**, and **2** showed absorption peaks at 280, 310, and 323 nm in water. The absorption spectrum was very much similar to that of **4** and to the sum of the absorption spectra of 2,3-naphtho-18-crown-6 and of 3,4-dimethoxytoluene. Poly(methacrylic acid) and its alkali metal salts did not show significant peaks at wavelength longer than 250 nm. Thus, the absorption peaks of the polymers are due to the naphthocrown moiety. On addition of alkali and alkaline earth metal cations, the changes in absorption spectra of the polymers were too small to use as a means for detecting cations. On excitation with 285 nm light, **1a**, **1b**, and **2** showed the fluorescence at 315–440 nm in water. When the fluorescence intensity at 400 nm was monitored, the peaks of the excitation spectrum was observed at 323 and 285 nm. This suggested that the fluorescence was originated from the naphthocrown moiety. The slight shift (~5 nm) of the fluorescence peak from **1b** to longer wavelength may be due to the excimer formation of some naphthalene moieties. When excited at 285 nm, fluorescence quantum yields (Φ) of **1a**, **1b** and **2** were found to be 0.058, 0.027, and 0.037, respectively. The Φ value changed with the excitation wavelength.

Fluorescence in the presence of univalent cations

Figure 1 shows the changes in fluorescence spectra of **2** on addition of thallium chloride (TlCl) in water. The fluorescence intensity simply decreased with increasing TlCl concentration. The fluorescence intensity of **2** in the presence of TlCl ($[\text{TlCl}]/[\text{crown units}] = 5$) was 1/10 of the fluorescence intensity in the absence of TlCl. The I/I_0 ratio for **2** on addition of alkali metal chlorides was shown in Figure 2, where I and I_0 are the fluorescence intensity in the presence and absence of salts, respectively. The I/I_0 values decreased with increasing cations added. If compared at the same cation-crown unit ratio, the I/I_0 values decreased in the order $\text{Tl}^+ \gg \text{Cs}^+ > \text{Rb}^+ \sim \text{K}^+ \sim \text{Na}^+ \sim \text{Li}^+$. The same order was observed for **1a**. This order was not consistent with the order of the cation binding ability of 18-crown-6 or dibenzo-18-crown-6. The binding abilities of 18-crown-

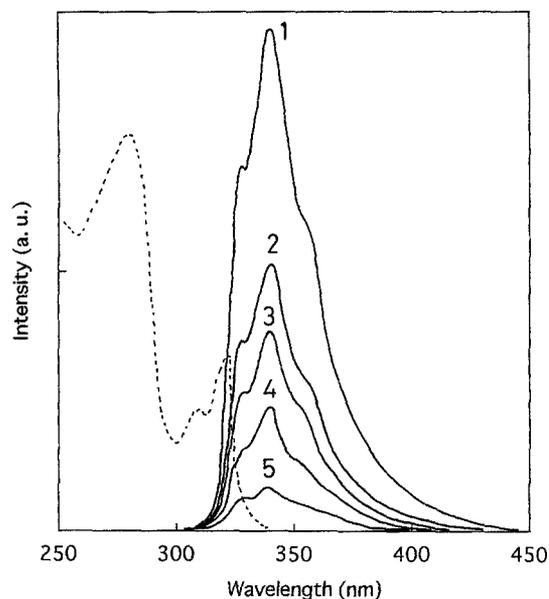


Fig. 1. Changes in fluorescence spectra of **2** on addition of thallium chloride (TlCl). The dotted line shows absorption spectrum of **2**. [Crown units] = 1×10^{-4} mol/L. Concentrations of TlCl in mol/L: (1) 0; (2) 5×10^{-5} ; (3) 1×10^{-4} ; (4) 2×10^{-4} ; (5) 5×10^{-4} .

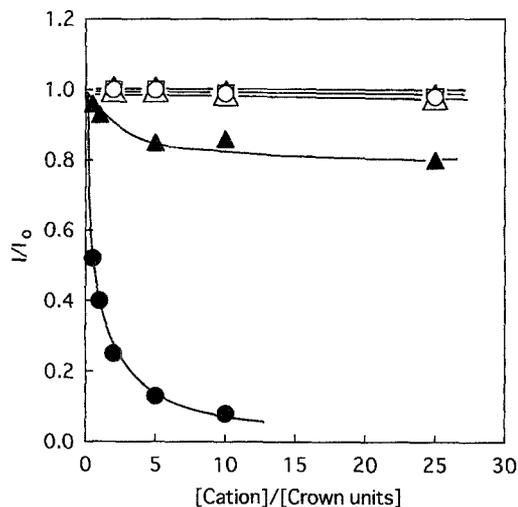


Fig. 2. Effect of alkali metal chlorides on the fluorescence intensity of **2** in water at 30 °C. I and I_0 are the fluorescence intensities in the presence and absence of salts, respectively. [Crown units] = 1×10^{-4} mol/L. Salts added: (○) NaCl; (△) KCl; (□) RbCl; (▲) CsCl; (●) TlCl.

6 and dibenzo-18-crown-6 for univalent cations were reported to decrease in the order $Tl^+ \sim K^+ > Rb^+ > Cs^+ > Na^+ > Li^{+(17)}$ and $K^+ > Tl^+ > Na^+ \sim Rb^+ > Cs^+ > Li^{+(18)}$ respectively. The liquid-liquid extraction of alkali metal picrates by the model compound **4** was carried out at 25°C to check the cation selectivity. A chloroform

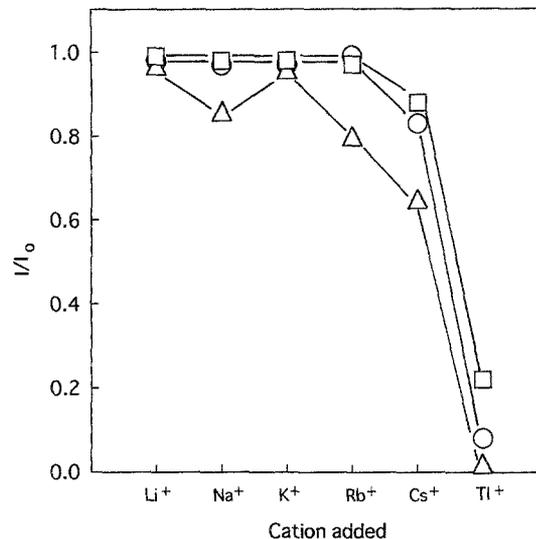


Fig. 3. I/I_0 values for **1a** (□), **1b** (△), and **2** (○) in the presence of salts. The anion of the salts was Cl^- . [Crown units] = 1×10^{-4} mol/L. [Cation]/[Crown units] = 10.

solution of **4** (5×10^{-4} mol/L) was mixed with an equal volume of an aqueous picric acid solution (6×10^{-5} mol/L) containing LiOH (1×10^{-2} mol/L) and metal chlorides (5×10^{-2} mol/L). After efficient agitation, the concentration of picrate in the aqueous phase was determined spectrophotometrically. The fraction of picrate salts extracted decreased in the order $K^+ > Rb^+ > Cs^+ > Na^+ > Li^+$. Tl^+ could not be checked because of the low solubility of thallium chloride in water. The fraction of Cs^+ picrate extracted was 1/5 of that of K^+ picrate. The magnitude of decrease in fluorescence intensity of **1a** was 15% on addition of CsCl ([CsCl]/[crown units] = 10). However, on addition of LiCl, NaCl, KCl or RbCl ([salt]/[crown units] = 10), the magnitude of decrease in fluorescence intensity was below 3%. This finding suggests that the decrease in fluorescence intensity of the polymers on addition of salts is due to the external heavy-atom effect of cations bound to the crown ether cavity. In Figure 3 the I/I_0 values for **1a**, **1b**, and **2** in the presence of salts ([cation]/[crown units] = 10) were shown. No significant differences in I/I_0 values for **1a** and **2** were observed in the presence of univalent cations, except Tl^+ . The I/I_0 values for Cs^+ - and Rb^+ -**1b** systems were found to be lower than those for Cs^+ - and Rb^+ -**1a** systems. Since the content of the crowned naphthalene units in **1b** was 14 times as high as that of **1a**, effective binding of Cs^+ and Rb^+ by **1b** is assumed to occur by a cooperative action of neighboring crown units as has been reported for the binding of large cations to poly(crown ethers).⁽¹⁹⁾

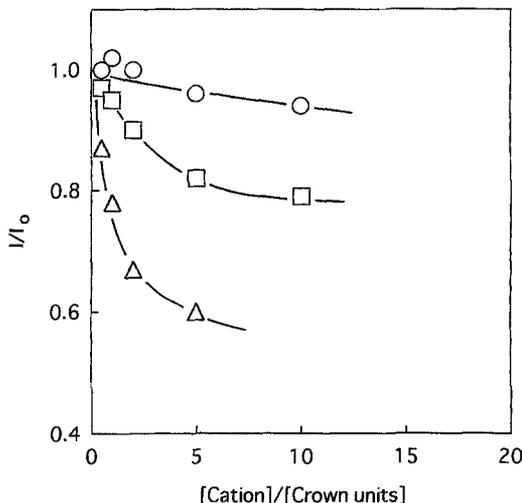


Fig. 4. Effect of alkaline earth metal chlorides on the fluorescence intensity of **2** in water at 30 °C. [Crown units] = 1×10^{-4} mol/L. Salts added: (○) CaCl_2 ; (□) SrCl_2 ; (△) BaCl_2 .

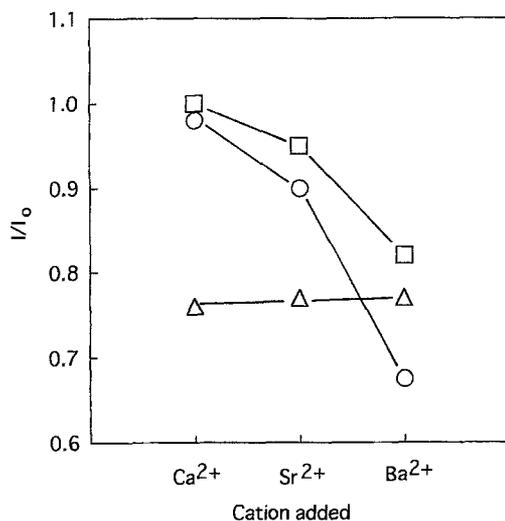


Fig. 5. I/I_0 values of **1a** (□), **1b** (△), and **2** (○) in the presence of alkaline earth metal chlorides. [Crown units] = 1×10^{-4} mol/L. [Cation]/[Crown units] = 2.

Fluorescence in the presence of divalent cations

The effect of alkaline earth metal salts on the I/I_0 value of **2** was studied. As shown in Figure 4 the I/I_0 values decreased with increasing the concentration of salts added and the magnitude increased in the order $\text{Ca}^{2+} < \text{Sr}^{2+} < \text{Ba}^{2+}$. Figure 5 shows the I/I_0 values for **1a**, **1b**, and **2** in the presence of alkaline earth metal cations ([cation]/[crown units] = 2). Although the I/I_0 values for **1a** and **2** decreased in the order $\text{Ba}^{2+} > \text{Sr}^{2+}$

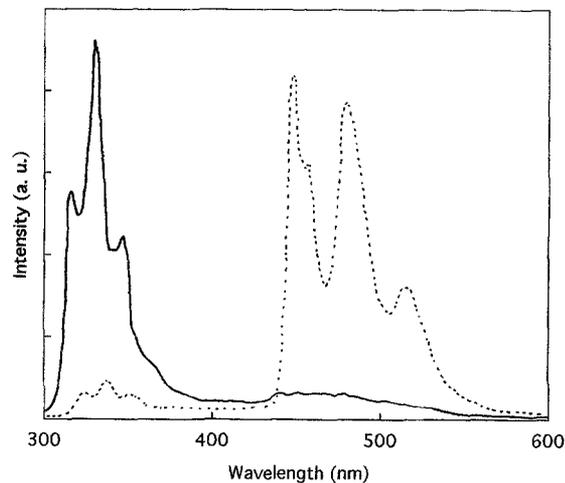


Fig. 6. Emission spectra of **4** in ethanol-methanol (4:1, v/v) mixture glasses at 77 K in the absence (solid line) and presence (dotted line) of TiClO_4 . $[\mathbf{4}] = 1.23 \times 10^{-4}$ mol/L, $[\text{TiClO}_4]/[\mathbf{4}] = 5.7$.

$> \text{Ca}^{2+}$, the I/I_0 values of **1b** were 0.75–0.78 in the presence of Ca^{2+} , Sr^{2+} , and Ba^{2+} . No cation selectivity was observed. The contraction of the polymer coil in water on addition of divalent cations may induce an aggregation of the hydrophobic crowned naphthalene units in the polymer. The aggregation of the crowned naphthalene units in polymer gives low I/I_0 values because of self quenching. **1b** was precipitated on addition of divalent cations at $[\text{cation}]/[\text{COO}^-] > 2$. For **1b**-alkaline earth metal cation system the binding of cations to the cavity of the crowned naphthalene units was not important for the decrease of I/I_0 values. Thus the fraction of the crowned naphthalene units in the polymer was an important factor for the fluorescent chemosensor showing high cation selectivity.

Heavy-atom effect and phosphorescence

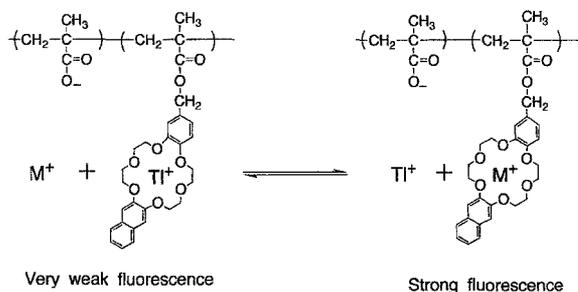
When the model compound **4** was excited with 285 nm light, emission was observed at 310–550 nm in uncracked ethanol-methanol (4:1, v/v) glasses at 77 K in vacuo (Figure 6). The emission at 310–380 nm is fluorescence. The emission spectrum at 435–550 nm was the same as the phosphorescence spectrum observed for 2,3-naphtho-18-crown-6 (life time $\tau_p = 3.8$ sec) at the same conditions. Thus this emission was confirmed to be the phosphorescence from the naphthocrown moiety of **4**. The phosphorescence excitation spectrum monitored at 480 nm was the same as the fluorescence excitation spectrum monitored at 350 nm. This means that the phosphorescence occurred from the naphthocrown moiety excited directly. As shown in Figure 6, addition of

Table I. Changes of phosphorescence intensity of **4** on addition of cations^a

Cation	Li ⁺	Na ⁺	K ⁺	Rb ⁺	Cs ⁺	Tl ⁺	Ca ²⁺	Sr ²⁺	Ba ²⁺
[cation]/[4]	5.12	5.48	5.58	5.48	5.49	5.70	2.14	2.16	2.19
P/P ₀	1.05	1.05	1.10	1.58	3.06	15.4	1.15	1.31	1.80

^aIn ethanol-methanol (4:1, v/v) glasses at 77K. [**4**] = 1.23×10^{-4} mol/L. P and P₀ are the phosphorescence intensity in the presence and absence of cations, respectively.

Tl⁺ caused a large decrease of the fluorescence intensity and a large increase in the phosphorescence. Effect of cations on the phosphorescence intensity of **4** is shown in Table 1. Heavy metal cations such as Tl⁺, Cs⁺, Rb⁺ and Ba²⁺ strongly enhanced the phosphorescence intensity of **4**. Thus the strong decrease in fluorescence intensity of **1a** and **2** on addition of cations such as Tl⁺, Cs⁺, or Ba²⁺ is due to the external heavy-atom effect which enhances the S₁-T₁ intersystem crossing efficiency, decreasing the fluorescence intensity. Sousa et al.^(5,6) have suggested the heavy-atom effect on the fluorescence decrease of naphthocrown ethers. Thus the observed decrease in the fluorescence intensity of **1a** and **2** can be governed by both the cation binding ability of crowned naphthalene units and the magnitude of the heavy-atom effect of cations bound to the crown ether cavity.



Sousa and coworkers have synthesized several crown ether compounds designed to signal the presence of alkali metal cations by showing enhanced fluorescence intensity. A scheme involved the displacement by a potassium ion of a quencher such as Cs⁺ complexed by a fluorescent crown ether.⁽²⁰⁾

In the present system the naphthocrown units complexed with Tl⁺ did not show significant fluorescence. When cations which can be bound to the crown ether cavity were added to the Tl⁺-crown complexes, Tl⁺ can be displaced by the cations added, resulting in the increase of the fluorescence intensity. The enhanced fluorescence responding to cations will be favored for practical applications. Effect of alkali metal chlorides on

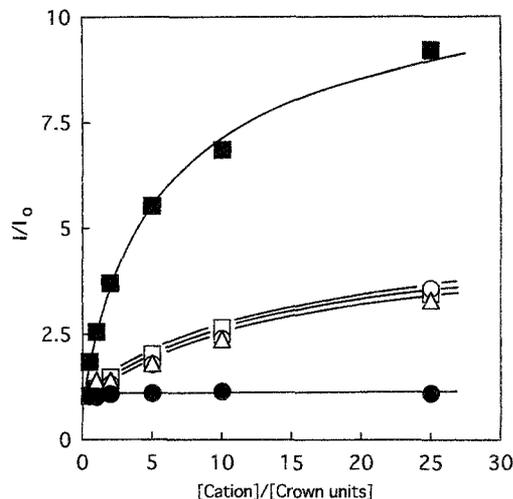


Fig. 7. Effect of alkali metal chlorides on the fluorescence intensity of **2** solution containing TlCl. [Crown units] = 0.99×10^{-4} mol/L, [TlCl]/[Crown units] = 0.5. Salts added: (●) LiCl; (△) NaCl; (■) KCl; (○) RbCl; (□) CsCl

the I/I_0 values of an aqueous solution of **2** containing TlCl ([TlCl]/[crown units] = 0.5) was shown in Figure 7. The I/I_0 values were observed to increase with salts added. The magnitude of the enhanced fluorescence increased in the order LiCl < NaCl ~ RbCl ~ CsCl < KCl. This order was roughly consistent with the order of the cation binding ability of 18-crown-6. K⁺ which can be strongly bound to crown ether units remarkably enhanced the fluorescence intensity. Rb⁺ and Cs⁺ which can be expected to be bound to 18-crown-6 or dibenzo-18-crown-6 more strongly than Na⁺ showed the same I/I_0 value as that of Na⁺. Although the displacement of Tl⁺ by Rb⁺ or Cs⁺ can occur more easily than by Na⁺, the external heavy-atom effect of Cs⁺ or Rb⁺ bound to the crown ether cavity may reduce the I/I_0 values.

Figure 8 shows the effect of alkaline earth metal chlorides on the fluorescence intensity of **2** solution containing TlCl. The I/I_0 values increased in the order Ca²⁺ < Sr²⁺ < Ba²⁺. This order was consistent with the order of the binding ability of alkaline earth metal cations to 18-crown-6 and dibenzo-18-crown-6. The I/I_0 value at cation/crown ratio of 5 was 3.1 which was smaller than that expected from the binding ability of Ba²⁺ to dibenzo-18-crown-6. This may be due to the external heavy-atom effect of Ba²⁺ bound to naphthocrown moiety.

The effect of alkylamine hydrochlorides on the fluorescence intensity of **2** solution containing TlCl was also studied. The I/I_0 values increased with increasing alkylamine hydrochlorides added as shown in Figure 9.

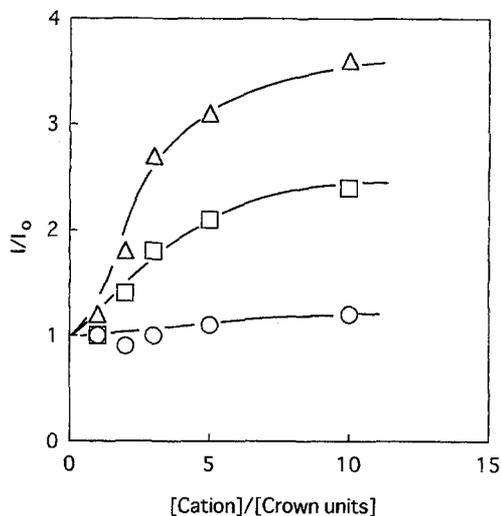


Fig. 8. Effect of alkaline earth metal chlorides on the fluorescence intensity of **2** solution containing TlCl. [Crown units] = 1×10^{-4} mol/L, [TlCl]/[Crown units] = 0.5. Salts added: (○) CaCl₂; (□) SrCl₂; (△) BaCl₂.

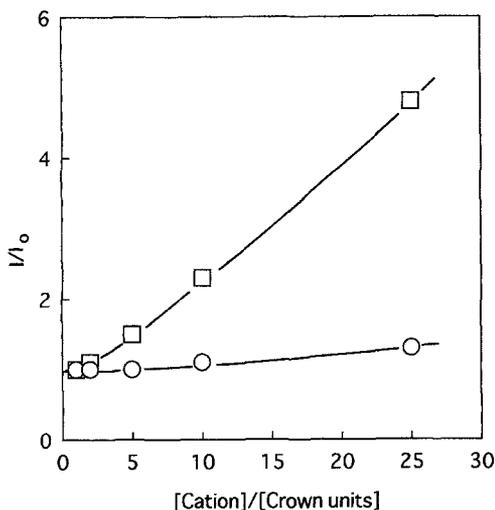


Fig. 9. Effect of alkylamine hydrochlorides on the fluorescence intensity of **2** solution containing TlCl. [Crown units] = 1×10^{-4} mol/L, [TlCl]/[Crown units] = 0.5. Ammonium salts: (○) CH₃CH₂NH₃Cl; (□) C₆H₅CH₂NH₃Cl

The increase of I/I_0 values for benzylamine hydrochloride was higher than that for ethylamine hydrochloride. The anionic groups $-\text{COO}^-$ in the polymer chain increase the concentration of cations close to the polymer-bound crown ether units. Furthermore, benzylamine hydrochloride which has hydrophobic phenyl moieties may be strongly bound to naphthocrown units by the hydrophobic bond which was reported to play an im-

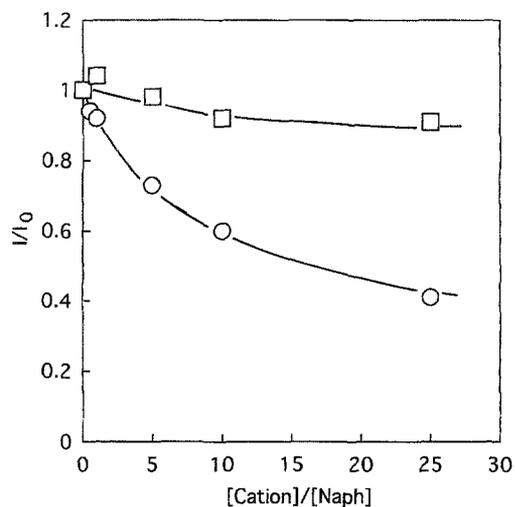


Fig. 10. Effect of KCl (□) and CsCl (○) on the fluorescence intensity of **3** solution containing TlCl. [Naphthyl units] = 7×10^{-3} mol/L, [TlCl]/[Naphthyl units] = 2.

portant role for the binding of alkylammonium salts to polyanions bearing crown ether moieties.⁽²¹⁾

To check the indispensability of crown ether moiety in the present system, effect of cations on the fluorescence properties of the copolymer (**3**) of methacrylic acid and 2-vinylnaphthalene was studied. As observed for **1a-b** and **2**, on addition of alkali metal cations the intensity of the fluorescence from **3** decreased in the order $\text{Tl}^+ \gg \text{Cs}^+ > \text{Rb}^+ \sim \text{K}^+ \sim \text{Li}^+$. However, the increase in the I/I_0 values for aqueous solution of **3** containing TlCl ([TlCl]/[naphthyl units] = 2) was not observed when K^+ or Cs^+ was added. As shown in Figure 10, addition of K^+ or Cs^+ caused further decrease of the fluorescence intensity of the system. This was quite different from the fact observed for **1a-b** and **2**. The decrease of the fluorescence intensity from **3** on addition of cations may be caused by the external heavy-atom effect of cations added and/or by the self quenching of the excited naphthalene moiety due to aggregation of the chromophore in the polymer chain. The aggregation can be induced by the contraction of polymer coil when cations were added.

CONCLUSIONS

The fluorescence properties of the anionic polymers which have naphtho-18-crown-6 moieties were studied in water at 30 °C. The polymers showed a fluorescence peak around 340 nm. When Tl^+ , Cs^+ , or Ba^{2+} was added to the aqueous solution of the polymers, the fluorescence

intensity largely decreased. It was suggested that the decrease of the fluorescence intensity of the polymers was caused by the external heavy-atom effect of the cations bound to the cavity of the naphthocrown moieties. A system which shows the increase of the fluorescence intensity on addition of cations was devised using a cation complexation competition method. The crown ether moiety in the polymers was indispensable for the system.

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