

Ternary inclusion complexes of γ -cyclodextrin with sodium 1-pyrenesulfonate and cationic and anionic organic compounds having an alkyl chain in aqueous solution

Sanyo Hamai

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Abstract The interactions of an organic anion, 1-pyrenesulfonate (PS), with γ -cyclodextrin (γ -CD) and organic cations such as quaternary ammonium compounds (or organic anions such as 1-decanesulfonate) have been examined by means of absorption and fluorescence spectroscopy. At a low concentration of PS, γ -CD forms a 1:1 inclusion complex with PS. PS forms organic cation–organic anion complexes with quaternary ammonium compounds. The organic cation–organic anion complexes of PS form ternary inclusion complexes with γ -CD. Equilibrium constants for the formation of these complexes have been evaluated from the fluorescence intensity change. As an alkyl chain in the quaternary ammonium compound is lengthened, the equilibrium constant for the formation of the ternary inclusion complex is increased. Although PS does not form complexes with organic anions such as 1-decanesulfonate, the organic anions are bound to the γ -CD cavity accommodating a PS molecule to form ternary inclusion complexes. However, the equilibrium constants for the organic anions (1-decanesulfonate etc.) are significantly less than those for the quaternary ammonium compounds. The small equilibrium constants for the organic anions can be ascribed to the electrostatic repulsion between PS and the organic anions.

Keywords γ -Cyclodextrin · Sodium 1-pyrenesulfonate · Quaternary ammonium compounds · Alkylsulfonates · Absorption spectra · Fluorescence spectra

Introduction

Cyclodextrins (CDs) are cyclic oligosaccharides, which are composed of D-glucopyranose residues [1, 2]. CDs, which have six, seven, and eight D-glucopyranose residues, are called α -CD, β -CD, and γ -CD, respectively. Because CDs have a relatively hydrophobic cavity, an organic molecule of appropriate dimensions is bound to the CD cavity to form an inclusion complex [1, 2].

The interactions of β - and γ -CD with pyrene have been extensively studied [3–9]. β -CD forms a ternary inclusion complex with pyrene and alcohol [6, 8, 10, 11]. In the ternary inclusion complex, an alkyl group of alcohol is most likely bound to the β -CD cavity accommodating a pyrene molecule. In γ -CD solution, pyrene exhibits the excimer fluorescence, which is due to the 2:2 γ -CD–pyrene inclusion complex. There are several studies on the excimer fluorescence of pyrene derivatives as well as that of pyrene in γ -CD solution. Herkstroeter et al. have found that sodium 1-pyrenebutyrate exhibits the excimer fluorescence in γ -CD solution [12, 13]. They have suggested that the excimer fluorescence is due to a 2:2 γ -CD-1-pyrenebutyrate inclusion complex of a barrel type. The interactions of CD with sodium 1-pyrenesulfonate (PS) have also been examined [14, 15]. Harada and Nozakura have found that the excimer fluorescence is observed for PS in γ -CD solution [16]. PS is less hydrophobic than pyrene because of the substitution of a sulfonate group. Consequently, the interactions of CD with PS would be weaker than those with pyrene.

It has been reported that an organic cation forms a complex with an organic anion [17, 18]. Through a series of studies on the interactions of CD with two kinds of guest molecules, we have been interested in the formation and properties of ternary inclusion complexes among CD, an

S. Hamai (✉)
Department of Chemistry, Faculty of Education and Human
Studies, Akita University, 1-1 Tegata Gakuen-machi,
Akita 010-8502, Japan
e-mail: hamai@ipc.akita-u.ac.jp

organic cation, and an organic anion [19]. We have examined the interactions of CD with organic cation–organic anion complexes, whose two components have an aromatic ring(s); the thionine-2-naphthalenesulfonate complex [20a], the Methylene Blue–acid orange 7 complex [20b], the Methylene Blue– α -naphthol orange complex [20c], the resorufin–1,1'-diheptyl-4,4'-bipyridyl dibromide complex [20d], and the tetrakis(4-*N*-methylpyridyl)porphyrin–disodium phthalate complex [20e].

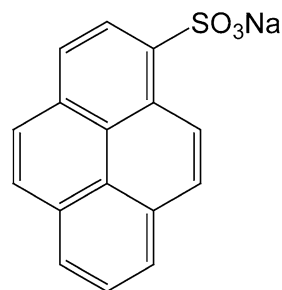
In the formation of a ternary inclusion complex of a guest having an alkyl chain, an alkyl chain is expected to be bound to the CD cavity, because an alkyl chain is hydrophobic. From capillary electrophoretic studies, it has been suggested that γ -CD forms a ternary inclusion complex with a complex of tetrakis(4-sulfonatophenyl)porphyrin (TSPP)–trimethyloctylammonium (TMOA) cation, which has a long alkyl-chain [20f]. Because TSPP is a large molecule, only a sulfonatophenyl moiety is bound to the γ -CD cavity; most part of a TSPP molecule resides outside the γ -CD cavity. Consequently, TSPP may interact with TMOA outside the γ -CD cavity. The equilibrium constant for the formation of the ternary inclusion complex of γ -CD–resorufin–1,1'-diheptyl-4,4'-bipyridyl dibromide from γ -CD and the resorufin–1,1'-diheptyl-4,4'-bipyridyl dibromide complex is $1,340 \text{ mol}^{-1} \text{ dm}^3$, which is significantly greater than that ($40.9 \text{ mol}^{-1} \text{ dm}^3$) of the ternary inclusion complex of γ -CD–resorufin–1,1'-dimethyl-4,4'-bipyridyl dibromide [20d]. The large difference in the equilibrium constant between the ternary inclusion complexes containing 1,1'-diheptyl-4,4'-bipyridyl dibromide and 1,1'-dimethyl-4,4'-bipyridyl dibromide has been explained by the incorporation of a heptyl chain of 1,1'-diheptyl-4,4'-bipyridyl dibromide into the γ -CD cavity simultaneously accommodating a resorufin molecule.

1,1'-Diheptyl-4,4'-bipyridyl dibromide (1,1'-dimethyl-4,4'-bipyridyl dibromide) has both an aromatic ring and an alkyl chain. To clarify the interactions between an alkyl chain and a guest ion within the CD cavity, it is preferable to use an organic ion having an alkyl chain alone. In addition, the guest ion, whose most part is incorporated into the γ -CD cavity, is suitable for the examination of the interactions between the alkyl chain and the guest ion within the γ -CD cavity as well as the electrostatic interactions between an organic cation and an organic anion. Thus, we have selected quaternary ammonium compounds and 1-pyrenesulfonate (PS) as organic cations and an organic anion, respectively; quaternary ammonium cations do not have an aromatic moiety but a long alkyl-chain, whereas PS has an aromatic moiety which is expected to be buried deeply into the γ -CD cavity. In this study, we aimed to investigate the interactions between an alkyl chain and a PS anion within the γ -CD cavity. In addition, alkylsulfonates and an alkylsulfate, which are organic anions having a long alkyl-chain, have been used to examine the

interactions with a PS anion within the γ -CD cavity. In the presence of γ -CD, we have also examined the electrostatic interactions between two kinds of organic ions with the same or opposite charges.

Experimental

Sodium 1-pyrenesulfonate (PS) was purchased from Molecular Probes, Inc. and used as received.



Sodium 1-pyrenesulfonate (PS)

γ -Cyclodextrin (γ -CD), which was obtained from Wako Pure Chemical Industries, Ltd., was used without further purification. Trimethyloctylammonium bromide (TMOA), decyltrimethylammonium bromide (DeTMA), dodecyltrimethylammonium chloride (DoTMA), benzyltrimethylammonium chloride (BTMA), sodium 1-decanesulfonate (SDeS), sodium 1-undecanesulfonate (SUnS), and tetramethylammonium chloride (TeMA), which were purchased from Tokyo Chemical Industries Co., Ltd., were used as received. Sodium 1-dodecylsulfate (SDoS) obtained from Nacalai Tesque Inc. was used as received. The concentrations of these organic ions having a long alkyl-chain were well below their cmcs, respectively. When the ionic strength of solution was held at $3.0 \times 10^{-2} \text{ mol dm}^{-3}$, TeMA was employed. In the concentration range used, TeMA was found not to affect the absorption and fluorescence spectra of PS within experimental errors.

Absorption spectra were recorded on a Shimadzu UV-2450 spectrophotometer. Fluorescence spectra were taken with a Shimadzu RF-501 spectrofluorometer equipped with a cooled Hamamatsu R-943 photomultiplier. The fluorescence spectra were corrected for the spectral response of the fluorometer. Spectroscopic measurements were made at $25 \pm 0.1 \text{ }^\circ\text{C}$. Conductivity was measured with a TOA CM-20E conductivity meter.

As stated above, PS in γ -CD solution exhibits the excimer fluorescence at high PS concentrations such as $2 \times 10^{-5} \text{ mol dm}^{-3}$ [16]. To avoid the formation of the PS excimer, the PS concentration in this study has been lowered to $5.0 \times 10^{-7} \text{ mol dm}^{-3}$, at which the excimer

fluorescence has not been observed in the presence of γ -CD. In the measurements of absorption spectra of PS solution containing a surfactant in the absence of γ -CD, the PS concentration was $2.0 \times 10^{-6} \text{ mol dm}^{-3}$.

Results and discussion

Inclusion interactions of γ -CD with PS

Figure 1 shows absorption spectra of PS ($5.0 \times 10^{-7} \text{ mol dm}^{-3}$) in aqueous solution in the absence and presence of γ -CD. Upon the addition of γ -CD, the absorption maxima of PS shift to longer wavelengths, suggesting the formation of an inclusion complex of γ -CD with PS. Figure 2 exhibits fluorescence spectra of PS ($5.0 \times 10^{-7} \text{ mol dm}^{-3}$) in aqueous solution containing several concentrations of γ -CD. When the γ -CD concentration is increased, the fluorescence intensity is reduced without band shifts, indicating the formation of the inclusion complex of γ -CD with PS. In Fig. 2, no excimer fluorescence of PS in γ -CD solution is observed in contrast to the results of Harada and Nozakura [16], because the PS concentration is very low in this study. Consequently, γ -CD most likely forms a 1:1 inclusion complex with PS.



where K_1 is the equilibrium constant for the formation of the 1:1 γ -CD–PS inclusion complex, and $\gamma\text{-CD} \cdot \text{PS}$ represents the 1:1 inclusion complex. When a 1:1 γ -CD–PS inclusion complex is produced, a double reciprocal plot for the fluorescence intensity shows a linear relationship [21]:

$$1/(I_f - I_f^0) = 1/a + 1/(aK_1[\gamma\text{-CD}]) \quad (2)$$

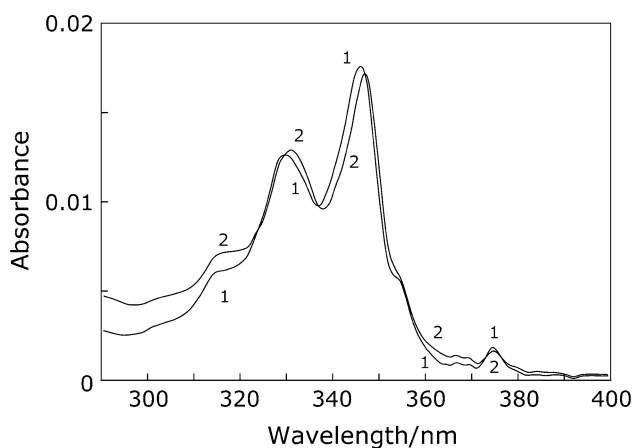


Fig. 1 Absorption spectra of PS ($5.0 \times 10^{-7} \text{ mol dm}^{-3}$) in aqueous solution in the absence (spectrum 1) and presence (spectrum 2) of γ -CD ($1.0 \times 10^{-2} \text{ mol dm}^{-3}$)

where I_f and I_f^0 are the fluorescence intensities in the presence and absence of γ -CD, respectively, a is an instrumental constant including the fluorescence quantum yields of free PS and the 1:1 γ -CD–PS inclusion complex, and $[\gamma\text{-CD}]$ is the concentration of γ -CD. Figure 3 exhibits the double reciprocal plot for a PS solution containing γ -CD. This plot in Fig. 3 shows a straight line, indicating the formation of the 1:1 γ -CD–PS inclusion complex. From this plot, the K_1 value is estimated to be $140 \pm 10 \text{ mol}^{-1} \text{ dm}^3$, which is less than half of the K_1 value ($300 \text{ mol}^{-1} \text{ dm}^3$) for pyrene [7]. This suggests that the hydrophobicity of PS is weaker than that of pyrene. Although the K_1 value has been reported to be $1 \text{ mol}^{-1} \text{ dm}^3$ from a simulation of the PS excimer fluorescence intensity [16], a direct evaluation of a K_1 value based on Eq. 1 is more reliable than an indirect evaluation using the excimer fluorescence intensity.

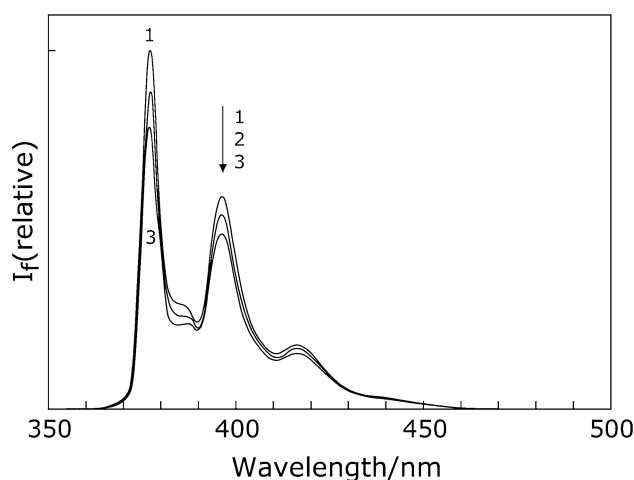


Fig. 2 Fluorescence spectra of PS ($5.0 \times 10^{-7} \text{ mol dm}^{-3}$) in aqueous solution containing several concentrations of γ -CD. Concentration of γ -CD: (1) 0, (2) 3.0×10^{-3} , and (3) $1.0 \times 10^{-2} \text{ mol dm}^{-3}$. $\lambda_{\text{ex}} = 340 \text{ nm}$

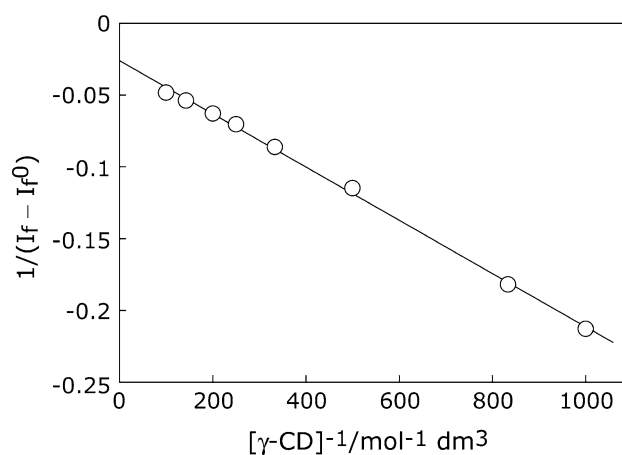


Fig. 3 Double reciprocal plot for the fluorescence intensity of PS ($5.0 \times 10^{-7} \text{ mol dm}^{-3}$) in aqueous solution containing γ -CD. $\lambda_{\text{ex}} = 340 \text{ nm}$. $\lambda_{\text{obs}} = 376 \text{ nm}$

Interactions of PS with quaternary ammonium compounds

When TMOA was added to a PS solution, the absorption maxima were reduced in intensity, suggesting the formation of an organic cation–organic anion complex (or an organic cation–organic anion pair [22, 23]) between PS and TMOA.



Here, K_2 is the equilibrium constant for the formation of a 1:1 PS–TMOA complex (PS · TMOA). With an increase in the TMOA concentration, the PS fluorescence was quenched without a shift of the fluorescence band. This finding also suggests the formation of the PS–TMOA complex. From the fluorescence intensity change by the addition of TMOA, the K_2 value has been evaluated to be $190 \pm 20 \text{ mol}^{-1} \text{ dm}^3$ (Table 1).

For the quaternary ammonium compounds, which have an alkyl chain longer than that of TMOA, the ionic strength may strongly affect the formation of an organic cation–organic anion complex. Figure 4 illustrates absorption spectra of PS ($2.0 \times 10^{-6} \text{ mol dm}^{-3}$) solutions containing several concentrations of DeTMA at a fixed ($3.0 \times 10^{-2} \text{ mol dm}^{-3}$) and an unfixed (less than $1.0 \times 10^{-3} \text{ mol dm}^{-3}$) ionic strength. Under the both conditions of the ionic strength, the absorption intensity is reduced without a peak shift, as the DeTMA concentration increases, although the spectral change at the unfixed ionic strength is greater than that at the fixed ionic strength. The insert in Fig. 4 represents the DeTMA concentration dependence of the absorbance at 346 nm in the absence of TeMA. The absorbance monotonously decreases with an increase in the DeTMA

concentration. These findings suggest that micelles are not formed by the addition of DeTMA. Consequently, the absorption spectral changes are due to the complex formation of PS with DeTMA. For DoTMA, similar absorption spectral changes were observed.

As in the case of TMOA, other quaternary ammonium compounds, DeTMA, DoTMA, and BTMA, exhibited similar fluorescence changes, indicating the formation of the organic cation–organic anion complexes. Figure 5 shows double reciprocal plots for the fluorescence intensity

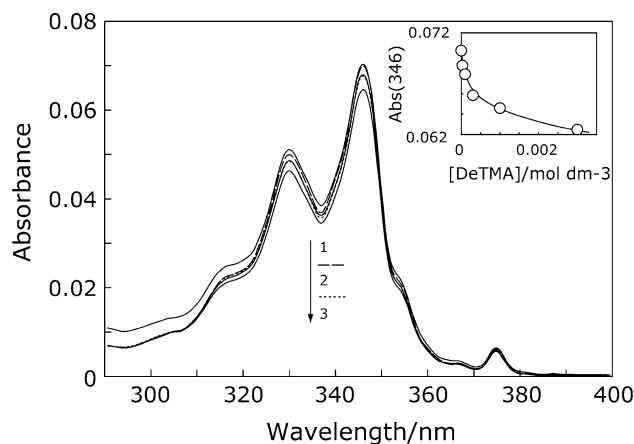


Fig. 4 Absorption spectra of PS ($2.0 \times 10^{-6} \text{ mol dm}^{-3}$) in aqueous solution containing DeTMA in the absence (curves 1, 2, and 3) and presence (dashed and dotted curves) of TeMA. TeMA was added in order to maintain the ionic strength at $3.0 \times 10^{-2} \text{ mol dm}^{-3}$. Concentration of DeTMA: (1) 0, (2) 1.0×10^{-4} , and (3) $1.0 \times 10^{-3} \text{ mol dm}^{-3}$. Dashed curve: [DeTMA] = 0 mol dm^{-3} . Dotted curve: [DeTMA] = $2.0 \times 10^{-3} \text{ mol dm}^{-3}$. The insert represents the dependence of the absorbance of PS at 346 nm on the DeTMA concentration in the absence of TeMA

Table 1 The K_2 and K_3 values for the quaternary ammonium compounds, and the K_4 values for the quaternary ammonium compounds, alkylsulfonates, and SDoS

Compound	K_2 ($\text{mol}^{-1} \text{ dm}^3$)	K_3 ($\text{mol}^{-1} \text{ dm}^3$)	K_4 ($\text{mol}^{-1} \text{ dm}^3$)
TMOA	190 ± 20	1,110	1.51×10^3
	30 ± 20^a	103^a	28^a
DeTMA	$3,100 \pm 400$	9,240	2.05×10^5
	820 ± 110^a	$4,030^a$	3.00×10^{4a}
DoTMA	$10,300 \pm 1,400$	43,400	3.19×10^6
	$8,000 \pm 2,400^a$	$4,990^a$	3.63×10^{5a}
BTMA	46 ± 6	138	45
SDeS			6.11
SUnS			219
SDoS			573
			382^a

^a Values evaluated at an ionic strength of $3.0 \times 10^{-2} \text{ mol dm}^{-3}$ using TeMA

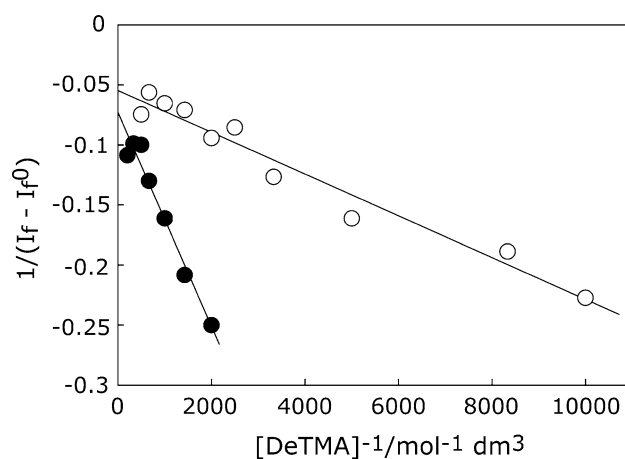


Fig. 5 Double reciprocal plots for the fluorescence intensity of PS ($5.0 \times 10^{-7} \text{ mol dm}^{-3}$) in aqueous solution containing DeTMA in the absence and presence of TeMA. Open circles: [TeMA] = 0 mol dm^{-3} . Closed circles: the ionic strength of solution was held at $3.0 \times 10^{-2} \text{ mol dm}^{-3}$ using TeMA. $\lambda_{\text{ex}} = 340 \text{ nm}$. $\lambda_{\text{obs}} = 376 \text{ nm}$

of PS solution containing DeTMA. Open circles represent the data at an unfixed ionic strength (without TeMA), while closed circles represent the data at an ionic strength of $3.0 \times 10^{-2} \text{ mol dm}^{-3}$ (with TeMA). The plot for the former data exhibits a straight line, suggesting that the ionic strength does not exert too large effects on the complex formation in the DeTMA concentration range up to about $3 \times 10^{-3} \text{ mol dm}^{-3}$. Here, we discuss the data under the conditions of the unfixed ionic strength, and later we discuss the data at a fixed ionic strength of $3.0 \times 10^{-2} \text{ mol dm}^{-3}$. From the fluorescence intensity change in the absence of TeMA, the K_2 values for DeTMA, DoTMA, and BTMA have been estimated to be $3,100 \pm 400$, $10,300 \pm 1,400$, and $46 \pm 6 \text{ mol}^{-1} \text{ dm}^3$, respectively, and their K_2 values are summarized in Table 1. The K_2 value for the quaternary ammonium compounds except for BTMA, which possesses not a long alkyl-chain but a benzyl group, increases on going from TMOA to DoTMA; the K_2 value increases with an increase in the length of an alkyl chain. The length effects of an alkyl chain in the quaternary ammonium compounds on the K_2 value suggest that the hydrophobic interactions operate between a PS molecule and a quaternary ammonium compound.

Ternary inclusion complexes of γ -CD with PS and quaternary ammonium compounds

Inclusion complexes are formed between poly(ethylene glycol) and not β -CD but α -CD [24]. In addition, it has been reported that 1,1'-diheptyl-4,4'-bipyridyl dibromide scarcely forms an inclusion complex with γ -CD, due to the γ -CD cavity being too large to closely include a hydrophobic heptyl-chain of 1,1'-diheptyl-4,4'-bipyridyl dibromide [25]. To examine the interactions between γ -CD and a long alkyl-chain of a quaternary ammonium compound, the conductivity of DoTMA solution ($1.4 \times 10^{-4} \text{ mol dm}^{-3}$) was measured in the absence and presence of γ -CD. A variation in the conductivity was less than 3% upon the addition of γ -CD of $1.0 \times 10^{-2} \text{ mol dm}^{-3}$, suggesting little or no interactions of γ -CD with DoTMA. Therefore, we have neglected the formation of an inclusion complex of γ -CD with quaternary ammonium compounds.

Figure 6 illustrates absorption spectra of PS ($5.0 \times 10^{-7} \text{ mol dm}^{-3}$) in aqueous solution containing γ -CD and TMOA. As shown in Fig. 1, the absorption peaks are reduced in intensity by the addition of γ -CD ($3.0 \times 10^{-3} \text{ mol dm}^{-3}$). Further addition of TMOA ($1.0 \times 10^{-2} \text{ mol dm}^{-3}$) to the PS solution containing γ -CD results in a red-shift of the absorption maxima, with a slight decrease in intensity. In the absence of γ -CD, the absorption maxima of PS were not shifted by the addition of TMOA but were slightly reduced in intensity. Consequently, the red-shift of the absorption maxima suggests the formation of a ternary

inclusion complex among γ -CD, PS, and TMOA. When TMOA is added to PS ($5.0 \times 10^{-7} \text{ mol dm}^{-3}$) solution containing γ -CD ($3.0 \times 10^{-3} \text{ mol dm}^{-3}$), the fluorescence peak at about 376 nm shifts to longer wavelengths, accompanied by a slight decrease in the fluorescence intensity (Fig. 7). As already stated, the fluorescence band of PS is not shifted by the addition of only TMOA or γ -CD. Consequently, the peak shift in the presence of both TMOA and γ -CD is due to the formation of the ternary γ -CD–TMOA–PS inclusion complex. Taking into account the cavity size of γ -CD, a single TMOA molecule is most likely bound to the γ -CD cavity accommodating a PS molecule. Addition of γ -CD to PS

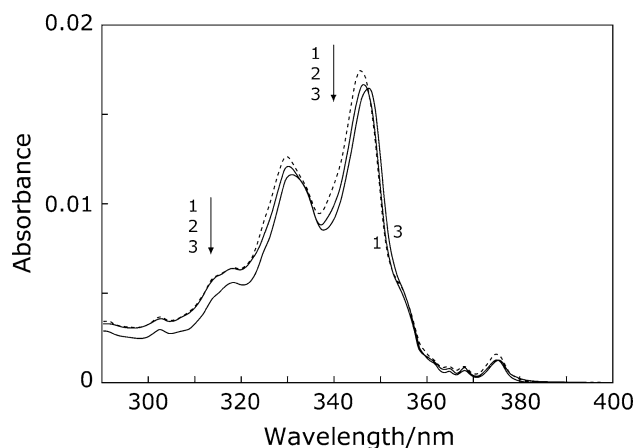


Fig. 6 Absorption spectra of PS ($5.0 \times 10^{-7} \text{ mol dm}^{-3}$) in aqueous solution containing γ -CD and TMOA. Spectrum 1 (dotted curve): $[\gamma\text{-CD}] = 0$ and $[\text{TMOA}] = 0 \text{ mol dm}^{-3}$, spectrum 2: $[\gamma\text{-CD}] = 3.0 \times 10^{-3}$ and $[\text{TMOA}] = 0 \text{ mol dm}^{-3}$, and spectrum 3: $[\gamma\text{-CD}] = 3.0 \times 10^{-3}$ and $[\text{TMOA}] = 1.0 \times 10^{-2} \text{ mol dm}^{-3}$

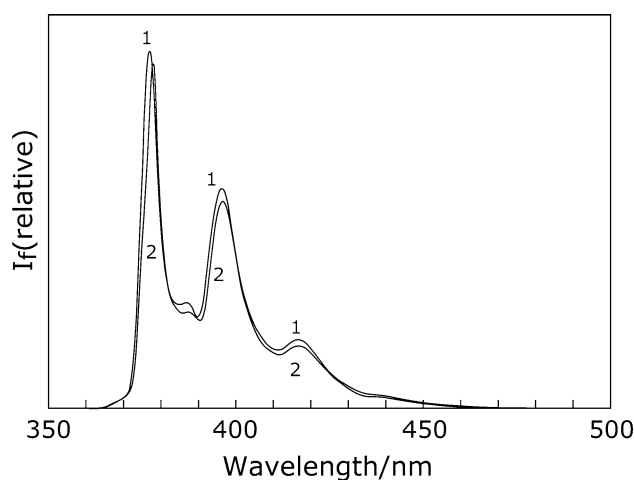
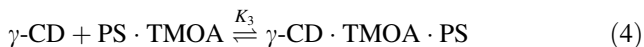


Fig. 7 Fluorescence spectra of PS ($5.0 \times 10^{-7} \text{ mol dm}^{-3}$) in aqueous solution containing γ -CD ($3.0 \times 10^{-3} \text{ mol dm}^{-3}$) and TMOA. Concentration of TMOA: (1) 0 and (2) $3.0 \times 10^{-2} \text{ mol dm}^{-3}$. $\lambda_{\text{ex}} = 340 \text{ nm}$

solution containing TMOA resulted in a fluorescence change similar to that caused by the addition of TMOA to PS solution containing γ -CD:



where K_3 is the equilibrium constant for the formation of the 1:1:1 γ -CD–TMOA–PS inclusion complex ($\gamma\text{-CD} \cdot \text{TMOA} \cdot \text{PS}$). Because the absorbance of PS solution is very small in this study, the fluorescence intensity is proportional to the concentration of a fluorescent species. For PS solution containing γ -CD and TMOA, the fluorescence intensity, I_f , is represented by the sum of the fluorescence intensities of free PS, the 1:1 γ -CD–PS inclusion complex, the 1:1 PS–TMOA complex, and the 1:1:1 γ -CD–TMOA–PS inclusion complex:

$$I_f = b[\text{PS}] + c[\gamma\text{-CD} \cdot \text{PS}] + d[\text{PS} \cdot \text{TMOA}] + e[\gamma\text{-CD} \cdot \text{TMOA} \cdot \text{PS}] \quad (5)$$

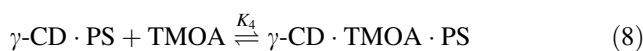
Here, b , c , d , and e are constants including the fluorescence quantum yields of free PS, the 1:1 γ -CD–PS inclusion complex, the 1:1 PS–TMOA complex, and the 1:1:1 γ -CD–TMOA–PS inclusion complex, respectively. Using the equilibrium constants, Eq. 5 can be rewritten as

$$I_f = \frac{(b + cK_1[\gamma\text{-CD}] + dK_2[\text{TMOA}] + eK_2K_3[\gamma\text{-CD}][\text{TMOA}])[\text{PS}]_0}{(1 + K_1[\gamma\text{-CD}] + K_2[\text{TMOA}] + K_2K_3[\gamma\text{-CD}][\text{TMOA}])} \quad (6)$$

where $[\text{PS}]_0$ is the initial concentration of PS. To obtain the K_3 value, we first evaluated values of c/b and d/b . Simulating the γ -CD concentration dependence of the fluorescence intensity for PS solution containing γ -CD alone and the TMOA concentration dependence of the fluorescence intensity for PS solution containing TMOA alone, values of c/b and d/b at $\lambda_{\text{ex}} = 340$ and $\lambda_{\text{obs}} = 376$ nm were estimated to be 0.584 and 0.718, respectively. The K_1 and K_2 values have already been evaluated. On the basis of Eq. 6, the K_3 value can be estimated from a simulation of the fluorescence intensity for PS solution containing γ -CD and TMOA, using values of b , e , and K_3 as variables. As a function of γ -CD concentration, Fig. 8 exhibits the observed fluorescence intensities and a best fit simulation curve (solid curve) for the fluorescence intensity of PS solution containing TMOA (1.0×10^{-2} mol dm $^{-3}$). The simulation curve well fits the observed fluorescence intensity data. From the simulation, a K_3 value of $1,110$ mol $^{-1}$ dm 3 is evaluated (Table 1). If the γ -CD–TMOA–PS inclusion complex is not formed (only the γ -CD–PS inclusion complex and the PS–TMOA complex are formed), the fluorescence intensity is represented by

$$I_f = \frac{(b' + c'K_1[\gamma\text{-CD}] + d'K_2[\text{TMOA}])[\text{PS}]_0}{(1 + K_1[\gamma\text{-CD}] + K_2[\text{TMOA}])} \quad (7)$$

where b' , c' , and d' are constants including the fluorescence quantum yields of free PS, the 1:1 γ -CD–PS inclusion complex, and the 1:1 PS–TMOA complex, respectively. Values of c'/b' and d'/b' are equal to the values of c/b and d/b , respectively. A dotted curve in Fig. 8 is a best fit simulation curve based on the scheme, in which the γ -CD–TMOA–PS inclusion complex is not formed. This simulation curve does not reproduce the observed fluorescence intensities, confirming the formation of the 1:1:1 γ -CD–TMOA–PS inclusion complex. In PS solution containing both γ -CD and TMOA, there is an equilibrium besides Eq. 4, which leads to the formation of the ternary inclusion complex:



where K_4 is the equilibrium constant for the formation of the 1:1:1 γ -CD–TMOA–PS inclusion complex from the 1:1 γ -CD–PS inclusion complex and TMOA. The K_4 value can be calculated from a relation among the equilibrium constants, $K_4 = K_2K_3/K_1$. For TMOA, a K_4 value of 1510 mol $^{-1}$ dm 3 is estimated (Table 1).

DeTMA and DoTMA exhibited fluorescence intensity changes similar to that for TMOA, indicating the formation of the ternary inclusion complexes including DeTMA and

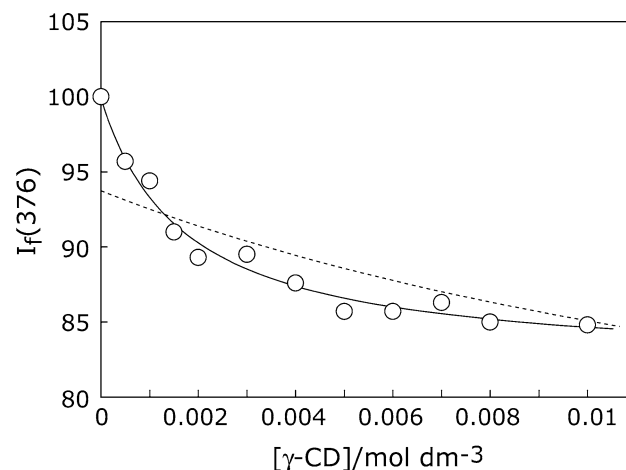


Fig. 8 Simulation for the observed fluorescence intensities of PS (5.0×10^{-7} mol dm $^{-3}$) in aqueous solution containing γ -CD and TMOA. A best fit simulation curve (solid curve) has been calculated on the basis of the scheme involving the formation of the 1:1:1 γ -CD–TMOA–PS inclusion complex. The evaluated K_1 and K_2 values have been used, and values of K_3 , b , and e have been assumed to be $1,110$, 2.45×10^8 , and 1.66×10^8 mol $^{-1}$ dm 3 , respectively. A best fit simulation curve (dotted curve), which has been based on the scheme not involving the formation of the 1:1:1 γ -CD–TMOA–PS inclusion complex, has been calculated with the evaluated K_1 and K_2 values and an assumed proportionality constant of 1.94×10^8 mol $^{-1}$ dm 3 . $[\text{TMOA}] = 1.0 \times 10^{-2}$ mol dm $^{-3}$. $\lambda_{\text{ex}} = 340$ nm. $\lambda_{\text{obs}} = 376$ nm

DoTMA, respectively. The K_3 values for DeTMA and DoTMA have been evaluated to be 9,240 and 43,400 $\text{mol}^{-1} \text{dm}^3$, respectively, and are summarized in Table 1. The K_3 value increases on going from TMOA to DoTMA, suggesting that an alkyl chain of the quaternary ammonium ion is bound to the γ -CD cavity in the ternary inclusion complexes. To further examine the effects of the alkyl chain on the formation of the ternary inclusion complex, the K_3 value has been evaluated for BTMA, which does not have an alkyl chain but a benzyl group as a hydrophobic moiety. In the case of BTMA, the benzyl group is most likely incorporated into the γ -CD cavity accommodating a PS molecule. A K_3 value of 138 $\text{mol}^{-1} \text{dm}^3$ has been obtained for BTMA (Table 1). This K_3 value is one to two orders of magnitude less than those for the other quaternary ammonium compounds examined. This supports that an alkyl chain is bound to the γ -CD cavity accommodating a PS molecule. The K_2 value for BTMA has been evaluated to be $46 \pm 6 \text{ mol}^{-1} \text{dm}^3$, which is significantly less than those for the other quaternary ammonium compounds. As in the case of TMOA, the K_4 values for DeTMA, DoTMA, and BTMA have been evaluated to be 2.05×10^5 , 3.19×10^6 , and $45 \text{ mol}^{-1} \text{dm}^3$, respectively (Table 1). The K_4 value as well as the K_3 value increases on going from TMOA to DoTMA. The trend in the magnitude of K_4 can be interpreted by the incorporation of an alkyl chain of the quaternary ammonium compound into the γ -CD cavity accommodating a PS molecule. The K_4 value for BTMA is significantly less than those for the other quaternary ammonium compounds, supporting that an alkyl group or a benzyl group is incorporated into the γ -CD cavity accommodating a PS molecule. The small K_4 value for BTMA may be partly due to the small K_2 value for BTMA, which is related to the strength of the interactions between PS and BTMA.

Because a long alkyl-chain in the quaternary ammonium compounds is bound to the γ -CD cavity accommodating a PS molecule, a cationic moiety ($(\text{CH}_3)_3\text{N}^{+-}$) resides in the water environment. A PS molecule is most likely incorporated into the γ -CD cavity from an aromatic moiety, protruding a sulfonate group into the water environment. Consequently, the cationic moiety of the quaternary ammonium compound and the sulfonate group of the PS molecule likely interact electrostatically with each other. When the cationic moiety interacts electrostatically with the sulfonate group, the K_3 value would be increased compared to when there are no electrostatic interactions between them. To confirm the electrostatic interactions between the two groups, we tried to use alcohols, which are non-ionic compounds having a long alkyl-chain, instead of the quaternary ammonium cations. However, the fluorescence spectral change was small, probably because the solubility of alcohol with a long alkyl-chain was very

small. Consequently, the K_3 value for alcohol could not be estimated. Thus, we have used alkylsulfonates and an alkylsulfate (1-dodecylsulfate (SDoS)), which are anionic species having a long alkyl-chain. In the case of alkylsulfonates (or SDoS), the electrostatic repulsion may work between a sulfonate group of an alkylsulfonate (or a sulfate group of SDoS) and a PS molecule. For this reason, the K_4 values for the alkylsulfonates and SDoS are expected to be less than those for the quaternary ammonium compounds.

Ternary inclusion complexes of γ -CD with PS and alkylsulfonates (or SDoS)

When SDoS was added to PS solution without γ -CD, the absorption spectrum of PS exhibited little or no change, indicating no formation of a complex between PS and SDoS. This is reasonable, because both PS and SDoS have the same negative-charge. Addition of SDoS to PS solution containing γ -CD ($3.0 \times 10^{-3} \text{ mol dm}^{-3}$) resulted in a slight red-shift of the absorption peak and a slight decrease in the absorbance of the peak, which were similar to the change in the absorption spectra upon the addition of quaternary ammonium compounds to PS solution containing γ -CD. This absorption spectral change suggests that a ternary inclusion complex is formed among γ -CD, SDoS, and PS. As the SDoS concentration is increased, the fluorescence intensity of PS solution containing γ -CD decreases, suggesting the formation of the ternary inclusion complex. Consequently, the fluorescence intensity for PS solution containing γ -CD and SDoS is represented by

$$I_f = (f + gK_1[\gamma\text{-CD}] + hK_1K_4[\gamma\text{-CD}][\text{SDoS}])[\text{PS}]_0 / (1 + K_1[\gamma\text{-CD}] + K_1K_4[\gamma\text{-CD}][\text{SDoS}]) \quad (9)$$

Here, f , g , and h are constants including the fluorescence quantum yields of free PS, the γ -CD–PS inclusion complex, and the γ -CD–SDoS–PS inclusion complex, respectively. The g/f value is equal to the estimated c/b value. The K_1 value has already been evaluated. Using values of f , h , and K_4 as parameters, a simulation for the fluorescence intensity has been performed. Figure 9 shows the observed fluorescence intensity as a function of γ -CD concentration and a best fit simulation curve (solid curve) calculated. From this simulation, a K_4 value of $573 \text{ mol}^{-1} \text{dm}^3$ is evaluated (Table 1). This K_4 value for SDoS is remarkably less than that for the quaternary ammonium compounds, except for BTMA. Although SDoS and DoTMA have a long alkyl-chain of the same length, a dodecyl chain, the K_4 value for DoTMA is more than 5,000 times greater than that for SDoS. This finding suggests that the electrostatic repulsion between the negative charges of PS and SDoS decelerates the formation of the ternary γ -CD–SDoS–PS inclusion complex, and that the electrostatic attraction between a negative charge of PS and a positive charge of DoTMA

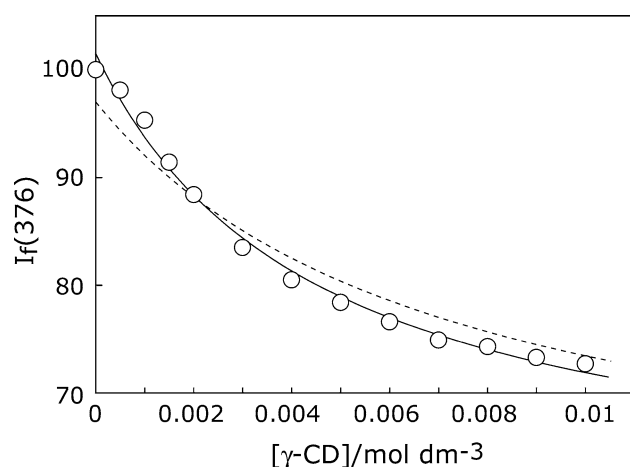


Fig. 9 Simulation for the observed fluorescence intensities of PS ($5.0 \times 10^{-7} \text{ mol dm}^{-3}$) in aqueous solution containing γ -CD and SDoS. A best fit simulation curve (solid curve) has been calculated on the basis of the scheme involving the formation of the 1:1:1 γ -CD-SDoS-PS inclusion complex. The evaluated K_1 value has been used. Values of K_4 , f , and h have been assumed to be 573, 2.03×10^8 , and $1.14 \times 10^8 \text{ mol}^{-1} \text{ dm}^3$, respectively. A best fit simulation curve (dotted curve), which has been based on the scheme not involving the formation of the 1:1:1 γ -CD-SDoS-PS inclusion complex, has been calculated with a proportionality constant of $2.30 \times 10^8 \text{ mol}^{-1} \text{ dm}^3$. $[\text{SDoS}] = 1.0 \times 10^{-3} \text{ mol dm}^{-3}$. $\lambda_{\text{ex}} = 340 \text{ nm}$. $\lambda_{\text{obs}} = 376 \text{ nm}$

accelerates the formation of the ternary γ -CD-DoTMA-PS inclusion complex. From simulations similar to that for SDoS, the K_4 values for alkylsulfonates have been evaluated. In Table 1, the K_4 values for the alkylsulfonates are also summarized. The K_4 value increases on going from SDeS to SDoS; the K_4 value increases with increasing the length of the alkyl chain. This finding can be explained in terms of the invasion of the alkyl chain into the γ -CD cavity accommodating a PS molecule. As in the case of SDoS, the K_4 value ($6.11 \text{ mol}^{-1} \text{ dm}^3$) for SDeS is more than 30,000 times less than that for DeTMA, which has the same length of the alkyl chain as SDeS. This also indicates the electrostatic effects on the formation of the ternary inclusion complex among γ -CD, PS (an organic anion), and an organic cation (or an organic anion).

Effects of the fixed ionic strength on the complex formation

The formation of an organic cation–organic anion complex is expected to be influenced by the ionic strength. As shown in Fig. 4, the absorption spectral change for PS solution of a fixed ionic strength ($3.0 \times 10^{-2} \text{ mol dm}^{-3}$) upon the addition of DeTMA is less than that for PS solution without TeMA, in which the ionic strength is significantly low but is not held constant. The double reciprocal plot (open circles in Fig. 5) for the fluorescence intensity of the later PS solution containing various

concentrations of DeTMA exhibits a straight line, although the ionic strength is not fixed. This suggests that the ionic strength does not exert too large effects on the complexation of PS with DeTMA at ionic strengths less than about $3 \times 10^{-3} \text{ mol dm}^{-3}$. In the absence of TeMA, the K_2 value for the formation of the PS-DeTMA complex is evaluated to be $3,100 \pm 400 \text{ mol}^{-1} \text{ dm}^3$ from the plot (open circles) in Fig. 5. At an ionic strength of $3.0 \times 10^{-2} \text{ mol dm}^{-3}$, the K_2 value for DeTMA is evaluated to be $820 \pm 400 \text{ mol}^{-1} \text{ dm}^3$ from the plot (closed circles) in Fig. 5. This small K_2 value indicates that the formation of the PS-DeTMA complex is retarded at an ionic strength of $3.0 \times 10^{-2} \text{ mol dm}^{-3}$; TeMA decelerates the formation of the PS-DeTMA complex. As in the case of DeTMA, the K_2 values for TMOA and DoTMA have been obtained at an ionic strength of $3.0 \times 10^{-2} \text{ mol dm}^{-3}$ using TeMA, and are summarized in Table 1. The K_2 values for TMOA and DoTMA in the presence of TeMA are less than those in the absence of TeMA, respectively. At an ionic strength of $3.0 \times 10^{-2} \text{ mol dm}^{-3}$, the K_2 value is increased with an increase in the length of an alkyl chain of a quaternary ammonium compound. This finding suggests that the hydrophobic interactions operate in the formation of the organic cation–organic anion complex at this ionic strength.

We also examined the effects of TeMA (fixed ionic strength) on the formation of the γ -CD-PS inclusion complex. From the fluorescence intensity change, a K_1 value of $110 \pm 10 \text{ mol}^{-1} \text{ dm}^3$ was estimated at an ionic strength of $3.0 \times 10^{-2} \text{ mol dm}^{-3}$. This K_1 value in the presence of TeMA is slightly less than that ($140 \pm 10 \text{ mol}^{-1} \text{ dm}^3$) in the absence of TeMA. Because γ -CD is a neutral species, the small K_1 value in the presence of TeMA may be due to the so-called salt effects.

As in the cases without TeMA, the formation of the ternary inclusion complexes for TMOA, DeTMA, and DoTMA was examined at an ionic strength of $3.0 \times 10^{-2} \text{ mol dm}^{-3}$. The K_3 values obtained from simulations similar to those in the absence of TeMA are tabulated in Table 1, which also summarizes the K_4 values obtained from the relation among the equilibrium constants. The K_3 and K_4 values in the presence of TeMA are less than those in the absence of TeMA, respectively. At an ionic strength of $3.0 \times 10^{-2} \text{ mol dm}^{-3}$, the K_3 and K_4 values increase on going from TMOA to DoTMA. This trend in the magnitude of the K_3 and K_4 values at a fixed ionic strength is the same as the trend in the absence of TeMA, suggesting that the hydrophobic interactions accelerate the formation of the ternary inclusion complex of γ -CD with PS and a quaternary ammonium compound.

For the anionic compound having a long alkyl-chain, SDoS, the K_4 value at an ionic strength of $3.0 \times 10^{-2} \text{ mol dm}^{-3}$ was estimated to be $382 \text{ mol}^{-1} \text{ dm}^3$ from

a simulation similar to that in the absence of TeMA (Table 1). The addition of TeMA does not cause an increase in the K_4 value of SDoS, although TeMA may be expected to reduce the electrostatic repulsion between PS and SDoS. A K_4 value of $382 \text{ mol}^{-1} \text{ dm}^3$ in the presence of TeMA is about 70% of that in the absence of TeMA. In the formation of the γ -CD–PS inclusion complex, the K_1 value in the presence of TeMA is about 80% of that in the absence of TeMA. The ratio (70%) of the K_4 value in the presence of TeMA to that in the absence of TeMA is close to the ratio (80%) for the K_1 value. Consequently, TeMA seems to exert the so-called salt effects on the formation of the γ -CD–SDoS–PS inclusion complex. For the effects of the fixed ionic strength on the K_4 value of SDoS, however, further study may be necessary.

Conclusions

At a low concentration of PS, it forms a 1:1 inclusion complex with γ -CD. The 1:1 γ -CD–PS inclusion complex encapsulates a TMOA cation to form a 1:1:1 ternary inclusion complex of γ -CD, PS, and TMOA. Similarly, the 1:1 γ -CD–PS inclusion complex forms ternary inclusion complexes with other quaternary ammonium compounds (DeTMA, DoTMA, and BTMA). PS, which is an organic anion, forms 1:1 organic cation–organic anion complexes with the quaternary ammonium compounds. The equilibrium constants for the formation of these complexes have been evaluated. The K_4 value, which is the equilibrium constant for the formation of the ternary inclusion complex from the γ -CD–PS inclusion complex, increases with an increase in the length of an alkyl group of the quaternary ammonium compounds. As in the case of the quaternary ammonium cations, alkylsulfonates and an alkylsulfate (SDoS), which are organic anions, also form ternary inclusion complexes with γ -CD and PS. However, the K_4 values for the SDeS and SDoS are significantly less than those for the quaternary ammonium compounds having an alkyl chain of the same length as SDeS and SDoS, respectively. This indicates that the electrostatic attraction or repulsion operates between PS and a co-included guest ion in the formation of the ternary inclusion complex. For the alkylsulfonates, the K_4 value also increases as the alkyl chain is lengthened, indicating that the alkyl chain enters the γ -CD cavity including a PS molecule. When the ionic strength of solution has been held at $3.0 \times 10^{-2} \text{ mol dm}^{-3}$ using TeMA, the trends in the magnitude of the K_2 , K_3 , and K_4 values for the quaternary ammonium compounds are similar to those in the absence of TeMA; the K_2 , K_3 , and K_4 values increase on going from TMOA to DoTMA. In the presence of TeMA, however, the magnitudes of the K_2 , K_3 , and K_4 values are less than those in the absence of TeMA,

respectively. The K_4 value for SDoS at an ionic strength of $3.0 \times 10^{-2} \text{ mol dm}^{-3}$ is also less than that in the absence of TeMA.

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