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Inclusional Association of Phenolphthalein with Cyclodextrins in the Presence of Polyelectrolytes and Ionic Detergents As Studied by the Temperature-Jump Technique

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ABSTRACT: The forward (k_f) and backward (k_b) rate constants and the association constants (K) of the inclusional association of phenolphthalein (PP) dye into the cavities of α- and β-cyclodextrins (CD) are determined using a temperature-jump technique in the presence of simple electrolytes, polyelectrolytes, and ionic detergents. The kinetic parameters are obtained very accurately using the substantial changes in the absorbance of PP in the course of the inclusion process. The apparent values of k_f and K decrease on the addition of hydrophobic macroions and detergents having long alkyl groups, whereas k_b increases. The driving forces of the inclusion process of PP or hydrophobic and cationic macroions with CD's are the van der Waals and hydrophobic interactions between the hydrophobic groups of the guest molecules and the inner wall of the cavity of the cyclodextrin.

Introduction

As is well-known, cyclodextrin (abbreviated as CD hereafter) is one of the most appropriate compounds to mimic enzymic systems.[1-5] This is because the cavity of a CD molecule can provide a hydrophobic environment for a guest molecule in an aqueous medium and can form complexes with a variety of molecular species. Among many guest molecules, dye molecules have been used for study of the inclusional associations, since the chromophoric changes accompanied with the association are really convenient for studying the static and dynamic properties. The inclusional association of phenolphthalein (PP), a typical indicator, with β-CD has been reported by Lautsch et al.[6] and recently by Taguchi.[7] Studying a kinetic analysis of the PP + CD systems has the advantage that the absorption peak of the dye disappears completely due to the inclusion as is shown below in Figure 1, and accurate determination of the kinetic and static parameters may be performed. Most of the dye molecules studied hitherto exhibited very small shifts in absorption peak by the inclusional association.

It has been reported that alkyl groups of ionic detergents and polyelectrolytes may be included in the cavities of CD's.[8-14] The following sections discuss in detail the

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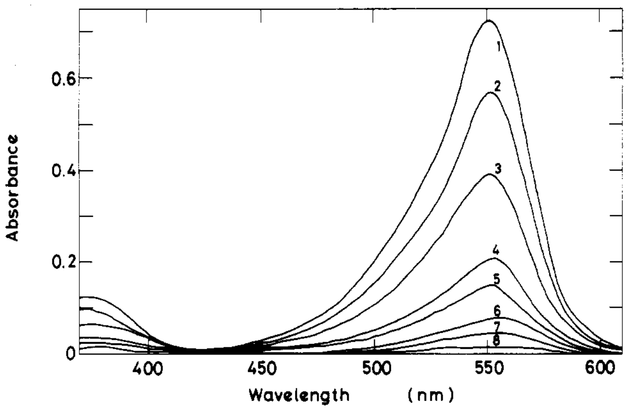


Figure 1. Absorption spectra of PP in the presence of β-CD at 25 °C. $[PP]_0 = 2.5 \times 10^{-5}$ mol dm^{-3}, in Sörensen glycine (II) buffer (pH 10.4). Curves: (1) $[\beta\text{-CD}]_0 = 0$ mol dm^{-3}, (2) 10^{-5}, (3) 4×10^{-5}, (4) 10^{-4}, (5) 1.5×10^{-4}, (6) 3×10^{-4}, (7) 6×10^{-4}, (8) 5×10^{-3}.

forward and backward reaction rates of the inclusions between PP and α-CD, and PP and β-CD, and the influences of simple electrolytes, polyelectrolytes, and ionic detergents on them, using temperature-jump measurements in order to study of the role of the hydrophobicities of the guest and host molecules.

Experimental Section

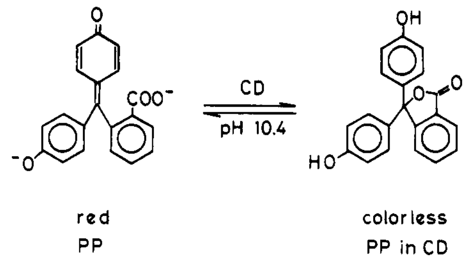
Materials. α- and β-Cyclodextrins (α-CD and β-CD) were purchased from Nakarai Chemical Co. (Kyoto) and used without further purification. Phenolphthalein (PP) was guaranteed grade obtained from Nakarai Chemical. Glycine, sodium chloride, and sodium hydroxide, which was used for the preparation of Sörensen glycine buffer, were guaranteed grade of Merck. The details of the preparation of poly(4-vinyl-*N*-ethylpyridinium bromide) (C2PVP), poly(4-vinyl-*N*-propylpyridinium bromide) (C3PVP), poly(4-vinyl-*N*-benzylpyridinium chloride) (BzPVP), and a copolymer of 4-vinyl-*N*-benzylpyridinium chloride (95%) and 4-vinyl-*N*-*n*-hexadecylpyridinium bromide (5%) (C16BzPVP) have been described in previous papers.[15,16] The degree of polymerization of the parent polymer, i.e., poly(4-vinylpyridine), was 3800 by viscometry. Hexadecyltrimethylammonium bromide (CTAB), sodium dodecyl sulfate (NaDS), and hydrobromide of poly(L-lysine) (PLL) were obtained from Sigma. The molecular weight of PLL was 79 000. A copolymer of diethyldiallylammonium chloride and sulfur dioxide (DECS) was a strongly basic polyelectrolyte prepared by Harada et al.[17,18] Sodium poly(ethylene sulfonate) (NaPES; degree of polymerization 770) and sodium poly(styrene sulfonate) (NaPSS; molecular weight 6.3×10^6) were gifts from the Hercules Powder Co. (Wilmington, DE) and the Dow Chemical Co. (Midland, MI), respectively. These samples were converted to their acid forms by passing them through columns of mixed beds of cation- and anion-exchange resins. Sodium salts were prepared by neutralization with NaOH. Sodium salts of chicken blood DNA (NaDNA) were purchased from Calbiochem. Co. (Los Angeles, CA). Deionized water obtained with cation- and anion-exchange resins was further distilled for the purification and preparation of solutions.

Temperature-Jump Measurements. The temperature-jump measurements were made on a rapid reaction analyzer (RA-1200, Union Engineering, Hirakata, Osaka).[19] Temperature jumps of ca. 4 °C were produced by the discharge of a 20-kV coaxial, which gives a heating time of 1.2 μs. The discharge heats the cell volume of solution (ca. 0.3 mL) between two gold-plated electrodes. A Tektronix oscilloscope (Beaverton, OR; types 7623A, 7A18, and 7B53A) was used. Temperature-regulated water at 21 ± 0.5 °C and in some cases at 26 ± 0.5 or 31 ± 0.5 °C was circulated in the measuring cell.

Results and Discussion

Static Parameters of Inclusional Association of PP with α-CD and β-CD. Figure 1 shows the absorption spectra of PP in the presence of β-CD. Impressively, the absorption peaks simply decreased as the concentration of β-CD increased, and the peak shift was negligibly small. The absorption peak disappeared entirely when an excess amount of β-CD was added! This simple and significant feature of the absorption changes is advantageous for accurate determination of the association equilibrium constant, *K*.

Scheme I



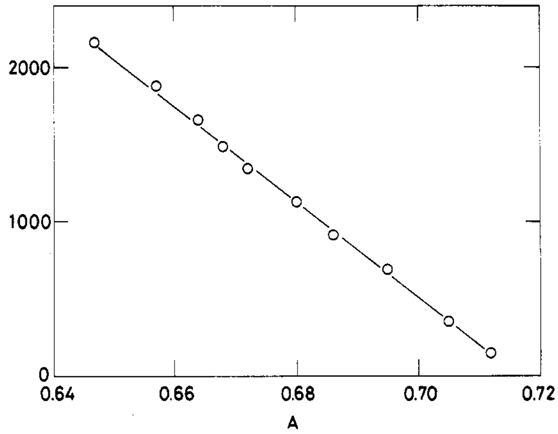


Figure 2. Plots of $A/[\beta\text{-CD}]_0$ against A for PP + β-CD mixtures at 25 °C. $[PP]_0 = 2.5 \times 10^{-5}$ mol dm^{-3}, $[\beta\text{-CD}]_0 = 3 \times 10^{-4}$–$5 \times 10^{-3}$ mol dm^{-3} at 550 nm, in Sörensen glycine (II) buffer (pH 10.4).

It has been clarified that PP is transformed into colorless lactonoid dianion within the cavity of CD (see Scheme I).[7] We assumed 1:1 type association for the PP + CD systems.

$$\text{PP} + \text{CD} \rightleftharpoons \text{complex} \qquad (1)$$

In our systems, the absorption of the complex was safely assumed to be zero. *K* may be evaluated from one of the following three equations.

$$A/[\text{CD}]_0 = -KA + [\text{PP}]_0\beta K \qquad [\text{PP}]_0 \ll [\text{CD}]_0 \quad (2)$$

$$[\text{PP}]_0/(A_0 - A) + (A_0 - A)/\beta A_0 = 1/K\beta[\text{PP}]_0 + 2/\beta \qquad [\text{PP}]_0 = [\text{CD}]_0 \quad (3)$$

$$(A_0/A) - 1 = K[\text{CD}]_0 - K(A_0 - A)/\beta \qquad [\text{PP}]_0 = \text{constant} \quad (4)$$

Here, A and A_0 are the peak absorbances of PP in the presence of CD's and in their absence. $[\text{CD}]_0$ and $[\text{PP}]_0$ denote the total concentrations of CD and PP. β indicates the molar extinction coefficient of PP (β = 26 200 mol^{-1} dm^3 cm^{-1}) at 551 nm and pH 10.4. The reference value of β for PP at pH 10.5 in 0.1 N NaCl was 30 600 mol^{-1} dm^3 cm^{-1} at 553 nm.[7] The K values were obtained from the slopes of the plots of $A/[\text{CD}]_0$ against A, $[\text{PP}]_0/(A_0 - A) + (A_0 - A)/\beta A_0$ against $[\text{PP}]_0^{-1}$, and $(A_0 - A)/A$ against $[\text{CD}]_0$ in eq 2–4, respectively.

Figure 2 shows a typical example of the plots using eq 2. The linearity was excellent, and K was 3.1×10^4 mol^{-1} dm^3 at pH 10.4 and at 25 °C. When the concentrations of PP and CD were equal; reliable values of K were estimated from eq 3. The figure demonstrating this has been omitted here, but the K value of 3.1×10^4 mol^{-1} dm^3 was obtained for PP + β-CD systems at 25 °C and at pH 10.4.

Table I
Static and Kinetic Data of the Inclusional Association of PP with CD at 25 °C[a]

CD	K, mol^{-1} dm^3	ΔG, kcal mol^{-1} dm^3	ΔH, kcal mol^{-1} dm^3	ΔS, eu	k_f, mol^{-1} dm^3 s^{-1}	k_b, s^{-1}
α-CD	106	-2.8	-5.7	-9.4	1.45×10^5	1300
β-CD	31 000	-6.1	-8.2	-6.9	3.66×10^7	1180

[a] In Sörensen glycine (II) buffer (pH 10.4). The experimental uncertainty is believed to be within ±5% for K, ±8% for k_f and k_b, ±0.02 for ΔG, ±0.05 for ΔH, and ±2 for ΔS, respectively.

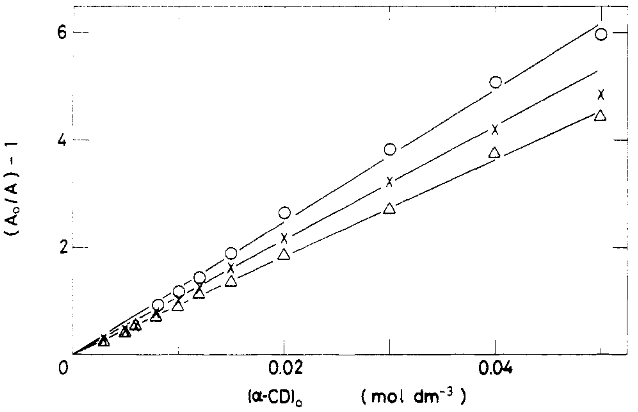


Figure 3. Plots of $(A_0/A) - 1$ against $[\alpha\text{-CD}]_0$ for PP + α-CD mixtures at 25 (○), 30 (×), and 35 °C (△). $[\mathrm{PP}]_0 = 5 \times 10^{-5}$ mol dm^{-3}, $[\alpha\text{-CD}]_0$ = 0–0.05 mol dm^{-3}, at 550 nm, in Sörensen glycine buffer (pH 10.4). The K values were 123, 106, and 91 mol^{-1} dm^3 at 25, 30, and 35 °C, respectively.

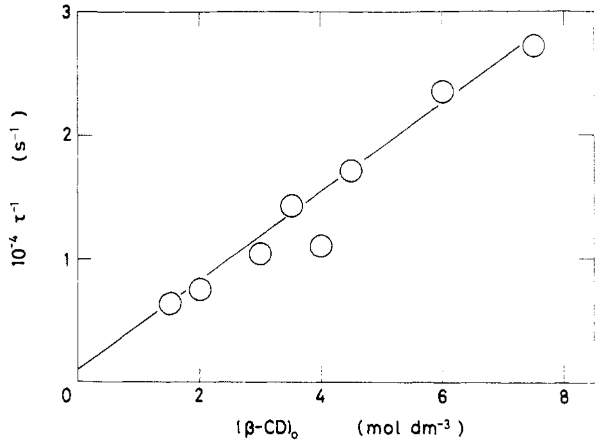


Figure 4. Plots of τ^{-1} against $[\beta\text{-CD}]_0$ for PP + β-CD mixtures at 25 °C. $[\mathrm{PP}]_0 = 2.5 \times 10^{-5}$ mol dm^{-3}, at 550 nm, in Sörensen glycine (II) buffer (pH 10.4). k_f, k_b, and K were 3.66×10^7 mol^{-1} dm^3 s^{-1}, 1.18×10^3 s^{-1}, and 3.10×10^4 mol^{-1} dm^3, respectively.

Figure 3 shows an example of the plots of $A_0/A - 1$ against $[\mathrm{CD}]_0$ for PP + α-CD systems at 25, 30, and 35 °C. The linearities were excellent, which strongly supports the formation of a 1:1 type inclusional complex between PP and CD.

The equilibrium association constants thus evaluated and the free energy (ΔG), enthalpy (ΔH), and entropy (ΔS) of the associations from their temperature dependencies are compiled in Table I. Note here that the values of k_f, k_b, K, ΔG, ΔH, and ΔS for PP + β-CD were reported to be 3.7×10^7 mol^{-1} dm^3 s^{-1}, 1.0×10^3 s^{-1}, 37 000 mol dm^{-3}, -6.1 kcal mol^{-1}, -5.8 kcal mol^{-1}, and 1 eu, respectively, at similar experimental conditions as ours (but at 20 °C and in 0.1 N NaCl).[7] The parameters for PP + α-CD have been found for the first time here.

It is interesting to note that the association constants of β-CD with PP dyes were much larger than those of α-CD. This is explained by the fact that the size of the inner cavity of β-CD fits for PP molecule; PP can be included completely in the cavity of β-CD, whereas α-CD has a space to include only one of the three phenyl groups of PP.

Kinetic Parameters of Inclusional Association of PP with α-CD and β-CD. Assuming a 1:1 association mechanism, reciprocal relaxation times, τ^{-1}, are given corresponding to eq 2–4 as

$$\tau^{-1} = k_f[\mathrm{CD}]_0 + k_b \qquad [\mathrm{PP}]_0 \ll [\mathrm{CD}]_0 \tag{5}$$

$$\tau^{-1} = k_f K^{-1}[(1 + 4K[\mathrm{PP}]_0)^{1/2} - 1] + k_b \qquad [\mathrm{PP}]_0 = [\mathrm{CD}]_0 \tag{6}$$

$$\tau^{-1} = k_f[(K^{-1} + [\mathrm{CD}]_0 + [\mathrm{PP}]_0)^2 - 4[\mathrm{CD}]_0[\mathrm{PP}]_0]^{1/2} \tag{7}$$

Here, k_f and k_b are the forward and backward reaction rate constants. Typical plots are shown in Figure 4 for the PP + β-CD system ($[\mathrm{PP}]_0 \ll [\mathrm{CD}]_0$) using eq 5. The k_f and k_b values were estimated to be 3.66×10^7 mol^{-1} dm^3 s^{-1} and 1180 s^{-1}, respectively. The kinetic parameters for the same system obtained using eq 6 were 3.70×10^7 mol^{-1} dm^3 s^{-1} and 1170 s^{-1}, respectively. The agreement between the two plots was excellent. Importantly, the k_f values obtained were of the order of 10^5–10^7 mol^{-1} dm^3 s^{-1}. These values are below those for the diffusion-controlled reaction. The kinetic parameters are given in Table I. Clearly, k_f of β-CD was much larger than that of α-CD. This result supports that the PP molecules are included adequately into the cavities of the β-CD. It should be noted here that the inequality β-CD > α-CD in k_f values is also consistent with the important role of hydrophobic interactions in the course of inclusion, because the hydrophobicity for β-CD is stronger than that for α-CD. Note that the magnitudes of k_f for the α-CD + PP inclusions were similar to those for the inclusional association of α-CD with the azo dye molecules substituted with OH, etc.[20,21] This result suggests that the rate-determining step of the host–guest association is the breakdown of the water structure inside CD and/or around PP. The important role of the dehydration to the association process was discussed earlier by Cramer et al.[20] However, they also showed that some kinds of azo dyes had very small k_f and k_b values because of the steric hindrance.[20]

The k_b values were quite insensitive irrespective of the kind of cyclodextrins, which supports that the rate-determining step for the backward reaction is the association (or hydration) of water molecules around phenyl groups of the inner cavity of PP molecule. Cramer et al.[20,21] proposed that the rate-determining steps of both association and dissociation were the release or binding of water molecules.

Influences of Polyelectrolytes and Ionic Detergents on the Static and Kinetic Parameters of Inclusional Association of PP with α-CD or β-CD. The apparent association constants (K) and the forward and backward reaction rate constants (k_f and k_b) in the presence of polyelectrolytes or ionic detergents were evaluated using one of the eq 2–4 and eq 7 for K, and k_f and k_b, respectively. The K values obtained are shown in Figure 5. All of the simple electrolytes such as KCl and $\mathrm{CaCl_2}$ and the anionic polyelectrolytes (NaPES, NaPSS, and NaDNA) did not affect the K values. This simply implies that the salts do not interact so much with any of PP, CD, or PP–CD.

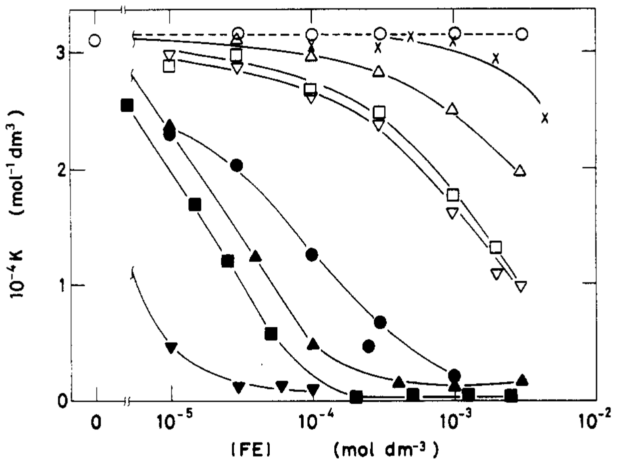


Figure 5. Influence of foreign salts on K for PP + β-CD reactions. $[PP]_0 = [\beta\text{-CD}]_0 = 5 \times 10^{-5}$ mol dm^{-3}, at 550 nm, in Sörensen glycine (II) buffer (pH 10.4): (---) KCl, CaCl$_2$, NaPSS, NaDNA; (○) NaPES; (×) PLL; (△) DECS; (□) C2PVP; (▽) C3PVP; (●) NaDS; (▲) BzPVP; (■) CTAB; (▼) C16BzPVP.

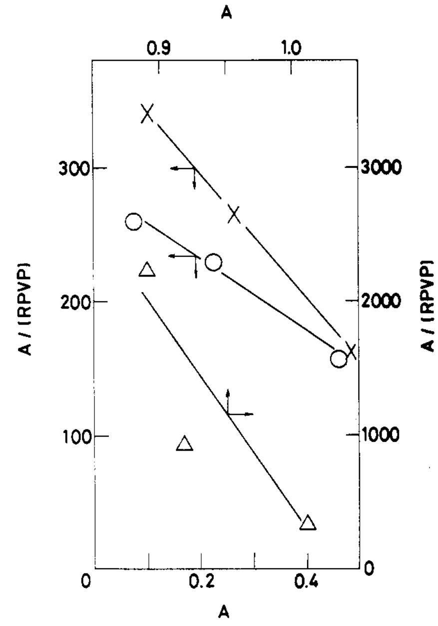


Figure 6. Modified Benesi–Hildebrand plots of $A/[\text{RPVP}]$ against A for PP + RPVP mixtures at 25 °C in Sörensen glycine (II) buffer (pH 10.4): (○) C2PVP; (×) C3PVP; (△) BzPVP.

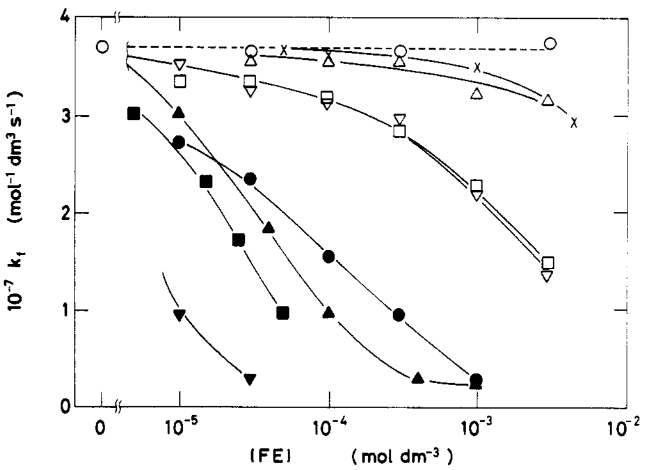


Figure 7. Influence of foreign salts on k_f for PP + β-CD reactions. $[PP]_0 = [\beta\text{-CD}]_0 = 5 \times 10^{-5}$ mol dm^{-3}, at 550 nm, in Sörensen glycine (II) buffer (pH 10.4): (---) KCl, CaCl$_2$, NaPSS, NaDNA; (○) NaPES; (×) PLL; (△) DECS; (□) C2PVP; (▽) C3PVP; (●) NaDS; (▲) BzPVP; (■) CTAB; (▼) C16BzPVP.

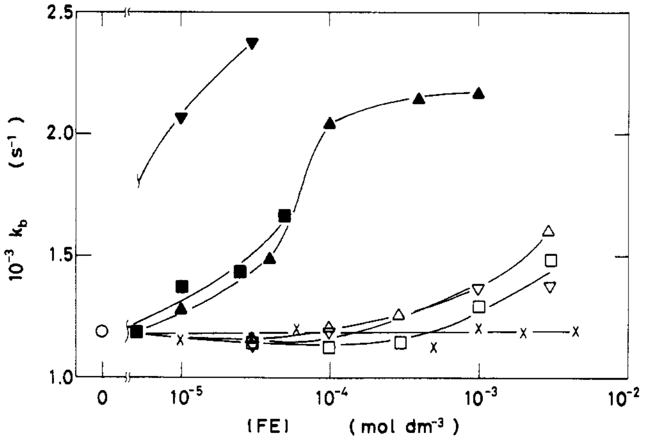


Figure 8. Influence of foreign salts on k_b for PP + β-CD reactions. $[PP]_0 = [\beta\text{-CD}]_0 = 5 \times 10^{-5}$ mol dm^{-3}, at 550 nm, in Sörensen glycine (II) buffer (pH 10.4): (×) PLL; (△) DECS; (□) C2PVP; (▽) C3PVP; (▲) BzPVP; (■) CTAB; (▼) C16BzPVP.

However, addition of the macrocations decreased the K values substantially, and the magnitudes of the decreasing effect were in the order PLL < DECS < C2PVP < C3PVP < BzPVP < C16BzPVP. Previously, we reported that PP molecules were bound on the cationic macroions strongly in the order DECS < C2PVP < C3PVP < BzPVP < C16BzPVP.[15] PP molecules are anionic and strongly hydrophobic substrates. Thus, the decreasing action of the macrocations on the K is interpreted in terms of the association of PP with the macrocations by the electrostatic and hydrophobic interactions. The binding constants of PP with C2PVP, C3PVP, and BzPVP were determined directly from the hypochromic effect in this work. The modified Benesi–Hildebrand plots are shown in Figure 6. From the slopes of the linear relations, the association constants were evaluated to be 270, 460, and 12 000 mol^{-1} dm^3 for the PP + C2PVP, PP + C3PVP, and PP + BzPVP systems, respectively.

The association between CD and the macrocations except C16BzPVP is safely neglected compared with the strong binding between PP and the macrocations.[9] The inclusional association of C16BzPVP molecules with CD molecules has been investigated from esterolysis[9] and the conductometric studies.[22] Both PP and CD were bound with the C16BzPVP macroions and reduced the reaction rate between free PP and CD significantly.

The ionic detergents (anionic NaDS and cationic CTAB) decreased K values as is shown in Figure 5. PP substrates have been reported to be bound with both NaDS and CTAB,[9,15] and the inclusional association took place between the ionic detergents and CD molecules.[8] The association constants for the associations of NaDS + α-CD, NaDS + β-CD, CTAB + α-CD, and CTAB + β-CD were 111 (160), 356, 1110, and 2240 mol^{-1} dm^3, respectively.[8,14] The values in parentheses are ones obtained in our laboratory recently.[14] Thus, the decreasing effect of CTAB and NaDS is interpreted by the binding of these detergents with both of PP and CD molecules.

Figure 7 shows the influence of macroions and ionic detergents on the k_f of the inclusional association between PP + β-CD. The k_f values decreased especially by the addition of hydrophobic and cationic macroions. The influence of electrolyte addition on the k_f values was quite similar to that on the K values described above. These observations are interpreted by the binding interactions of reactant molecules (PP and CD) with the electrolytes and the resulted depression of the activities of the reactants in the activated-complex theory.

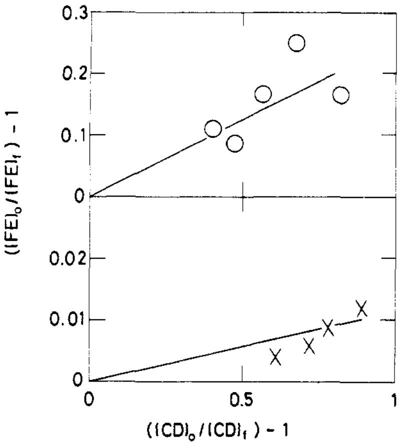


Figure 9. Plots of $([FE]_0/[FE]_f) - 1$ against $([CD]_0/[CD]_f) - 1$ for PP + β-CD + BzPVP (○) and PP + β-CD + C3PVP (×) systems at 25 °C.

The apparent backward rate constants, k_b, with foreign salts are shown in Figure 8. Clearly, the strongly hydrophobic macrocations increased k_b. The main factor for this is ascribed to the fact that the activated complex, the structure of which is close to the reactant states, was bound with the macroions much more strongly than with the product, i.e., inclusional compound of CD with PP.

Note that the parameters K, k_f, and K_b in the presence of foreign salts are the apparent values and not real ones. Determination of the real individual rate constants in the ternary systems, PP + CD + foreign electrolytes (FE), is not so easy. Here we consider three kinds of reactions given by eq 8–10. The further associations of the products

$$\mathrm{PP} + \mathrm{CD} \underset{k_{10}}{\overset{k_{01}}{\rightleftharpoons}} \mathrm{PP{-}CD} \tag{8}$$

$$\mathrm{PP} + \mathrm{FE} \underset{k_{20}}{\overset{k_{02}}{\rightleftharpoons}} \mathrm{PP{-}FE} \tag{9}$$

$$\mathrm{CD} + \mathrm{FE} \underset{k_{30}}{\overset{k_{03}}{\rightleftharpoons}} \mathrm{CD{-}FE} \tag{10}$$

with any of reactant molecules such as PP–CD + FE were neglected in this discussion. It should be noted that the association constants between PP and CD (K_1) and between PP and FE (k_2) are not independent from each other but correlated by eq 11

$$K_1/K_2 = (k_{01}/k_{10})/(k_{02}/k_{20}) = ([\mathrm{PP{-}CD}]/[\mathrm{PP}]_f[\mathrm{CD}]_f)/([\mathrm{PP{-}FE}]/[\mathrm{PP}]_f[\mathrm{FE}]_f) = [([\mathrm{CD}]_0/[\mathrm{CD}]_f) - 1]/[([\mathrm{FE}]_0/[\mathrm{FE}]_f) - 1] \tag{11}$$

where subscripts f and 0 denote the free state and the total quantity. Furthermore, $[\mathrm{FE}]_f$ and $[\mathrm{CD}]_f$ are given by the observable quantities such as $[\mathrm{PP}]_0$, $[\mathrm{PP}]_f$, $[\mathrm{FE}]_0$, and K_1 as

$$[\mathrm{PP}]_f = [\mathrm{FE}]_0 - [\mathrm{PP}]_0 + [\mathrm{PP}]_f + K_1[\mathrm{PP}]_f[\mathrm{CD}]_0/(1 + K_1[\mathrm{PP}]_f) \tag{12}$$

$$[\mathrm{CD}]_f = [\mathrm{CD}]_0/(1 + K_1[\mathrm{PP}]_f) \tag{13}$$

Thus, K_2 is evaluated from eq 11. Figure 9 shows the plots of $([FE]_0/[FE]_f) - 1$ against $([CD]_0/[CD]_f) - 1$ for the systems PP + β-CD + C3PVP and PP + β-CD + BzPVP. The rough values of K_2 between PP and C3PVP and between PP and BzPVP were estimated from the slopes to be 360 and 7800 mol^{-1} dm^3, respectively. These values agree well with the association constants obtained directly spectrophotometrically, i.e., 460 and 12 000 mol^{-1} dm^3, respectively.

The parameters k_{01}, k_{10}, k_{02}, and k_{20} are evaluated from eq 14 and 15 when the reaction 8 is in preequilibrium:[22]

$$\tau_{\mathrm{I}}^{-1} = k_{01}([\mathrm{CD}]_f + [\mathrm{PP}]_f) + k_{10} \tag{14}$$

$$\tau_{\mathrm{II}}^{-1} = k_{02}\{[\mathrm{FE}]_f(k_{01}[\mathrm{PP}]_f + k_{20})/(k_{01}[\mathrm{CD}]_f + k_{01}[\mathrm{PP}]_f + k_{20}) + [\mathrm{PP}]_f\} + k_{20} \tag{15}$$

However, the evaluation of the kinetic parameters was not made because the τ_{II}^{-1} values were not able to be determined in our temperature-jump measurements.

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Registry No. PP, 77-09-8; α-CD, 10016-20-3; β-CD, 7585-39-9; NaPSS, 62744-35-8; NaPES, 9002-97-5; PLL, 25988-63-0; DECS, 27577-32-8; C2PVP, 25619-82-3; C3PVP, 42845-23-8; NaDS, 151-21-3; BzPVP, 30109-97-8; CTAB, 57-09-0; (C16BzPVP)(BzPVP) (copolymer), 40780-43-6; KCl, 7447-40-7; $\mathrm{CaCl_2}$, 10043-52-4.

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