1. INTRODUCTION

It is well known that anions play important roles in the fields of chemistry, biology, medicine, and environmental science: therefore, considerable attention has been focused on designing new receptors that can selectively recognize and sense anions [1-3]. By directional hydrogen bond interactions, receptor molecules that possess functional groups, such as urea [4,5], thiourea [6,7], pyrrole [8], indole [9,10], and phenol [11-14], have proven to be particularly effective in binding anions. Although there have been extensive studies of hydrogen donating effects on anion binding by functional groups in artificial receptors, alcoholic hydroxyl groups have rarely been used as anion receptors [15-18].

CDs are naturally occurring cyclic oligomers of α-,β-linked D-glucose units, and they possess a unique truncated cone shape and several hydroxyl groups on their rims. Natural α-, β-, and γ-CDs contain six, seven, and eight glycopyranose units, respectively, thereby providing a choice of host CDs for binding different guest molecules. Using CDs as host molecules in aqueous media has been extensively investigated because of their hydrophobic cavities, which are capable of binding guest molecules [19, 20]; however, the molecular recognition of CDs in organic solvents has rarely been explored [21-28]. To address this situation we investigated the interaction between anions and CDs bearing alcoholic hydroxyl groups in organic solvents. We synthesized modified α- and β-CDs (1-3), in which the hydroxyls on C-2 and C-3 are protected by benzyl, acetyl, or propionyl groups; moreover, we investigated their anion binding properties in CD 3CN or CD 3CN/D 2O (99/1, v/v) using 1H-NMR titration experiments. The results demonstrate that CD-based receptors (1-3) effectively bind with AcO⁻ and H 2PO 4⁻ by cooperative intermolecular hydrogen bondings with alcoholic hydroxyl groups on C-6. The selectivity trends thought to be a function of the basicity of the anions and the size of the binding pocket in the receptors.

Key Words: Cyclodextrin, Anion receptor, Hydrogen bonding, Hydroxyl group, Acetate, Dihydrogen phosphate

2. EXPERIMENTAL SECTION

Melting points were measured by Stuart SMP3 melting point apparatus and were not corrected. 1H and 13C NMR spectra were measured on a JEOL ECX-500 (500 MHz for 1H, 125 MHz for 13C) and/or a JEOL ECX-400 (400 MHz for 1H, 100 MHz for 13C) spectrophotometers. IR spectra were recorded on HORIBA FT-720 spectrophotometer. Electrospray ionization (ESI) mass spectra were collected on a JEOL JMS-T100LP spectrometer. All chemicals were reagent grade and were used without further purification. α- and β-CDs, benzyl bromide, sodium hydride, tert-butylidemethylsilyl chloride (TBDMSCI), trifluoroboronic-diethyl ether complex (BF 3·OEt 2), N,N-dimethyl-4-aminopyridine (DMAP), triethyl amine, tetra n-butyl ammonium salts (n-Bu 4N X⁻, X =Cl, Br, I, NO 3, H 2PO 4, AcO) were purchased from Kanto Chemical Co., Tokyo Kasei Industry, Acros, and Aldrich. Hexakis (2,3-di-O-benzyl) α-CD (1a) [29], heptakis(2,3-di-O-benzyl) β-CD (1b)
ethyl acetate, 3/1 as an eluent to give a CD (2a) [31], heptakis(2,3-di-O-acetyl) β-CD (2b) [32], heptakis(6-O-TBDMSC) α-CD (5a) [29], heptakis(6-O-TBDMSC) β-CD (5b) [29], heptakis(2,3-di-O-benzyl-6-O-TBDMSC) α-CD (6a) [29], heptakis(2,3-di-O-benzyl-6-O-TBDMSC) β-CD (6b) [29], heptakis(2,3-di-O-acetyl-6-O-TBDMSC) α-CD (7a) [30] and heptakis(2,3-di-O-acetyl-6-O-TBDMSC) β-CD (7b) [30] were prepared according to the literature.

Synthesis of heptakis(2,3-di-O-propionyl-6-O-TBDMSC)α-CD (8a) and heptakis(2,3-di-O-propionyl-6-O-TBDMSC) β-CD (8b)

To a solution of 5a (0.50 g, 0.30 mmol), DMAP (0.29 g, 2.4 mmol) was diluted with hexane. The organic solution was washed with 5% HCl aqueous solution and water and then dried over anhydrous sodium sulfate. Removal of solvent gave solid residue, which was subjected to column chromatography on silica gel using hexane/ethyl acetate, 3/1 as eluent to give 8a (90% yield) as white solid. The corresponding 8b was synthesized by the same procedure using 5b instead of 5a.

8a: 1H-NMR (CDCl 3) 0.04 s (SiCH 3, 18H), 0.05 s (SiCH 3, 18H), 0.89 s (C(CH 3), 54H), 1.08 t (CH 3CH 2, J = 8.0 Hz, 18H), 1.09 t (CH 3CH 2, J = 8.0 Hz, 18H), 2.20-2.41 (m, CH 2CH 3, 24H), 3.70 (d, C 6H, J = 11.5 Hz, 6H), 3.86 (d, C 6H, J = 9.0 Hz, 6H), 4.03 (dd, C 6H, J = 8.5, 9.0 Hz, 6H), 4.12 (d, C 6H, J = 11.5 Hz, 6H), 4.67 dd, (C 6H, J = 3.0, 10.0 Hz, 6H), 5.13 (d, C 6H, J = 3.0 Hz, 6H), 5.37 dd, (C 6H, J = 8.0, 10.0 Hz, 6H). 13C-NMR (CDCl 3) -53.9 (SiCH 3), -50.5 (SiCH 3), 8.9 (CH 2CH 3), 8.9 (CH 2CH 3), 18.2 (C(CH 3)), 25.8 (C(CH 3)), 27.2 (C(CH 3)), 27.3 (C(CH 3)), 61.9 (CH 2O), 71.1 (CH), 71.3 (CH), 72.1 (CH), 74.6 (CH), 96.1 (CH), 172.6 (C=O), 174.1 (C=O). ESI-MS: 2352 (M+Na). Anal. Calc. for C 38H 38O 3Si: C, 52.55; H, 6.62. Found: C, 52.48; H, 6.72.

8b: 1H-NMR (CDCl 3) 0.03 s (SiCH 3, 21H), 0.04 s (SiCH 3, 21H), 0.88 s (C(CH 3), 63H), 1.08 t (CH 3CH 2, J = 8.0 Hz, 21H), 1.09 t (CH 3CH 2, J = 8.0 Hz, 21H), 2.23-2.55 (m, CH 2CH 3, 28H), 3.72 (d, C 6H, J = 11.6 Hz, 7H), 3.85-3.93 (m, C 6H, C 6H, 44H), 4.06 (d, C 6H, J = 11.6 Hz, 7H), 4.70 (dd, C 6H, J = 3.6, 10.0 Hz, 7H), 5.13 (d, C 6H, J = 3.6 Hz, 6H), 5.37 dd, (C 6H, J = 8.0, 9.6 Hz, 6H). 13C-NMR (CDCl 3) -53.9 (SiCH 3), -50.5 (SiCH 3), 8.9 (CH 2CH 3), 8.9 (CH 2CH 3), 18.2 (C(CH 3)), 25.9 (C(CH 3)), 27.2 (C(CH 3)), 27.3 (C(CH 3)), 61.9 (CH 2O), 71.1 (CH), 71.3 (CH), 72.1 (CH), 74.6 (CH), 96.1 (CH), 172.6 (C=O), 174.1 (C=O). ESI-MS: 2740 (M+Na). Anal. Calc. for C 40H 29O 3Si: C, 55.64; H, 8.30. Found: C, 55.52; H, 8.48.

Synthesis of heptakis(2,3-di-O-propionyl) α-CD (3a) and heptakis(2,3-di-O-propionyl) β-CD (3b)

To a solution of 8a (520 mg, 0.19 mmol) in dry dichloromethane (10 ml) was added BF 3 ·OEt 2 (0.24 ml, 1.95 mmol) under nitrogen atmosphere. The mixture was allowed to stir at r.t. for 6 h. The reaction mixture was washed with saturated NaHCO 3 , aqueous solution. The organic layer was separated and then dried over anhydrous sodium sulfate. Removal of solvent gave white solid residue, which was subjected to column chromatography on silica gel using chloroform/ methanol, 6/1 as an eluent to give 3a (80% yield) as white crystals. The corresponding 3b was synthesized by the same procedure using 8b instead of 8a.

3a: 1H-NMR (CDCl 3 ) 1.02 t (CH 3, J = 8.0 Hz, 18H), 1.05 t (CH 3, J = 8.0 Hz, 18H), 2.15-2.37 (m, CH 2CH 3, 24H), 3.31 (bs, OH, 6H), 3.75-3.90 (m, C 6H, C 6H, 18H), 4.00 (d, C 6H, J = 9.6 Hz, 6H), 4.68 (dd, C 6H, J = 3.2, 10.4 Hz, 6H), 5.01 (d, C 6H, J = 3.2 Hz, 6H), 5.45 (dd, C 6H, J = 8.4, 10.4 Hz, 6H). 13C-NMR (CDCl 3 ) 8.0 (CH), 8.1 (CH 2), 26.7 (CH 2), 26.8 (CH 2), 61.0 (CHOH), 70.2 (CH), 70.5 (CH), 72.2 (CH), 76.0 (CH), 96.2 (CH), 172.6 (C=O), 173.6 (C=O). ESI-MS: 1668 (M+Na). Anal. Calc. for C 47H 41O 37: C, 52.55; H, 6.62. Found: C, 52.38; H, 6.83.

Job Plot [33].

Job plots were carried out as following procedure. 1H-NMR sample solutions were made of [CDI, 2, or 3] + (quaternary ammonium salt [4]) ratio under the condition that [1, 2, or 3] + [4] = 3.0 mmol dm -3 in deuterated NMR solvent and, [1, 2, or 3] varied from 0 to 3.0 mmol dm -3 in 0.3 mmol dm -3 steps. The experimental observed parameter was the 1H-NMR chemical shift changes (Δδ) of the alcoholic OH and/or the methylene (H g and H h) protons of 1, 2 or 3 that was sensitive to complex formation. The data was plotted in the form Δδ × [1] + 10 -1 versus [1, 2, or 3] / [1, 2, or 3] + [4]), and the position of the maximum indicated the stoichiometry of the complex.

Association Constants (K a ) [34, 35].

Association constants (K a ) were obtained by 1H-NMR titration experiments, performed directly in the NMR tube using a micropipette to add known amounts (0, 50, 100, 150, 200, 250, 300, 350, 400, 450, 500 μl) of quaternary ammonium salts (4) stock solution (concentration = 16.5 mmol dm -3 ) in deuterated NMR solvent to a solution of CD derivative (1, 2 or 3) (700 μl, concentration = 2.38 mmol dm -3 ) in deuterated NMR solvent. The experimental observed parameter was the 1H-NMR chemical shift changes (Δδ) of the alcoholic OH and/or the methylene (H g and H h) protons of 1 that was sensitive to complex formation. A 1:1 association of CD (1, 2 or 3) and quaternary ammonium salt (4) was previously demonstrated, therefore, experimental data were fit to the equation of the 1:1 binding isotherm. All titration experiments were performed in deuterated NMR solvent at 298 K and 500 MHz.
The acetylation of 5a with anhydrous acetic acid at 100°C for 6 h gave hexakis(2,3-di-O-acetyl-6-O-TBDMSCI) α-CD (7a) in 87% yield [30]. O-Desilylation of 7a with BF3-OEt2 in dichloromethane at room temperature for 6 h gave hexakis(2,3-di-O-acetyl) α-CD (2a) in 88% yield [31]. The propionylation of 5a with anhydrous propionic acid in the presence of DMAP in dry triethyl amine at room temperature for 24 h gave hexakis(2,3-di-O-propionyl) α-CD (3a) in 80% yield. The corresponding heptakis(2,3-disubstituted) β-CD derivatives (1b, 2b and 3b) were synthesized in moderate yields from similar reaction procedure using β-CD instead of α-CD as shown in Scheme 1 [29-32]. The structures of the CD derivatives (1-3 and 5-8) were characterized by 1H- and 13C-NMR, ESI-MS and elemental analysis.

We investigated the anion binding properties of CDs using CDCl3 as a nonpolar solvent. The 1H-NMR spectra of the CDs showed broad signals. When the temperature was increased, the signals sharpened and could be identified (Figure 2). Moreover, we obtained sharp signals with the addition of tetra n-butyl ammonium chloride (Figure 3). Because generation of intramolecular hydrogen bonding and/or aggregation in CDCl3 is possible, evaluating the anion-binding properties of CDs (1-3) in CDCl3 is difficult.

However, the 1H-NMR spectra of α- and β-CD-based receptors (1-3) in CD3CN at ambient temperatures showed well-resolved spectra and no concentration-dependent shifts were observed around 1.0 × 10−5 mmol dm−3. At least in our experimental concentration range, these results strongly indicate the absence of any dimeric or oligomeric aggregation of the receptors from intermolecular hydrogen bonding.

Subsequently, we investigated the interaction of receptor (1) and anions (4) in CD3CN using 1H-NMR spectroscopy. We observed downfield shifts of the C-6-hydroxymethyl (OH, Hf, and Hg) protons of 1 with the addition of tetra n-butyl ammonium chloride (4a) to the solution of 1a. This indicates the formation of the complex (1a-4a) via intermolecular hydrogen bonding between the alcoholic OH protons of 1a and the anionic component of 4a (Figure 4). 4, induced chemical shift (Δδ, ppm) of 1a in the presence of 4a ([1a] = 2.38 mmol dm−3, [4a] = 11.9 mmol dm−3) in CD3CN at 298 K; ΔδOH = 0.64, ΔδHf = 0.13, ΔδHg = −0.11. Note that “~“ denotes a shift to a higher magnetic field). Furthermore, we observed similar downfield shifts of the C-6-hydroxymethyl protons of 1a with the addition of other anions (Br− (4b), I− (4c), and NO3− (4d)); however, the induced chemical shifts were very small. In contrast, the OH proton signal of 1a significantly broadened with the addition of basic anions such as AcO− (4e) and H2PO4− (4f). However, the methylene protons (Hf and Hg) adjacent to the C-6 hydroxyl groups exhibited similar induced chemical shifts with the addition of 4a. This observation supports the idea that the hydroxyl groups of 1a serve as binding sites for AcO− and H2PO4−. Moreover, we observed analogous induced chemical shifts when we evaluated other α- and β-CD-based receptors (1b, 2, and 3) with respect to the anions (4).
We confirmed the 1:1 stoichiometry of the complexes of the receptors (1-3) and the ammonium salts (4) by Job plots, which reached a maximum at a mole ratio of 0.5 (Figure 5) [33]. We then determined the association constants of the complexation between the receptors (1-3) and the anions (4a-4f) using a nonlinear regression method based on the chemical shifts of the 6-hydroxymethyl protons (Hf, Hg, and/or OH) of the receptors (1) (Figure 6) [34, 35]. The results are summarized in Table 1. The order of the anion binding ability of the receptors (1) in CD3CN was AcO− (4e) > H2PO4− (4f) >> Cl− (4a) > Br− (4b) > I− (4c), NO3− (4d). This trend can be understood on the basis of the anion basicity. AcO− and H2PO4− are strongly basic compared to other anions [36, 37]. The improved binding abilities of the α-CDBased receptors (1a, 2a, and 3a) compared to those of the β-CDBased receptors (1b, 2b, and 3b) may be attributed to the more appropriate size of their binding pockets.

To investigate the effect of the addition of water on the binding affinity and selectivity for anions, we used an acetonitrile-water mixture (CD3CN/D2O 99/1 (v/v)) as the solvent. The methylene protons (Hf and Hg) adjacent to the C-6-hydroxyl groups of the receptors (1-3) exhibited similar induced chemical shifts with the addition of anions (Cl− (4a), AcO− (4e), and H2PO4− (4f)). The 1H-NMR chemical shift changes of the receptors (1-3) in the presence of the anions (Br− (4b), I− (4c), and NO3− (4d)) were negligible in CD3CN/D2O 99/1 (v/v).

To determine the association constants for the receptors (1-3) with the anions (Cl− (4a), AcO− (4e), and H2PO4− (4f)), we arrayed the binding isotherms using a nonlinear regression method. The results are summarized in Table 2. It is well-known that the nature of the solvent has a profound influence on binding constants, especially when hydrogen bonds are involved in the recognition process. We observed a drop in the affinity of the receptors toward...
Anion Recognition of 2,3-Disubstituted Cyclodextrin Derivatives in a Mixed Solvent of Acetone and Water

The weakening effect of the addition of water on the complex formation was because of the preferential solvation of the anion, which served to screen it from interaction with the receptors [38]. Interestingly, the selectivity of H2PO4 for AcO increased in CD3CN/D2O 99/1 (v/v) as the solvent. When we used a 2% volume of water in CD3CN (CD3CN/D2O 98/2 (v/v)) as the solvent, we observed no induced chemical shift changes in the receptors (1-3).

Table 1. The association constants (K $^{106}$ [M$^{-1}$] in CD3CN at 298 K) for 1:1 complexes of CD-based receptors (1, 2, and 3) and quaternary ammonium salts (4c) and free energy (-ΔG [kJ/mol]) in CD3CN at 298 K, as evaluated by 1H-NMR titration experiments.

| Receptor   | Cl$^{-}$ (4a) | Br$^{-}$ (4b) | AcO$^{-}$ (4e) | H$_2$PO$_4$$^{-}$ (4f) |
|------------|---------------|---------------|----------------|-----------------------|
| 1a         | 310           | 25            | 6900           | 3300                  |
|            | (14.2)        | (8.0)         | (21.6)         | (20.1)                |
| 1b         | 230           | 20            | 4000           | 2000                  |
|            | (13.5)        | (7.4)         | (20.5)         | (18.8)                |
| 2a         | 250           | 23            | 6900           | 3900                  |
|            | (13.7)        | (7.8)         | (21.6)         | (20.5)                |
| 2b         | 215           | 22            | 4000           | 2700                  |
|            | (13.3)        | (7.7)         | (20.5)         | (19.6)                |
| 3a         | 290           | 22            | 7000           | 4000                  |
|            | (14.0)        | (7.7)         | (21.9)         | (20.9)                |
| 3b         | 275           | 20            | 4000           | 2500                  |
|            | (13.9)        | (7.4)         | (20.9)         | (19.4)                |

a) Errors were estimated to be 10%.

b) The 1H-NMR chemical shift changes of the receptors (1-3) in the presence of the anions (1-4e), and NO$_3$ (4d) were negligible in CD3CN.

c) Anions were used as their $\sigma$BuN$^+$ salts.

4. CONCLUSION

In conclusion, we demonstrated that hexakis(2,3-di-O-substituted) α- and β-CD-based anion receptors (1-3) can effectively bind with AcO$^{-}$ in a 1:1 manner in CD3CN. This binding is facilitated by cooperative hydrogen bond interactions between the anion and the primary alcoholic hydroxyl groups on C-6. The binding strength of the receptors (1) toward the anions depends on the basicity of the anions and the size of the binding pocket of the receptors. Interestingly, the selectivity of H$_2$PO$_4$ for AcO$^{-}$ increased when we used a water/acetonitrile mixture (CD3CN/D2O 99/1 (v/v)) as the solvent. This was due to the higher basicity of the AcO$^{-}$ anion, which interacted strongly with water. We also note that CD-based receptors can display chiral recognition due to the chiral environment of the recognition sites. Thus, achieving further functionalization by introducing chromophore or fluorophore may be a promising technique that can be used in various applications [39, 40].

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Figure 6. 1H-NMR titration of receptors (1a) with anions (a) 4a: Cl$^{-}$, (b) 4b: Br$^{-}$, (c) 4e: AcO$^{-}$, (d) 4f: H$_2$PO$_4$ $^{-}$ in CD3CN at 298 K indicating a change of the chemical shift of the protons (OH, Hf and Hg) as a results of added 4. Points are experimental and curves are calculated by non-linear regression.

Table 2. The association constants (K $^{106}$ [M$^{-1}$]) in CD3CN/D2O (99/1, v/v) at 298 K for 1:1 complexes of CD-based receptors (1, 2, and 3) and quaternary ammonium salts (4c) and free energy (-ΔG [kJ/mol]) in CD3CN/D2O (99/1, v/v) at 298 K, as evaluated by 1H-NMR titration experiments.

| Receptor | Cl$^{-}$ (4a) | AcO$^{-}$ (4e) | H$_2$PO$_4$$^{-}$ (4f) |
|----------|--------------|---------------|-----------------------|
| 1a       | 250          | 450           | 1200                  |
|          | (13.7)       | (15.1)        | (17.0)                |
| 1b       | 110          | 350           | 510                   |
|          | (11.7)       | (14.5)        | (15.4)                |
| 2a       | 60           | 210           | 1000                  |
|          | (10.1)       | (13.9)        | (17.1)                |
| 2b       | 150          | 380           | 620                   |
|          | (12.4)       | (14.7)        | (15.9)                |
| 3a       | 160          | 290           | 1400                  |
|          | (12.6)       | (13.1)        | (17.9)                |
| 3b       | 160          | 500           | 1100                  |
|          | (12.6)       | (15.4)        | (17.4)                |

a) Errors were estimated to be 10%.

b) Anions were used as their $\sigma$BuN$^+$ salts.
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