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NMR Chemical Shift Methods for Binding Constant Determination of an Organic Anion and α-Cyclodextrin

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Internal reference compounds suitable for proton chemical shift measurements of organic anions in deuterium oxide solutions are proposed and used to determine the binding constant of sodium hexane-1-sulfonate (SHS) and α-cyclodextrin (α-CD). The chemical shift of the methyl proton of sodium methyl sulfate (MeS), referred to external sodium 4,4-dimethyl-4-silapentane-1-sulfonate (DSS), changes linearly with the α-CD concentration, because of the volume magnetic susceptibility effect. The chemical shifts of the SHS methyl proton, referred to external DSS and corrected for this magnetic susceptibility effect, as well as referred to internal MeS and methanol (MeOH), provide reliable binding constants of SHS and α-CD. Therefore, MeS and MeOH are appropriate internal standards for organic anions. The present results serve not only for choosing appropriate internal references and the internal or external standard method for chemical shift measurements but also for correcting the chemical shift referred to an external standard.

NMR chemical shifts have frequently been used to investigate intermolecular interactions in solutions, such as host–guest docking, surfactant micellization, and donor–accepter complexation. This method utilizes the difference between the chemical shifts of a molecular species in the free state and in the bound state.[1–3]

The chemical shift is usually measured using an external or internal reference. A convenient reference signal is one that is sharp and well separated from other signals in the NMR spectrum. The use of an internal reference signal has the advantage that no volume susceptibility corrections are necessary. These procedures are satisfactory only when specific solvent and solution effects are unimportant. Sodium 3-(trimethylsilyl)-2,2,3,3-tetradeuteriopropionate and sodium 4,4-dimethyl-4-silapentane-1-sulfonate (DSS) have often been used for such primary internal references in aqueous solution systems.[4,5] These compounds, however, form complexes with cyclodextrins (CDs). For aqueous CD solutions, therefore, tetramethylammonium chloride (TMA), sodium methanesulfonate (MS), sodium methyl sulfate (MeS), and methanol (MeOH) were recommended as secondary internal references, because they are practically unbound to CDs.[6,7] TMA forms the ion-pair complex with benzenesulfonate ion, an anion, by electrostatic and hydrophobic interactions.[7,8] For such an anion, MS and MeS were recommended as secondary internal standards.[7] However, MS and MeS have never been used to determine the binding constant of any anionic guest and CD.

On the other hand, the external standard method has the advantage of inertness to the system to be measured and the disadvantage of necessity of volume susceptibility correction.[4,5] The chemical shift of TMA referred to external DSS changes linearly with increasing concentration of additive and this molar shift is proportional to the product of the molar volume of the additive and the difference in volume magnetic susceptibility between water and the additive.[8] We corrected this magnetic susceptibility effect on the chemical shift to determine the binding constant of CD inclusion;[7,8] for instance, the values of the binding constants of acetonitrile and α-CD were the same whether an internal or an external reference was used.[7] Most of the chemical shifts referred to external standards have not been corrected for the volume magnetic susceptibility effect. These uncertainties about the choice of an internal standard and the correction of chemical shifts referred to an external standard will attract the interest of researchers who use chemical shift data to investigate intermolecular interactions.

In this work, we investigate the chemical shifts of the methyl protons of MeS and MS using external DSS in aqueous α-CD solutions and analyze these data in terms of the volume magnetic susceptibility effect and α-CD inclusion. The binding constant of sodium hexane-1-sulfonate (SHS) and α-CD is determined from chemical shift data of the methyl proton of SHS referred to internal MeS, MS, and MeOH and to external DSS. It is shown that MeS and MeOH are appropriate internal standards for SHS in aqueous α-CD solutions. The external standard method also provides a reliable binding constant for this system, if an appropriate correction for the volume magnetic susceptibility effect has been carried out.

Experimental

Materials. Commercial samples of TMA (Nacalai Tesque Co.), MS, MeS, 99.9 atom% D deuterium oxide, DSS (Aldrich), SHS (Tokyo Kasei Organic Chemicals Co.), MeOH (Wako Pure Chemicals Co.), and α-CD (Ensuiko Seitou Co.) were used as received. These chemicals are of reagent grade.

NMR Measurements. All 300 MHz proton NMR spectra were recorded with a Varian XL-300 NMR spectrometer at 294.2 ± 0.5 K. Deuterium oxide was used for the preparation of all solutions. These solutions were prepared in volumetric flasks, so

that the molarity scale was employed as the concentration unit.

The NMR spectra for the external reference were recorded using a Wilmad WGS-5BL cylindrical coaxial tube. A 5 mmol dm^{-3} (mM) DSS deuterium oxide solution was placed in the inner tube and a sample solution was placed in the outer tube. The chemical shift of the methyl proton of 1 mM MeS, MS, or MeOH was measured as a function of α-CD concentration. For the determination of the binding constant of SHS and α-CD, the chemical shift of the methyl proton of 5 mM SHS, referred to external DSS, was also determined as a function of α-CD concentration.

Using an internal standard of 1 mM MeS, MS, or MeOH, we measured the chemical shift of the methyl proton of 5 mM SHS as a function of α-CD concentration and determined the binding constant of SHS and α-CD. In reference to internal 5 mM DSS, the chemical shifts of internal secondary standards of MeOH, MeS, MS, and TMA were determined to be 3.343, 3.740, 2.800, and 3.176 ppm, respectively.

Some 500 MHz spectra were recorded with a Jeol Lambda 500 spectrometer at 298.2 K. The chemical shift of the methyl proton of 1 mM MS was measured as a function of α-CD concentration.

Results

Chemical Shifts of MeS and MS Referred to External DSS. The singlet peaks of the methyl protons of MeS and MS appeared around 3.7 and 2.8 ppm on the 300 MHz NMR spectra. As Fig. 1 shows, the chemical shift variations, $\Delta\delta$, referred to external DSS, of these protons of MeS and MS changed linearly with the α-CD concentration, C_{CD}:

$$\Delta\delta = \delta - \delta_0 = aC_{CD} \quad (1)$$

Here, δ_0 denotes the chemical shift in the absence of CD. In Table 1 the observed molar shifts for MeS and MS are shown, together with related data. These changes reflect two effects, namely, the magnetic susceptibility change and α-CD inclusion.

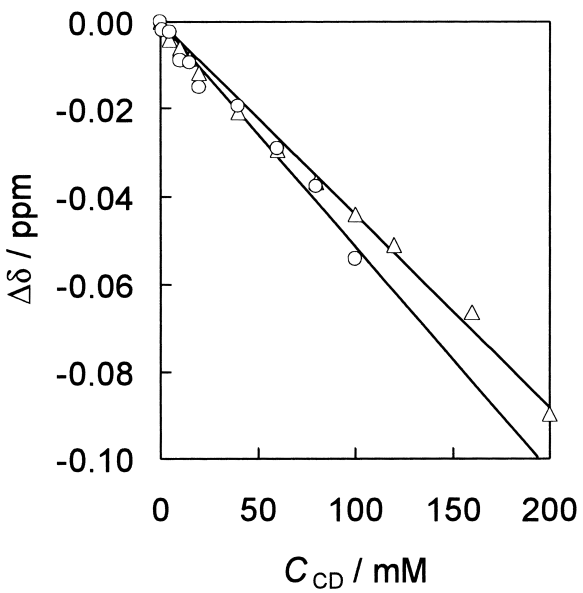

Fig. 1. Chemical shift variations of the methyl protons of MeS (triangles) and MS (circles), referred to external DSS, plotted against the α-CD concentration.

Table 1. Molar Chemical Shifts (ppm M^{-1}) of MS, MeS, MeOH, TMA, HDO, and α-CD with the α-CD Concentration, Determined by the External DSS Standard Method at 294.2 K

MeS	MS	TMA[a)]	MeOH[a)]	HDO[a)]	α-CD[b)]	Theory[c)]
−0.427	−0.494	−0.421	−0.401	−0.485	−0.420	−0.448

a) Taken from Ref. 6. b) Taken from Ref. 7. c) Taken from Ref. 8.

The volume magnetic susceptibility of an aqueous solution must change from that of deuterium oxide toward that of α-CD, as α-CD is added into water. From this viewpoint, we have given a theoretical a value for the aqueous α-CD solution:[8]

$$a = 4\pi(\chi_2 - \chi_w)V_2/3000 \quad (2)$$

Here, χ_w and χ_2 denote the volume magnetic susceptibilities of deuterium oxide and α-CD and V_2 is the molar volume of α-CD. Equation 2 holds true for ideal solutions that are contained in long and perfectly cylindrical coaxial tubes placed in a superconducting solenoid. In Eq. 2 we employed values of $\chi_w = -0.707\times10^{-6}$, $\chi_2 = -0.88\times10^{-6}$, and $V_2 = 611.4$ cm^3 mol^{-1} to obtain a theoretical value of $a = -0.448$ ppm M^{-1}. This χ_2 value was estimated from the volume magnetic susceptibilities of saccharides, because the volume magnetic susceptibility of α-CD in aqueous solution is not available.[8]

Because the observed a values for MeS and MS are close to the theoretical one (Table 1), most of the chemical shift changes are ascribed to the magnetic susceptibility effect. It is suggested that TMA is almost unbound to α-CD.[5] The a value for MeS is very close to that of TMA. This proximity suggests that MeS is also unbound to α-CD. However, the observed a value for MS is slightly larger than that of TMA. This difference suggests that MS is weakly bound to α-CD. If a completely unbound standard is available, the difference in chemical shift between it and MS is ascribed to α-CD inclusion. Furthermore, if this difference is determined very accurately over a wide concentration range of α-CD, one can estimate the binding constant of MS and α-CD.

Binding Constant Determination of α-CD and SHS Using External DSS. In the 300 MHz NMR spectrum of a deuterium oxide solution containing 5 mM SHS, the methyl proton of SHS appeared as a triplet signal around 0.8 ppm. The α-, β-, and intermediate methylene protons of SHS appeared as multiplet signals around 2.5, 1.5, and 0.9 ppm. We could determine most accurately the chemical shift of the methyl among these four signals of SHS. The chemical shift of this methyl signal of 5 mM SHS, referred to external DSS, is shown as a function of α-CD concentration in Fig. 2. This concentration dependence is caused by the 1:1 complex formation of SHS and α-CD:

$$\text{SHS} + \text{CD} = \text{SHS–CD} \quad (3)$$

Therefore, the observed chemical shift, δ, can be written as:

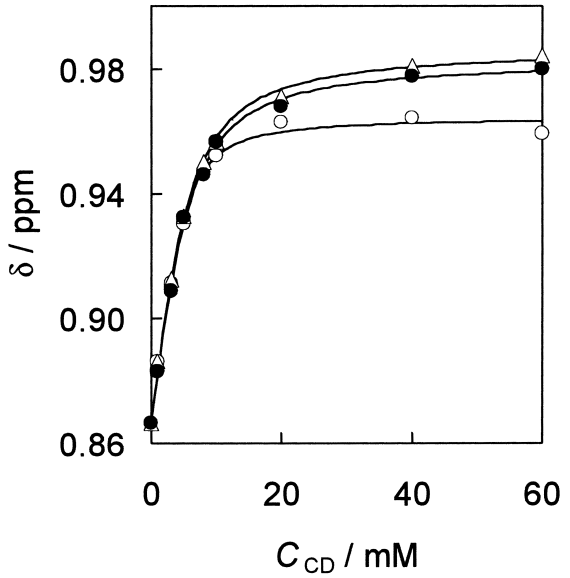

Fig. 2. Uncorrected (open circles) and corrected (open triangles) chemical shifts of the SHS methyl proton referred to external DSS and those referred to internal MeOH (closed circles), plotted against the α-CD concentration, while the SHS concentration was kept constant at 5 mM. Because the chemical shifts referred to internal MeS and MS standards overlap with the corrected and uncorrected external standard values, they are omitted for clarity. The solid lines are calculated from Eqs. 4–6 with the best fit binding constants and $\Delta\delta_{SHS-CD}$ values shown in Table 2.

$$\delta = ([SHS]\delta_{SHS} + [SHS\text{–}CD]\delta_{SHS-CD})/C_{SHS} = ([SHS]\delta_{SHS} + K_1[SHS][CD]\delta_{SHS-CD})/C_{SHS} \quad (4)$$

Here, δ_{SHS} and δ_{SHS-CD} denote the chemical shifts of the SHS methyl proton in the free and complexed states, K_1 is the equilibrium constant of complex formation, and C_{SHS} is the total concentration of SHS. The concentrations of free α-CD and SHS molecules are written as a function of C_{CD} and C_{SHS}:

$$[CD] = \{K_1C_{CD}-K_1C_{SHS}-1 + [(K_1C_{CD}-K_1C_{SHS}-1)^2 + 4K_1C_{CD}]^{1/2}\}/2K_1 \quad (5)$$

$$[SHS] = \{K_1C_{SHS}-K_1C_{CD}-1 + [(K_1C_{SHS}-K_1C_{CD}-1)^2 + 4K_1C_{SHS}]^{1/2}\}/2K_1 \quad (6)$$

Once δ_{SHS-CD} and K_1 are given, we can calculate δ at $C_{SHS} = 5$ mM as a function of C_{CD} from Eqs. 4–6. Thus, we determined the best fit values of $\Delta\delta_{SHS-CD} = 0.098$ ppm and $K_1 = 1172$ M^{-1} by nonlinear least-squares method, where $\Delta\delta_{SHS-CD}$ stands for the difference between the chemical shifts of SHS in the complexed and free states.

However, this analysis neglected the change in volume magnetic susceptibility of the aqueous α-CD solution. A corrected chemical shift of any proton in the aqueous α-CD solution can be calculated from Eq. 1 with the a value for TMA:

$$\delta_{cor} = \delta_{obsd} + 0.421C_{CD} \quad (7)$$

The open circles in Fig. 2 show the observed (uncorrected) chemical shifts, whereas the open triangles show the chemical shifts corrected using Eq. 7. The application of Eqs. 4–6 to these corrected chemical shifts yielded the best fit values of $\Delta\delta_{SHS-CD} = 0.120$ ppm and $K_1 = 510$ M^{-1} by nonlinear least-squares method. These values are summarized in Table 2.

Table 2. Binding Constants of SHS and α-CD and the Complexation-induced Chemical Shift Variations Determined from the Chemical Shifts of the SHS Methyl Proton, Referred to Internal and External Standards

Standard	K_1/M^{-1}	$\Delta\delta_{SHS-CD}$/ppm[a)]
Uncorrected external DSS	1172 (198)[b)]	0.098 (0.002)[b)]
Corrected external DSS	510 (39)	0.120 (0.001)
Internal MS	252 (33)	0.105 (0.003)
Internal MeS	430 (40)	0.126 (0.002)
Internal MeOH	516 (39)	0.117 (0.001)

a) $\Delta\delta_{SHS-CD}$ (= $\delta_{SHS-CD} - \delta_{SHS}$) for the SHS methyl proton.
b) Parentheses show standard deviations.

Binding Constant Determination of SHS and α-CD Using Internal Standards. For the determination of the binding constant of SHS and α-CD, the chemical shift of the methyl proton of 5 mM SHS, referred to an internal standard of 1 mM MeS, MS, or MeOH, was determined as a function of α-CD concentration up to 60 mM. The chemical shift values for MeOH are shown in Fig. 2. Because the values referred to internal MeS and MS standards overlap with corrected and uncorrected external standard values, they are omitted for clarity from Fig. 2. These chemical shifts were analyzed to determine the binding constant of SHS and α-CD by using Eqs. 4–6. As Table 2 shows, the binding constants, determined from three sets of the chemical shift data referred to internal MeS and MeOH and those referred to external DSS and then corrected for the magnetic susceptibility effect, are close to one another. Furthermore, these binding constants are close to the literature values of 500 and 379 M^{-1} obtained by the reaction kinetics[9] and the electric conductance.[10] However, it is notable that the binding constant determined from the chemical shift referred to internal MS is significantly smaller than these values. This discrepancy will be ascribed to some binding of MS to α-CD; then the signal of MS used as the internal standard will shift with the addition of α-CD.

Discussion

Chemical shifts of a nucleus in binary mixtures are determined as a function of composition and analyzed in terms of the difference in volume magnetic susceptibility between solute and solvent and intermolecular interactions (hydrogen bond, self-association, complex formation, acidic dissociation, and other reactions) between solute and solvent or two solutes.[4,5,11–14] For instance, the equilibrium formation constants of charge-transfer complexes have been determined by chemical shift measurements.[12,13] Recently, many artificial host molecules have been synthesized and chemical shift measurements have been used to determine their binding constants with a variety of guest compounds in aqueous solutions and organic solvents.[1,2] Because CDs, natural host molecules, include DSS into their cavities, DSS is an unsuitable internal standard.[6]

The addition of many solutes, such as saccharides, peptides,

and sodium chloride, into water can change the chemical shift of TMA, referred to external DSS, with the solute concentration. The reason for this concentration dependence was ascribed to the change in the magnetic susceptibility of water: the magnetic susceptibility of an aqueous solution approaches from that of water to that of the solute with its addition.[8] Thus, one must correct this effect on the chemical shift referred to the external standard. For instance, Eq. 7 gives an approximate method for correcting the observed chemical shift for the α-CD system. Instead of Eq. 7, a more rigorous equation consists of two correction terms:

$$\begin{aligned}\delta_{cor} &= \delta_{obsd} + 4\pi\{(\chi_{CD} - \chi_w)V_{CD}[CD] + \\ &\quad (\chi_{SHS-CD} - \chi_w)V_{SHS-CD}[SHS{-}CD]\}/3000 \\ &= \delta_{obsd} + 0.421[CD] + a_{SHS-CD}[SHS{-}CD] \qquad (8)\end{aligned}$$

Here χ_{CD} and χ_{SHS-CD} are the volume magnetic susceptibilities of α-CD and α-CD-SHS, V_{CD} and V_{SHS-CD} are the molar volumes of α-CD and α-CD–SHS, and a_{SHS-CD} denotes the molar shift of the α-CD–SHS complex caused by the volume magnetic susceptibility effect. To apply Eq. 8, we must estimate the a_{SHS-CD} coefficient from the observed chemical shift data by nonlinear least-squares method. Actually, we employed Eq. 7 under the assumption that a_{SHS-CD} is equal to an a_{CD} value of 0.421 ppm M^{-1}.

From chemical shifts obtained using internal and external standards, binding constants have been determined for various host-guest systems.[1–3,6–8,15–25] The external standard method has the advantage of inertness to the system to be investigated and the disadvantage of necessity of volume susceptibility correction. In most cases, uncorrected chemical shift data have been used for binding constant determination, resulting in substantial errors in the published chemical shifts and binding constants.[19–25] In a few cases, corrected external standard data as well as internal standard data have given reliable binding constants.[7,12,13]

Appropriate internal standards for binding constant determination should be as inert as possible to the system under investigation and should exhibit negligible changes in chemical shift with any molecular interactions. Such standards for aqueous systems include MeOH, TMA, MeS, MS, and HDO. Because MeOH is an uncharged molecule and has small binding constants of 0.9 M^{-1} and 0.3 M^{-1} for α-CD and β-CD, it is an excellent internal standard.[6] For the system of an anionic guest and α-CD, chemical shift data referred to internal MeOH gave reasonable binding constants.[15] Though the binding constants of TMA with CDs have not been determined, they would be smaller than that of MeOH. TMA is an excellent internal standard for neutral and cationic compounds. Because the signal of MeS appears at slightly higher field than the CD H5 proton signal, we can distinguish between these signals. For anionic compounds, MeS and MeOH are excellent internal standards and the HDO signal may be used as a good internal standard.[16] Because this HDO signal is very sensitive to temperature, temperature must be kept as constant as possible. Because the H1 proton of CD is located in the exterior of the cavity, its chemical shift remains almost unchanged with complexation. This proton signal was used as an internal standard.[17] Though DSS was used as the internal standard,[18] it is unsuitable for CDs because of its entrapment into the CD cavity.[6]

We attempted to determine the binding constants of MS and α-CD from two sets of the observed chemical shift data, referred to external DSS and to internal α-CD H1. These two binding constants are not reliable, because the observed changes in chemical shift are too small. On the other hand, the logarithms of binding constants of α-CD and sodium alkane-1-sulfonates change linearly with the number, n_C, of carbon atoms of alkane-1-sulfonates (n_C = 4 to 6).[9] From this linearity, the binding constant of MS is extrapolated to be 1.3 M^{-1}.

The thermodynamic binding constant is defined with the activities of reactants and products, instead of their concentrations. The activity coefficient of α-CD in water is available in the literature; for instance, the activity coefficient at C_{CD} = 0.06 mol kg^{-1} is 0.93.[26] However, this value cannot be employed in the presence of a guest and its complex with α-CD. It is more difficult to determine or estimate the activity coefficients of a guest and its complex in the equilibrium mixture. This will cause more errors in the binding constant estimated as the concentrations of reactants and products are increased.

Diffusion constants obtained by pulsed-field gradient NMR spectroscopy have been often used for binding constant determination. This method is based on the difference between the diffusion constants of a molecular species in the free and bound states, though it neglects the concentration dependence of the diffusion constant.[2,27] Because the diffusion constant slightly depends on the concentration, this dependence must be taken into consideration.[28–30] The chemical shift method has been employed to determine the binding constants of systems forming two or more complexes.[16,25,31] For these complicated systems, however, the diffusion constant method will be less useful than the chemical shift method.

Chemical shift data are utilized in all fields of chemistry. In the internal standard method it is usually not easy to find a completely inert reference compound suitable for the systems investigated. For aqueous solutions of organic anions, MeS and MeOH are appropriate internal references. In the external standard method the volume magnetic susceptibility of the sample slightly changes with the addition of any solute, so that the chemical shift must be corrected for this difference. Because this correction has not usually been carried out, the binding constants determined from the uncorrected chemical shifts are inaccurate. The present results serve not only for choosing appropriate internal references and the internal or external standard method for chemical shift measurements but also for correcting the chemical shift referred to an external standard.

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