Small-angle neutron scattering study of specific interaction and coordination structure formed by mono-acetyl-substituted dibenzo-20-crown-6-ether and cesium ions

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This study uses small-angle neutron scattering (SANS) to elucidate the coordination structure of the complex of mono-acetyl-substituted dibenzo-20-crown-6-ether (ace-DB20C6) with cesium ions (Cs+). SANS profiles obtained for the complex of ace-DB20C6 and Cs+ (ace-DB20C6/Cs) in deuterated dimethyl sulfoxide indicated that Cs+ coordination resulted in a more compact structure than the free ace-DB20C6. The data were fitted well with SANS profiles calculated using Debye function for scattering on an absolute scattering intensity scale. For this theoretical calculation of the scattering profiles, the coordination structure proposed based on density functional theory calculation was used. Consequently, we conclude that the SANS analysis experimentally supports the proposed coordination structure of ace-DB20C6/Cs and suggests the following: (1) the complex of ace-DB20C6 and Cs+ is formed with an ace-DB20C6/Cs molar ratio of 1/1 and (2) the two benzene rings of ace-DB20C6 fold around Cs+ above the center of the crown ether ring of ace-DB20C6.

Keywords: analysis; cesium; neutron

1. Introduction

Following the Fukushima Daiichi nuclear disaster in Japan in 2011, radioactive cesium was released into the northern Kanto and southern Tohoku areas [1–5]. Moreover, a huge amount of radioactive cesium still remains in the containment vessel of the atomic power reactors at the facility. The development of physicochemical techniques for removing cesium ions (Cs+) is required to decrease the radioactivity in these areas. The selective recognition of Cs+ from other cations, such as Na+ and K+ (11), is crucial for achieving remediation and for reducing the volume of secondary contamination.

Crown ethers [6–10] are macrocyclic organic compounds that exhibit electrostatic interactions between an alkali metal ion and the multiple oxygen atoms in the ether ring. As a result of these interactions, the alkali metal ion is bound inside the ring, forming a stable coordination complex in solution. Generally, the coordination between a crown ether and a metal ion is fully stabilized when the ratio of the ionic radius of the metal to the radius of the ring is approximately 1, whereas the stability decreases as the ratio deviates from 1 [11]. This size fitting effect for the coordination of the crown ethers particularly holds for alkali metals and alkaline earth metals. Nevertheless, the size recognition effect is not sufficient for the selective adsorption of Cs+ through changing the ring size of crown ethers to isolate Cs+ from other alkali metals, such as Na+ and K+ [11,12], which are abundant in the environment. Therefore, we believe that an extra interaction is needed to enhance the ionic selectivity of crown ethers for Cs+ before they can be used as a decontamination reagent.

Against this background, we focused on a derivative of benzo-crown ether [7,13], mono-acetyl-substituted dibenzo-20-crown-6-ether (ace-DB20C6) [14], that forms a stable complex with Cs+. On the basis of the density functional theory (DFT) calculation method [15,16], we have previously suggested that the stability
the complex formed by ace-DB20C6 and Cs⁺ (ace-DB20C6/Cs) arises from the interaction between the π-orbitals of the two benzene rings and the d-orbital of Cs⁺ [17] (Supplementary data). That is, π-electrons of the benzene rings would be donated to the vacant d-orbitals. The calculation indicated that Cs⁺ is stably bound above the center of the ether oxygen ring by the two benzene rings as shown in Figure 1 and ace-DB20C6 adopts the folded structure. However, the single-crystal structure of ace-DB20C6/Cs has not yet been confirmed experimentally.

In this work, we performed experiments to confirm the complex structure of ace-DB20C6/Cs for advancing the development of effective adsorbents for Cs⁺ in solution. We use small-angle neutron scattering (SANS) observations of ace-DB20C6/Cs in deuterated dimethyl sulfoxide (DMSO-d₆) to elucidate the coordination structure in solution. SANS profiles obtained for ace-DB20C6 and ace-DB20C6/Cs in DMSO-d₆ were analyzed based on the Guinier approach [18] and were compared against the SANS profiles calculated from the model of coordinate structure using the Debye formula [19–21] on an absolute scattering intensity scale. The SANS results provide an evidence that the coordination structure of ace-DB20C6/Cs is as predicted by the DFT calculation (Supplementary data).

2. Experimental

2.1. Materials

Reagent grade DMSO-d₆ and cesium perchlorate (CsClO₄) were purchased from Wako Pure Chemical Industries Co., Ltd. (Osaka, Japan) and used without further purification. The water used in this study was deionized by a Millipore Milli-Q purification system (Merck, Millipore, Billerica, MA). Ace-DB20C6 [14] was synthesized from a deprotonated phenoxide derivative of 3,5-dihydroxyacetophenone (Tokyo Chemical Industry Co., Ltd., Tokyo, Japan) and 1,3-bis[2-(2-chloroethoxy)ethoxy]benzene. Note that 1,3-bis[2-(2-chloroethoxy)ethoxy]benzene can be synthesized from deprotonated phenoxide of resorcinol (Tokyo Chemical Industry Co., Ltd.) and an excess amount of bis(2-chloroethyl)ether (Wako) according to the literature [22]. The mass density of ace-DB20C6 (d_{ace-DB20C6} = 1.293 g/mL) was measured by using a density meter (DMA-4500M, Anton Paar Co., Ltd., Graz, Austria).

2.2. UV/vis spectroscopic titration

UV/vis spectroscopic titration [23] was carried out by in situ addition of 10 μL aliquots of CsClO₄ (60 mM) in 3 mL of DMSO solution, containing 0.1 mM of ace-DB20C6, in order to describe the speciation diagram relating the complexation of ace-DB20C6/Cs. The change of UV/vis spectra during the titration was monitored with a V-560 spectrometer (JASCO, Tokyo, Japan) in the range of 265–360 nm, which corresponds to the absorption band of ace-DB20C6.

2.3. Sample preparation for SANS measurements

Four samples (samples 1 to 4, listed in Table 1) of the mixtures of ace-DB20C6/Cs and ace-DB20C6 in DMSO-d₆ for SANS measurement were prepared by dissolving 100 mM of ace-DB20C6 and 0–100 mM of CsClO₄ in DMSO-d₆, where the volume fraction of feed ace-DB20C6 (φ_{ace-DB20C6}) was 0.031. The concentrations of the feed ace-DB20C6 ([ace-DB20C6]_{fd}) and CsClO₄ ([CsClO₄]_{fd}) in DMSO-d₆, the concentrations of ace-DB20C6/Cs ([ace-DB20C6/Cs]_{eq}) in the equilibrium state, and the molar fractions of ace-DB20C6/Cs (f_{ace-DB20C6/Cs}) and ace-DB20C6 (f_{ace-DB20C6}) in the equilibrium state are shown in Table 1, where [ace-DB20C6/Cs]_{eq} = 100 mM – [ace-DB20C6]_{eq}, f_{ace-DB20C6/Cs} and f_{ace-DB20C6} were evaluated by the speciation study of ace-DB20C6/Cs complexation as will be explained in Section 4.1 in detail. Each solution from 1 to 4 was loaded into a quartz cell (path length: 2 mm). The quartz cell was then placed in the incident beam path of neutrons, and the SANS measurements were performed. DMSO-d₆ was used to

| Sample | [ace-DB20C6]_{fd} (mM) | [CsClO₄]_{fd} (mM) | [ace-DB20C6/Cs]_{eq} (mM) | f_{ace-DB20C6/Cs} | f_{ace-DB20C6} |
|--------|-----------------------|-------------------|--------------------------|-------------------|---------------|
| 1      | 100                   | 0                 | 0                        | 0                 | 1             |
| 2      | 100                   | 30                | 29.6                     | 0.296             | 0.704         |
| 3      | 100                   | 50                | 49.1                     | 0.491             | 0.509         |
| 4      | 100                   | 80                | 77.0                     | 0.770             | 0.230         |
provide sufficient neutron scattering contrast between solutes (ace-DB20C6/Cs and ace-DB20C6) and solvent (DMSO-6d6) and to decrease the incoherent scattering intensity from the solvent.

2.4. Small-angle neutron scattering measurements

SANS measurements were performed with the time-of-flight extended q-range SANS (EQ-SANS) spectrometer of the Spallation Neutron Source (SNS), Oak Ridge National Laboratory, USA [24]. A sample-to-detector distance of 4.0 m was employed with a single band of neutrons with wavelengths (λ) from 2.0 to 5.6 Å. This configuration of the EQ-SANS provides a momentum transfer, q (= (4πλsinθ/2), where θ is the scattering angle), range of 0.01 Å⁻¹ < q < 0.5 Å⁻¹. The divergence of the incident beam was defined by using a 25 mm diameter source aperture and a 10 mm diameter sample aperture. The scattered neutrons were detected with a two-dimensional position-sensitive 3He detector of 1.0 × 1.0 m, composed of tube detectors providing 256 × 192 pixels. Data reduction followed standard procedures, as implemented in the Mantid software package [25]. Briefly, the scattering data were corrected for wavelength-dependent sample transmission, for detector counting efficiency, and for instrumental background on a pixel-to-pixel basis. The reduced scattered intensity was then azimuthally averaged. Data output by the reduction were in absolute units of reciprocal centimeters through a scale factor determined by measuring a porous SiO2 standard [26]. After subtracting the scattering contribution of the empty quartz cell from that of the sample, the contribution to the signal resulting from the solvent (DMSO-6d6) was subtracted by considering the volume fraction of DMSO-6d6 in the sample solution. Incoherent scattering from hydrogen, estimated as a constant value, was also subtracted from the signal to produce net absolute scattered intensity. The corrected scattered intensity distributions are designated as I(q) hereafter.

3. Theoretical calculation of SANS profiles

We numerically analyzed the SANS profiles to test the coordination structure of ace-DB20C6/Cs. The scattering functions of ace-DB20C6/Cs and ace-DB20C6, IS(q) (X: ace-DB20C6/Cs or ace-DB20C6), in DMSO-6d6 were calculated using the Debye formula [19–21]. When the positions of all the atoms in the single molecule are known,

\[
I_S(q) = \frac{n}{\sum_i \Delta b_i^2 A_i(q)^2 + \sum_i \sum_j \Delta b_i \Delta b_j A_i(q) A_j(q) \sin qr_{ij}/qr_{ij} },
\]

where n [= 6.0 × 10¹⁴ cm⁻³] is the number of molecules per unit volume in solution, which can be defined as \(n = \phi_X/V_X\), where \(\phi_X\) and \(V_X\) are the volume fraction and the volume of the solute, respectively, and \(r_{ij}\) is the distance between the \(i\)th and \(j\)th atoms that depends on the positions of \(r_i\) and \(r_j\) of the \(i\)th and \(j\)th atoms, respectively, giving \(r_{ij} = |\vec{r}_i - \vec{r}_j|\). The scattering contrast difference between \(i\)th atom and DMSO-6d6 (Δbi) and the form factor amplitude for the \(i\)th atom [\(A_i(q)\)] are given by

\[
\Delta b_i = \frac{b_i}{v_i} - \rho_{\text{DMSO-6d6}}
\]

and

\[
A_i(q) = 4\pi \int_0^\infty x^2 \exp\left(-\frac{x^2}{2\sigma_i^2}\right) \sin q x \frac{q x}{q x} dx,
\]

where \(b_i\) and \(v_i\) are the neutron scattering length and the excluded volume of the \(i\)th atom, respectively. \(\rho_{\text{DMSO-6d6}} = 5.28 \times 10^6 \text{cm}^{-2}\text{mol}^{-1}\) is the neutron scattering length density of DMSO-6d6. Because the \(i\)th atom is capable of moving within the limit of the excluded volume, we assume that \(A_i(q)\) follows a Gaussian distribution function with standard deviation \(\sigma_i\), which is related to \(v_i\) by following the equation:

\[
\sigma_i = \frac{1}{\sqrt{2\pi}} v_i^{1/3}.
\]

We need to know the numeric values of \(\tau^7_i\), \(\tau^7_j\), and \(v_i\) in Equation (1) for calculating the experimental scattering curves of ace-DB20C6/Cs and ace-DB20C6. For \(\tau^7_i\) and \(\tau^7_j\), the positions of all the atoms in the single ace-DB20C6/Cs and ace-DB20C6 molecules in this study were given by our previous DFT calculations (Supplementary data) and the crystal structure analysis [27], respectively. The values of \(v_i\) were determined in the following manners, (1)–(3). For (1), we assumed that the radius of the \(i\)th atom was half the averaged bond length (\(l_{av,i}\)) between the \(i\)th atom and all neighboring atoms. However, the ionic radius of Cs⁺ (\(r_{Cs}^+\)) [28] was used to \(v_i = 4 \pi r_{Cs}^+ r_{Cs}^+/3\) for cesium in ace-DB20C6/Cs. For (2), the whole value of the apparent excluded volume for all atoms in single ace-DB20C6 [\(V_{\text{app}} = \Sigma(4\pi L_{av,i}^3)/3\)] is compared with the real volume [\(V_{\text{ace-DB20C6}} = M_{\text{ace-DB20C6}}/N_A a_{\text{ace-DB20C6}}\)] to obtain the adjustment factor, \(k\) (\(V_{\text{ace-DB20C6}} = kV_{\text{app}}\), where \(M_{\text{ace-DB20C6}}\) is the molecular weight of ace-DB20C6 (= 402.4) and \(N_A\) is Avogadro’s number. For (3), \(v_i\) was defined by \(v_i = k(4\pi L_{av,i}^3)/3\).
4. Results and discussion

4.1. UV/vis spectroscopic titration and speciation diagram

UV spectra obtained during the titration are shown in Figure 2. These spectra change as the concentration of CsClO₄ in DMSO increases; that is, the absorption maxima at around 275 nm decreases as the concentration of Cs⁺ increases. The absorption at 295 nm or higher increased slightly as highlighted in the inset of Figure 2.

The equilibrium constant for coordinating ace-DB20C₆/Cs (\( K = \frac{[\text{ace-DB20C₆/Cs}]_{\text{eq}}}{[\text{free Cs}]_{\text{eq}}[\text{ace-DB20C₆}]_{\text{eq}}} \)) can be calculated as \( K = 1.12 \times 10^3 \) (M⁻¹) with the HYPERQUAD program [29], which fitted all the UV/vis spectra obtained during the titration with complete consistency. [free Cs]eq is the concentration of uncoordinated Cs⁺ in the equilibrium state.

Here, we assume that ace-DB20C₆/Cs is formed with the molar ratio of ace-DB20C₆/Cs = 1/1 in the numerical analysis of the UV spectra obtained during the titration. When the molar ratio of ace-DB20C₆/Cs⁺ = 2/1 is considered as one of the coordination species in DMSO, the UV spectra experimentally obtained cannot be reproduced by the calculation using HYPERQUAD program [29]. This fact indicates that the complex between ace-DB20C₆ and Cs⁺ tends to be formed by the ratio of ace-DB20C₆/Cs = 1/1, and thus, the complex formed with the molar ratio of ace-DB20C₆/Cs = 2/1 is none or minor presumably in DMSO in this titration.

Based on the value of \( K \), [ace-DB20C₆/Cs]eq, [ace-DB20C₆]eq, and [free Cs]eq are calculated with the HySS program [30], giving the speciation diagram for all the components, ace-DB20C₆/Cs, ace-DB20C₆, and free Cs⁺, in DMSO. Figure 3 shows the speciation diagram of [ace-DB20C₆/Cs]eq, [ace-DB20C₆]eq, and [free Cs]eq in DMSO as a function of the titrated CsClO₄ concentration ([CsClO₄]tit). [ace-DB20C₆/Cs]eq increases from the initial stage of CsClO₄ titration, whereas [ace-DB20C₆]eq decreases simultaneously. Finally, almost all ace-DB20C₆ coordinates with Cs⁺ above [CsClO₄]tit = 0.2 (M). In contrast, [free Cs]eq increases linearly starting at [CsClO₄]tit = 0.1 (M). To examine the coordination structure of ace-DB20C₆/Cs in DMSO-d₆ with different f_{ace-DB20C₆/Cs} values (samples 1–4, see Table 1), SANS measurements were employed.

4.2. Concentration dependence of ace-DB20C₆/Cs SANS profiles

Figure 4 shows the SANS profiles obtained for samples 1–4, which had different values of f_{ace-DB20C₆} and f_{ace-DB20C₆/Cs} as shown in Table 1. The value of \( \phi_{\text{ace-DB20C₆}} + \phi_{\text{ace-DB20C₆/Cs}} \) is equal to 0.031 in all samples, where \( \phi_{\text{ace-DB20C₆/Cs}} \) is the volume fraction of ace-DB20C₆/Cs. In case of such dilute solution system, the
SANS profile can be reproduced approximately solely by the form factor of the solute [31], because the inter-particle interaction of the solutes, which is accounted for by a function termed the structure factor, is negligible. Therefore, all SANS profiles from samples 1 to 4 are solely attributed to the form factors of ace-DB20C6/Cs and ace-DB20C6.

The scattering intensity in the low-\(q\) region (\(q < 0.1 \text{ Å}^{-1}\)) and the \(q\) dependence in the higher-\(q\) region (\(q > 0.2 \text{ Å}^{-1}\)) exhibit systematic changes with increasing \(f_{\text{ace-DB20C6/Cs}}\). In the low-\(q\) region, the forward scattering intensity \(I(q)\) at the limit of \(q \rightarrow 0\), \(I(q) = 0\), slightly increases in the range of 0.02 to 0.03 (cm\(^{-1}\)). In contrast, in the high-\(q\) region, the scattering intensity level starts to decrease according to the power law for scattering, \(I(q) \sim q^{-\alpha}\), where the exponent \(\alpha\) characterizes the \(q\) dependence. The characteristic \(q\) position, which starts to decrease in intensity at this position, moves toward higher \(q\) as the Cs\(^+\) concentration increases, indicating that the average size of the solutes becomes smaller. We carried out an analysis of the SANS profiles to evaluate the average size of the solutes. We carried out the calculation of the scattering curves with absolute scattering intensity for both ace-DB20C6/Cs and ace-DB20C6.

A Guinier plot (\(\ln I(q)\) versus \(q^2\)), which fit the experimentally observed SANS profiles in Figure 5(a) are the best-fit lines for Equation (5), enabling \(R_{g,av}\) and \(I(q = 0)\) to be estimated from the slope and intercept of the line, respectively. The solid lines in Figure 5(a) are the best-fit lines for Equation (5), which fit the experimentally observed SANS profiles (filled circles) very well in the low-\(q\) region. The evaluated \(R_{g,av}\) for the solute and \(I(q = 0)\) are plotted as a function of \(f_{\text{ace-DB20C6/Cs}}\) (filled circles, Figure 5(b) and 5(c)). At \(f_{\text{ace-DB20C6/Cs}} = 0\) (ace-DB20C6 = 1) in sample 1, \(R_{g,av} (4.6 \text{ Å})\) indicates the size of the free ace-DB20C6 in DMSO-\(d_6\). \(R_{g,av}\) decreases linearly with \(f_{\text{ace-DB20C6/Cs}}\) (dashed line, Figure 5(b)), demonstrating that the ace-DB20C6/Cs adopts a more compact structure than the free ace-DB20C6.

4.3. Analyses of ace-DB20C6/Cs and ace-DB20C6 coordination structure

We carried out the calculation of the scattering curves with absolute scattering intensity for both ace-DB20C6/Cs and ace-DB20C6 in DMSO-\(d_6\) as described above. The results of the calculation with Equation (1) are shown in Figure 6. We note that the scattering curves for ace-DB20C6/Cs, \(I_{\text{ace-DB20C6/Cs}}(q)\) and ace-DB20C6, \(I_{\text{ace-DB20C6}}(q)\), in DMSO-\(d_6\) correspond to the cases of \(f_{\text{ace-DB20C6/Cs}} = 1\) and \(f_{\text{ace-DB20C6}} = 1\) (solution 1), respectively.

To test the DFT-derived coordination structure of ace-DB20C6/Cs, we compared the experimental data with the scattering curves calculated by the model. To test if the previously proposed coordination structure of ace-DB20C6/Cs (Figure 1(b)) is correct, the SANS profiles obtained for samples 1–4 was modeled according to the following:

\[
I(q) = f_{\text{ace-DB20C6/Cs}} I_{\text{ace-DB20C6/Cs}}(q) + f_{\text{ace-DB20C6}} I_{\text{ace-DB20C6}}(q).
\]

(6)

Only one parameter, \(f_{\text{ace-DB20C6}}\) (since \(f_{\text{ace-DB20C6}} = 1 f_{\text{ace-DB20C6/Cs}}\)), was refined to obtain the best fit for the data to reproduce the experimental SANS profile. Figure 5. (a) \(\ln I(q)\) plotted as a function of \(q^2\), according to Equation (1). Solid black lines show best-fit theoretical lines from Guinier’s law. Average radius of gyration, \(R_{g,av}\), and \(I(q = 0)\) (filled circles) with error are plotted as a function of \(f_{\text{ace-DB20C6/Cs}}\) value, shown Table 1, in (b) and (c), respectively. Dashed line in (b) is a visual guide.
Figure 6. Theoretical scattering profiles for ace-DB20C6/Cs, $I_{\text{ace-DB20C6/Cs}}(q)$ and ace-DB20C6, $I_{\text{ace-DB20C6}}(q)$ in DMSO-$d_6$, shown by dashed and solid lines, respectively. Profiles were reproduced by the Debye formula (Equation (1)).

Table 2. Summary of characteristic parameters determined by model analysis of SANS (see Equation (6)) for ace-DB20C6/Cs and ace-DB20C6 mixture in DMSO-$d_6$.

| Sample | $f_{\text{ace-DB20C6/Cs}}$ | 1 | 2 | 3 | 4 |
|--------|--------------------------|---|---|---|---|
|        | 0.91 ± 0.06              | 0.64 ± 0.03 | 0.47 ± 0.02 | 0.28 ± 0.02 |

Note that the difference between the values of $f_{\text{ace-DB20C6/Cs}}$ obtained here and those shown in Table 1 provides information whether the coordination structure of ace-DB20C6/Cs proposed is correct or not. The solid black lines in Figure 4 show the best-fit theoretical scattering curves from Equation (6). The values of the parameter obtained here for $f_{\text{ace-DB20C6/Cs}}$ are summarized in Table 2. These parameter values shown in Tables 1 and 2 are consistent within 15%. This result leads us to the conclusion that SANS analysis experimentally supports the coordination structure of ace-DB20C6/Cs and lend credence to the proposal that the driving force behind Cs$^+$ coordination is an interaction between the $\pi$-electrons of the two benzene rings and the $d$-orbital of Cs$^+$.

5. Conclusion

The coordination structure of ace-DB20C6/Cs, which we studied by SANS, is important for understanding its stability. Guinier analysis of the SANS profiles of samples 1 to 4 showed that ace-DB20C6/Cs is more compact than ace-DB20C6. Moreover, these SANS profiles can be reproduced by the structure obtained from DFT calculations for ace-DB20C6/Cs and the crystal structure analysis of ace-DB20C6. The confirmation of the predicted coordination structure presented here will enable developing a deeper understanding of the special interaction between the $\pi$-electrons of the benzene rings and Cs$^+$ that will contribute to the further development of these materials for separating radioactive Cs in solution.

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Disclosure statement

No potential conflict of interest was reported by the authors.

Supplemental data

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