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Short Communication

Identification of number and type of cations in water-soluble Cs^+ and Na^+ calix[4]arene-bis-crown-6 complexes by using ESI-TOF-MS

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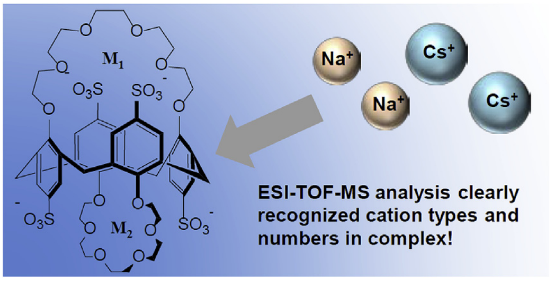
HIGHLIGHTS

- Water-soluble calix[4]arene-bis-crown-6 (W-BisC6) was synthesized for Cs^+ removal.
- W-BisC6-cations complex was prepared in the presence of both Cs^+ and Na^+.
- Number and type of cations in W-BisC6-cations complex was identified by ESI-TOF-MS.
- Helpful for rapid characterization of complex during Cs^+-wastewater treatment.

GRAPHICAL ABSTRACT



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ABSTRACT

The treatment of cesium-contaminated wastewater has become one of the biggest issues. The selective Cs^+ removal from wastewater containing competitive alkali metal ions such as Na^+ is desired to reduce the volume of sludge. Therefore, the present work focused on water-soluble calix[4]arene-bis-crown-6 (W-BisC6) to selectively capture Cs^+. For characterization of the complex, UV–vis spectroscopy is commonly used, however, due to the limited availability of information it can be hard to quickly identify the specific structures of some complexes. In this work, the electrospray ionization time of flight spectrometry (ESI-TOF-MS) is successfully utilized to identify the number and type of cations in W-BisC6-cation complexes. ESI-TOF-MS accurately recognized 4 types of complex (W-BisC6–Na^+, W-BisC6–Cs^+, W-BisC6–$2Na^+$, W-BisC6–Na^+–Cs^+), and the experimental and simulated results were almost perfectly matched. It also revealed the difficulty of W-BisC6–$2Cs^+$ complex formation under the present conditions. Thus, this technique is significantly helpful for rapid identification of the specific structures of complexes during Cs^+-contaminated wastewater treatment.

1. Introduction

The treatment of ^{137}Cs-contaminated wastewater has become one of the biggest issues in Japan after the Fukushima nuclear power plant accident in 2011. The current treatment consists of a combination of adsorption by zeolite and flocculation. However, the volume of ^{137}Cs-containing sludge is increasing on a daily basis (Tokyo Electric Power Company, 2017). Furthermore, the long half-life of ^{137}Cs ($t_{1/2} = 31.2$ years) poses storage problems. Therefore, the volume of sludge generated should be minimized as much as possible.

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Selective cesium capture from wastewater, especially in the presence of competitive alkali metal ions such as Na^+, is strongly desired to reduce the volume of sludge. Calix[4]arene is a macrocyclic compound well-known as a building block for synthetic receptors of various molecules (Gutsche, 1998; Mandolini and Ungaro, 2000; Asfari et al., 2001). Calix[4]arene-bis-crown-6 (BisC6) **1** (Fig. 1) showed particularly high selectivity for cesium removal from radioactive liquid wastes containing other alkali metal ions (Asfari et al., 1995; Lamare et al., 1997; Mohapatra et al., 2006; Zhou et al., 2013). This is due to the suitable size of the cavity in BisC6, as well as stabilization from the crown ether's oxygen donors and π-electrons of the phenyl groups in the calixarene. Furthermore, water-soluble properties are desirable for complexation with Cs^+ in the aqueous phase, improving Cs^+/Na^+ selectivity (Nicod et al., 1998; Mathieu et al., 2001; Pellet-Rostaing et al., 2001, 2003). Thus, water-soluble BisC6 is a promising compound for the selective removal of ^{137}Cs from wastewater.

Complexation with Cs^+ is commonly judged by changes in absorbance using Ultraviolet–visible (UV–vis) spectroscopy. However, there is limited information available from UV–vis analysis, which makes it difficult to identify the specific structure of complexes. It becomes more complicated when the ligands form complexes with several kinds of ions. In order to understand the nature of complex formation in detail, specific information, such as the molecular weight of the complex and coordination number of the ions, will be very important.

In general, electrospray ionization mass spectrometry (ESI-MS) is applied for the characterization of calixarene derivatives. ESI is a soft ionization desorption technique, which makes it possible to ionize calixarenes without fragmentation. Since 2000, the number of reports describing the identification of cation–calixcrown complexes has increased. However, it is still not known whether the identification of water-soluble cation–calixcrown complexes is possible using ESI-MS. Furthermore, ESI combined with time of flight mass spectrometry (ESI-TOF-MS) has never been applied for cation–calixcrown identification to the best of our knowledge. This work sheds light on the effectiveness of ESI-TOF-MS analysis for the identification of cation type and number in water-soluble Na^+ and Cs^+ BisC6 (W-BisC6) complexes.

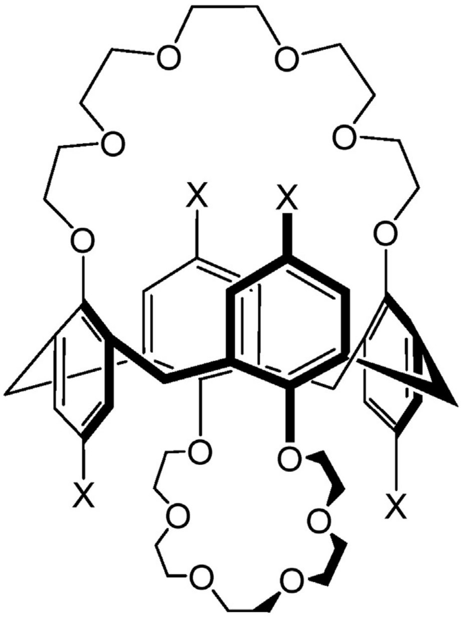

Fig. 1. Structures of BisC6 **1** (X = H) and W-BisC6 **2** ($X = SO_3Na$).

2. Experimental

2.1. Synthesis of W-BisC6

W-BisC6 **2** was prepared from calix[4]arene via BisC6 **1** according to reports by Asfari et al. (1995) and Nicod et al. (1998). The detailed procedure and NMR results are summarized in the Supporting information (SI).

2.2. UV–vis studies

For UV–vis analysis, 4 sets of **2** and Cs^+ mixed water solution were prepared. The concentration of **2** was fixed to 1.3×10^{-6} M, Cs^+ concentration were set to 1.0×10^{-4} M, 2.0×10^{-4} M, 4.0×10^{-4} M, and 8.0×10^{-4} M, respectively. The pH of each solution was adjusted to 11 by NaOH addition. UV–vis spectra between 190 and 250 nm of were recorded on a U-5100 (Hitachi Ltd.).

2.3. ESI-TOF-MS studies

For ESI-TOF-MS analysis, mixed solution of **2** (1.6×10^{-5} M) and Cs^+ (1.3×10^{-6} M) was prepared, which was analyzed by using a micrOTOF II (Bruker Corporation). The measurement conditions of ESI-TOF-MS are following: scanning range: $m/z = 50–3000$; capillary voltage: 4000 V; end plate offset: −500 V; dry heater: 30 °C; sample flow rate: 180 μL/h; solvent: H_2O. The simulation values were calculated based on elemental composition of W-BisC6 and their complexes and natural isotope ratio of each element.

3. Results and discussion

3.1. UV–vis studies

The UV–vis studies of **2** were carried out in the presence and absence of 4.0×10^{-4} M Cs^+ (Fig. 2). The absorbance was reduced in the presence of Cs^+ compared to that in the absence of Cs^+, indicating that Cs^+ was incorporated in **2**. This result is in agreement with the previous work (Nicod et al., 1998).

The stability constant, β_n, of the W-BisC6–Cs^+ complex was determined using equation (1) which corresponds to the equilibrium shown in equation (2), where n is the coordination number of Cs^+. Cs^+ concentrations of 1.0×10^{-4}, 2.0×10^{-4}, 4.0×10^{-4} and 8.0×10^{-4} M were analyzed. Foster-Hammick-Wardley plots

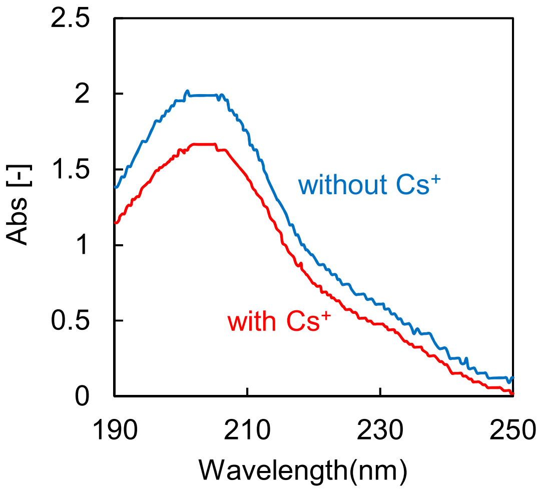

Fig. 2. UV–vis spectra of W-BisC6 in the presence and absence of Cs^+: $[\mathbf{2}] = 1.3 \times 10^{-6}$ M and $[Cs^+] = 4.0 \times 10^{-4}$ M, pH = 11.