Sodium-23 NMR Studies of Sodium Ion Ensembles with a 1,3-Alternate-Shaped Calix[4]arene

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Abstract: Sodium-23 NMR longitudinal magnetization recovery (L.M.R.) study has been carried out to clarify the sodium ion exchange in ensembles with 1,3-alternate-shaped calix[4]arene **1** for the first time. The line width $\nu_{1/2}$ of a sharp singlet for NaClO₄ in the absence of **1** is 65 Hz: upon addition of **1** a singlet peak was broadened to 1100 Hz ($\nu_{1/2}$). The life times (τ) of Na⁺ were estimated to be $(20\text{--}3.8) \times 10^{-3}$ s for τ_A and $(5.0\text{--}2.0) \times 10^{-3}$ s for τ_B , by the simulations of sodium-23 NMR L.M.R. curves. The life times of **1**-Na⁺ Ensemble are larger than those for 18-crown-6. This implies that Na⁺ cation is bound deeply in the cavity formed by two OCH₂CO groups of **1**, the complex being classified as a “nest-in-type”.

Key words: sodium-23 NMR, longitudinal magnetization recovery, life time, 1,3-alternate-shaped calix[4]arene, sodium ion, spin-lattice relaxation, molecular tweezer, molecular recognition

1 Introduction

The complexation of alkali-metal ions by supramolecules is a subject of substantial current interest, because organoalkali substrates are of fundamental importance both in modern organic synthesis (1-3) and in molecular devices (4). Calixarene has been receiving increasing attention in the field of supramolecular chemistry (5). It has been found that the ester derivatives show the ionophoric nature and are capable of binding alkali metal, alkaline earth metal, diazonium ions as crown ethers do (6-10). In particular, the 1,3-alternate-shaped calix[4]arene possessing two ester groups **1** exhibits moderate selectivity towards Na⁺ (11). This is attributable to the internal size of the ionophoric cavity made up by the two OCH₂C=O groups, which is comparable with the ion size of Na⁺

(12). In order to understand the selectivity for the metals, it is of great significance to access the kinetic properties of sodium ion ensembles with 1,3-alternate-shaped calix[4]arene (**Fig. 1**). Among NMR spectroscopic methods, it is known that sodium-23 NMR longitudinal magnetization recovery (L.M.R.) studies could provide further insights into the binding dynamics of included sodium ion (13). Herein, we describe systematic studies through ²³Na NMR L.M.R. of an ionophoric 1,3-alternate-shaped calix[4]arene ester **1**. The main purpose of this work is to clarify the sodium ion exchange between encapsulated sodium ion and solvated sodium ion.

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Fig. 1 Substrates **1** and **1-Na⁺ Ensemble**.

2 Experimental

2.1 Materials

2-(Ethoxycarbonylmethoxy)xylene **2** was used as a reference compound. The synthesis of 1,3-alternate-shaped 25,27-dipropoxy-26,28-bis(ethoxycarbonylmethoxy)-calix[4]arene **1** was described previously (14).

2.2 NMR Measurements

NMR samples consisted of 0.5 ml of solution in 5-mm o.d. tubes which were sealed under vacuum after degassing by 5 freeze-pump-thaw cycles. All glass-ware were washed with 0.01 M ethylenediaminetetraacetic acid (EDTA) solution to remove paramagnetic impurities. Perdeuteriotetrahydrofuran (THF-*d*₈) and perdeuteriomethanol (CD₃OD) were used as a solvent. ²³Na NMR spectra were recorded on a Varian Gemini-300 spectrometer operated at 300 MHz in the Fourier transform mode to study the spectroscopic behaviors of sodium perchlorate (NaClO₄) in the absence and the presence of **1**. The L.M.R. curves were estimated from the time (τ) evolution of the heights of spectra taken by inversion recovery method (15). As shown in **Fig. 2**, when the resonance frequencies of ²³Na nuclei in two environments are almost the same magnitude, the total longitudinal magnetization is proportional to the heights of spectra.

3 Results and Discussion

As shown in **Fig. 2**, we found that the addition of the calixarene derivatives **1** made the ²³Na NMR spectra very broad at 25°C. So, the line width $\nu_{1/2}$ of a sharp singlet for NaClO₄ in the absence of **1** is 65 Hz: upon addition of **1** a singlet peak was broadened to 1100 Hz

Fig. 2 Partial ²³Na NMR for Na⁺ in the Absence (1) and the Presence (2) of **1** at 25°C. [Na⁺] = 8.0 × 10⁻³ M, [**1**] = 2.0 × 10⁻² M, CDCl₃-THF-*d*₈ (3:1 v/v).

($\nu_{1/2}$). The line shapes of the spectra in the absence and the presence of **1** were single Lorentzians at 25°C. Further examination of the ²³Na NMR spectra, the L.M.R. curves between 0°C and 60°C showed single exponential decays. This suggests that, in 1,3-alternate-shaped calix[4]arene ester **1**, the CH₂CO₂Et groups suppress the motion of Na⁺. In contrast, the ²³Na NMR spectrum of NaClO₄ was not affected at all by the addition of the reference compound **2** (even at 8.0 × 10⁻² M). This means that **2** does not form the complex with Na⁺.

The calixarene derivative **1** shows a doublet (3.80, 3.90 ppm) for the ArCH₂Ar protons and this split pattern was not affected by the measurement temperature (0 - 60°C). This indicates that **1** adopts a 1,3-alternate conformation (5) and the oxygen-through-the annulus rotation is inhibited by the CH₂CO₂Et groups (16). It is reported that **1** can bind Na⁺ through interactions with two oxygens in the OCH₂CO moiety and the association constant (K_a) is $\log K_a = 3.5$ (11). Hence, we consider that **1** exists totally as a Na⁺ ensemble under the measurement conditions. The large association constant observed for **1** is rationalized as for the fitness between the ionophoric cavity formed by two ester groups and the ionic size of Na⁺. These ¹H NMR data are in line with the ²³Na NMR spectral data discussed above.

Thus, the temperature dependence of ^{23}Na NMR can be attributed to the chemical exchange reaction between two sites A and B (**Equation 1**).

The spin-lattice relaxation rates R_A and R_B between 0°C and 60°C attained from the slopes of the L.M.R. curves were equal to $5300 \sim 1700 \text{ S}^{-1}$ and $130 \sim 60 \text{ S}^{-1}$, respectively. This indicates that the interaction of the nuclear quadrupole moment with electric field gradients becomes very large between a sodium nucleus and oxygen atoms of the OCH_2CO groups in **1-Na⁺ Ensemble**. We can calculate the life times of Na^+ with the simulations of the L.M.R. curves and also the evolution of the longitudinal magnetization $M_z(\tau)$ is estimated as a following **equation 2** (15): where R_A and R_B are given by the spin-lattice relaxation rate, the life times, and the fractional population. The life times (τ) of Na^+ were estimated to be $(20 \sim 3.8) \times 10^{-3} \text{ s}$ for τ_A and $(5.0 \sim 2.0) \times 10^{-3} \text{ s}$ for τ_B , respectively. As shown in **Fig. 3**, the life times of Na^+ were efficiently enhanced in the presence of **1**. In particular, the life time (τ_A : $2.0 \times 10^{-2} \text{ s}$ at 25°C) of **1-Na⁺ Ensemble** is larger than those (τ_A between $10^{-4} \sim 10^{-6} \text{ s}$ at 23°C) for 18-crown-6 (13). This implies that Na^+ cation is bound deeply in the cavity formed by two OCH_2CO groups of **1**, the complex being classified as a “nest-in-type”. As the cavity size of 18-crown-6 is greater than the size of Na^+ cation, the complex is not so stable. That is, the greater τ_A , the larger association constant obtains.

The foregoing results demonstrate that, in 1,3-alternate-shaped calix[4]arene **1**, the motion of Na^+ cation is

Fig. 3 Plots of ^{23}Na NMR Life Times τ_A (○ in the Presence of **1**) and τ_B (● in the Absence of **1**) versus Temperature. $[\text{Na}^+] = 8.0 \times 10^{-3} \text{ M}$, $[\mathbf{1}] = 2.0 \times 10^{-2} \text{ M}$, $\text{CDCl}_3\text{-THF-}d_8$ (3:1 v/v).

completely suppressed and two OCH_2CO groups of **1** play an important role to freeze the fluctuational motion of Na^+ cation.

In conclusion, the present paper shows the first study on ^{23}Na NMR life times of Na^+ cation included in 1,3-alternate-shaped calix[4]arene. It is clear that the calixarene skeleton efficiently suppresses the molecular motion of Na^+ cation through complexation. Further examination on the conformational motions in 1,3-alternate-shaped calix[4]arene possessing two ester groups as molecular machine is now under investigation.

Equation 1

$$\frac{M_z^0 - M_z(\tau)}{M_z^0} = 2[C_1 \exp(-R_A \tau) + C_1 \exp(-R_B \tau)]$$

Equation 2

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