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Structural analysis of macrocyclic polyethres using positron annihilation measurements

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The structural analysis of crown ether was carried out with positron annihilation lifetime spectroscopy. The lifetime of *o*-Ps was increased with the number of ether group from 0.91 ns to 1.51 ns. The radius of nanoscale open space of crown ether calculated by using Tao-Eldrup equation showed good agreement with the cavity size of crown ether measured with other analytical method such as XRD etc, and this suggested that the annihilation site of *o*-Ps was in the cavity of crown ether. In comparison between B18C6 and DB18C6, it was found that the lifetime of *o*-Ps was changed from *ca.* 1.1 ns to *ca.* 1.3 ns with the number of benzene ring and the relative intensity of pick-off annihilation of *o*-Ps was influenced by the number of benzene ring. The change of the lifetime of *o*-Ps would be due to the influence of chemical modification on the shape of the crown ether ring, and the difference of the relative intensity between them seems to be caused by the inhibition of positronium generation by benzene in molecule.

Key words: positron, positronium, polyether, crown ether and PALS

1. INTRODUCTION

The evaluation of the separation support such as the ion-exchanger and chelator is important for the elucidation of degradation mechanism and development of new material. In general, the following two properties are required for the separation support, 1) high reactivity to the guest ion and molecule, 2) high selectivity for the objective substances. Many studies of crown ethers on reactivity and selectivity have been carried out. It is well known that the separation supports are modified chemically and this influences its reactivity. Because positron annihilation spectroscopy (PAS) has potential for 1) the analysis of the solution and gel phase, which is difficult with X-ray diffraction (XRD), 2) the evaluation of the nanoscale open space size and electronic state near the annihilation site of positrons by the analysis of the lifetime spectrum and line shape of photopeak [1, 2], PAS seems to be a powerful tool to analyze separation support with high sensitivity.

Macrocyclic polyether, which is called crown ether and one of the separation supports, has unique property, namely the interior of crown ether ring is hydrophilic and the cation and molecule, whose size is similar to the cavity size of crown ether, are selectively taken into the cavity [3, 4]. Because the exterior of the crown ether ring is hydrophobic, the cation and molecule trapped in the cavity can be transported into the organic solution phase. Having these specific characters, crown ethers are used for the separation of congeners [5, 6, 7], isotopes [8, 9] and biopolymers [10, 11]. Because crown ethers are also applied to supermolecular chemistry and molecular recognition chemistry by using the ability of molecular recognition, crown ethers play very important roles in the field of separation science and life science. Although XRD and molecular orbital (MO) calculation are used for the analysis of crown ether [12, 13], these methods are difficult to analyze the solution phase, in which chemical reactions occur. Thus, it is very important to analyze the solute in solution phase.

As PAS has been used for the analysis of the solution and gel phase [14-16], it seems to be suitable for the structural analysis of crown ether. Mahmood et al attempted to analyze 12C4, 15C5 and 18C6 with PAS [17], and evaluated the cavity size, phase transition and the effect of the extrinsic defect and conformation change to the cavity size. Bokare et al also reported the structural analyses of 18C6 and 18C6-NH_4^+ complex by using *S*-parameter evaluation [18]. We applied positron annihilation lifetime spectroscopy (PALS) for the analysis of the structure of crown ether having benzene ring and the effect of the introduction of benzene ring to the crown ether ring.

2. EXPERIMENTAL

Benzo-12-Crown-4 (B12C4), Benzo-15-Crown-5 (B15C5), Benzo-18-Crown-6 (B18C6), Dibenzo-18-Crown-6 (DB18C6), and Dibenzo-24-

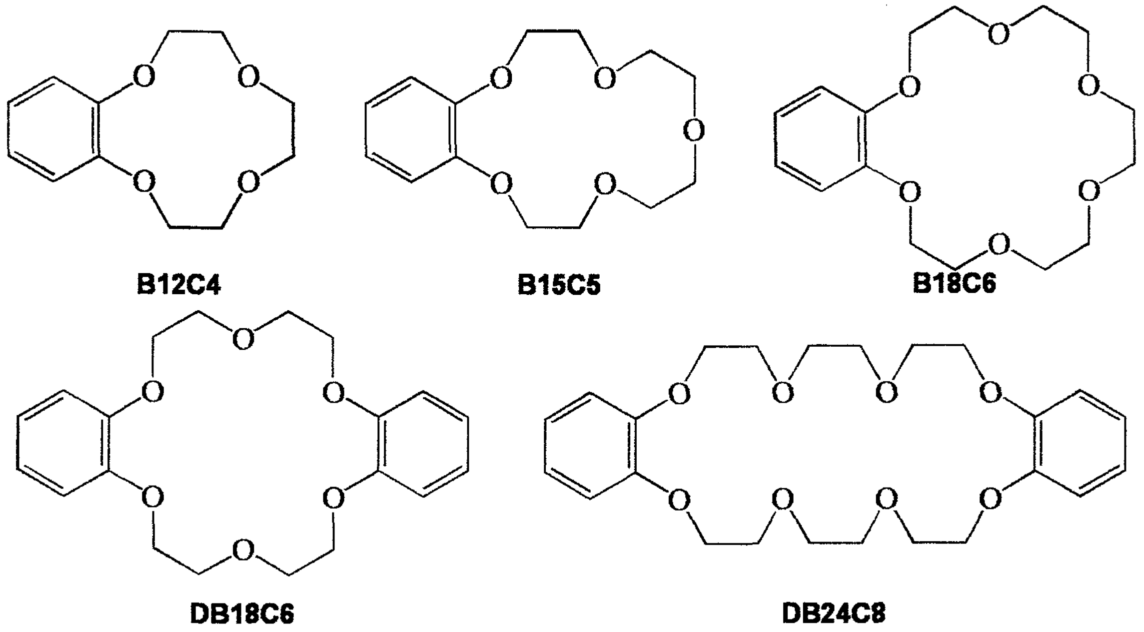

Figure 1. Chemical structures of crown ethers

Crown-8 (DB24C8) were purchased from Tokyo Chemical Industry, and used without further purification. Chemical structures of crown ethers are shown in Fig. 1. Samples were packed into two aluminum cases. ^{22}Na (46 kBq) covered with Kapton^{TM} film was used as a positron source, and was sandwiched between target samples. Samples were separated from the positron source by thin nickel foils of 5 μm thickness. The total count in each lifetime measurement was 3x10^{6}. The measurements were carried out at 293 K with relative humidity of 40 %, and a time resolution was *ca.* 240 ps. The obtained lifetime spectra were analyzed using PATFIT program [19, 20], to obtain the lifetimes and the relative intensities.

3. RESULTS AND DISCUSSION

We analyzed the lifetime spectrum of B12C4 by using PATFIT program. The obtained lifetime and relative intensity of *o*-Ps were τ_3 = 0.92±0.02 ns and I_3 = 25.8±0.6 %, respectively. The lifetimes and relative intensities of all crown ethers were summarized in Table 1. The lifetime of *o*-Ps was increased with the number of ether group from 0.92 ns to 1.51 ns. The values of τ_3 for B12C4, B15C5 and B18C6 showed good agreement with those for 12C4, 15C5 and 18C6 reported by Mahmood et al. [17]. They analyzed the cavity sizes at low temperature, because the lifetime of *o*-Ps was influenced by phase transition, conformational change and extrinsic defects at around room temperature. On the other hand, the measurements of PALS in our study were carried out at 293 K and the similar results for cavity sizes were obtained. As for the reason of this discrepancy, the crown ether rings used in our study are attached to benzene and this makes the crown ether ring more rigid. The lifetimes of *o*-Ps in B18C6 and DB18C6 were *ca.* 1.1 ns and *ca.* 1.3 ns with the number of benzene ring. This discrepancy shows that the extension of electronic cloud inside of the cavity in crown ether is shrunk by the attachment of benzene, leading to the increase of rigidity of crown ether. It is well known that the selectivity of crown ether is changed according to the chemical modification even for the same number of ether group [21], which is considered as the change of flexibility of crown ether ring. The radius of nanoscale open space of each crown ether was estimated by using the lifetime of *o*-Ps in Table I and Tao-Eldrup equation expressed as follow [22, 23];

Table I Calculated values of τ_3 and I_3.

	τ_3	I_3
B12C4	0.92(2)	25.8(6)
B15C5	1.09(2)	23.6(3)
B18C6	1.08(2)	23.8(4)
DB18C6	1.27(3)	9.6(3)
DB24C8	1.51(2)	11.7(2)

The errors of 2SD in the last quoted digits are given in brackets.

Table II Calculated cavity radius of each crown ether.

	Cavity radius [Å]	
	This study	Mahmood et al.[a]
12C4	1.50(2)	1.4(1)
15C5	1.79(3)	1.8(1)
18C6	1.77(3)[B18C6] 2.03(4)[DB18C6]	1.8(1)
24C8	2.36(3)	

[a] ref. [17].

$$\tau_3 = 0.5\left\{1 - \frac{R}{R + 0.166} + \frac{1}{2\pi}\sin\left(\frac{2\pi R}{R + 0.166}\right)\right\}^{-1}, \quad (1)$$

where τ_3 and R are lifetime of *o*-Ps expressed in nano-second and so-called free volume hole (FVH) radius expressed in nano-meter, respectively. By using Eq. (1), the radius of FVH of B12C4 was estimated to be about 1.5 Å. The radii of FVH in crown ethers estimated by using Eq. (1) are listed in Table II, and the relationship between the radii of FVH and the number of ether group is shown in Fig. 2. As shown in Table II and Fig. 2, the radius of FVH was increased with the number of ether group from 1.5 Å to 2.4 Å. It is considered that the space in the vicinity of benzene and the cavity of crown ether are the plausible annihilation site of positron and positronium. In the case of DB18C6, it is reported that the distance between benzene rings was *ca.* 3.5 Å and cavity diameter of crown ether was *ca.* 4 Å [12, 13, 24]. As shown in Table II, the diameter of FVH of DB18C6 was about 4 Å and this value is close to the result for crown ether without benzene reported by Mahmood and the cavity size obtained by other method such as MO calculation and XRD, which suggests that the radius of FVH calculated by using Tao-Eldrup equation is the radius of cavity size of crown ether. Thus the pick-off annihilation of *o*-Ps is thought to occur according to the following process.

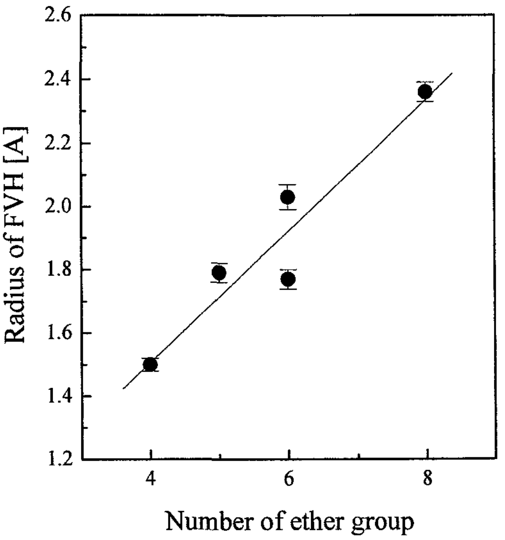

Figure 2. Calculated cavity radius of each crown ether as a function of ether group number

$$\begin{aligned} &\text{Crown} + o\text{-Ps} \rightarrow (\text{Crown-}o\text{-Ps}) \\ &\rightarrow \text{Crown} + 2\gamma. \end{aligned} \quad (2)$$

In this process, *o*-Ps would interact with ether group, which is the hydrophilic group. This reaction shows that *o*-Ps forms complex with crown ether by host guest interaction, because crown ether is an electron donor and a pick-off annihilation of *o*-Ps, which is a reaction of positronium atom with the extrinsic electron, can be considered as an electrophilic reaction.

The relative intensity corresponding to the lifetime of positron is important to analyze the generation process of positronium. The values of I_3 for B12C4, B15C5 and B18C6 having one benzene ring were almost the same value of *ca.* 24 %. The generation process of *o*-Ps was similar between these compounds, since these compounds have similar structure except for the ether group number. The relative intensities of *o*-Ps in DB18C6 and DB24C8 having two benzene rings, on the other hand, were about 10 %. This also shows that the generation process of the *o*-Ps was similar in DB18C6 and DB24C8. In comparison between B18C6 and DB18C6 having same number of ether group but different number of benzene, the value of I_3 for DB18C6 is less than half of those of B18C6. The difference of the relative intensity of the pick-off annihilation between one-benzene crown ether and two-benzene crown ether would be caused by the introduction of benzene, because the generation of positronium is inhibited by a molecule having low energy charge transfer state [25] and the charge transfer state is affected by the presence of the benzene having π-electron.

4. CONCLUSION

The structural analysis of crown ether was carried out with positron annihilation spectroscopy. The lifetime of *o*-Ps was increased with the number of ether group from 0.92 ns to 1.51 ns. The lifetimes of *o*-Ps in B12C4, B15C5 and B18C6 showed the good agreement with those of 12C4, 15C5 and 18C6 measured at low temperature. As the reason for this agreement, the crown ether rings used in this study seem to be rigid because of the existence of benzene ring. In comparison between B18C6 and DB18C6, the lifetimes of *o*-Ps were *ca.* 1.1 ns and *ca.* 1.3 ns. This discrepancy would be due to the difference of the rigidity of crown ether ring and/or the localization of electronic cloud. By using Tao-Eldrup equation, the radii of FVH of crown ether were calculated, and these values showed good agreement with the cavity sizes of crown ethers estimated by other analytical method. This suggests that *o*-Ps forms complex with crown ether by the host guest interaction and annihilates in the cavity of crown ether via pick-off annihilation. In comparison between B18C6 and DB18C6 having the same number of ether group but different number of benzene, the value of I_3 for DB18C6 is less than half of that for B18C6. The difference of the relative intensity of the pick-off annihilation between one-benzene crown ether and two-benzene crown ether would be caused by the different charge transfer rate brought by benzene.

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