NMR STUDY ABOUT THE STRUCTURE AND BEHAVIOR OF N-PERALKYLMAMINO-CYCLODEXTRINS IN AQUEOUS AND NON-AQUEOUS SOLVENTS

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ABSTRACT

$^1$H and $^{13}$C NMR spectra of the N-alkylamino-cyclodextrin(CD)s were measured in organic and aqueous solvents. It was found by the spectral analyses of the very broad signals of the glucose rings and N-alkyl groups that these CD derivatives strongly aggregate and the aggregation form is a reversed micelle type in organic solvents and is a normal micelle type in aqueous solvents.

1. INTRODUCTION

It is well known that CD is insoluble in organic solvents. Therefore, we introduce the long N-alkylamino chain to the 6 position of the glucose ring in the CD in order to be soluble in both organic and aqueous solvents. The N-peralkylamino-CDs show an amphiphilic property.

Recently, we report the syntheses of N-peralkylamino-$\beta$-CDs and their host-guest phenomena [1, 2]. On the way of the NMR analyses of these substituted CDs, we have found the unusual broad signals. Thus, we made various kinds of NMR measurements in order to get detailed information about the aggregation mode in these amphiphilic molecules.

In this paper, we report the interesting results of the NMR spectral analyses.

2. MATERIALS AND METHODS

Substituted γ-CDs (I-V) were chemically synthesized from bromo-γ-CD and N-alkylamines. The purification was done by the column chromatographic method. The purity was checked by \(^1\)H and \(^{13}\)C NMR spectroscopy. The smaller compounds were analyzed by TOF-MS spectra. The purity is ca. 99%. NMR spectra were measured by a JEOL α-500 spectrometer (for \(^1\)H: 499.65 MHz and for \(^{13}\)C: 122.5 MHz).

3. RESULTS AND DISCUSSION

3.1. NMR spectra of N-alkylamino CDs in organic solvents

γ-CD derivatives with eight alkylamino groups in the 6 position of the glucose skeleton of the CD were chemically synthesized. The alkylamino group (RNH) is; R: C\(_4\)H\(_9\) (I), C\(_6\)H\(_{13}\) (II), C\(_8\)H\(_{17}\) (III), C\(_{12}\)H\(_{25}\) (IV) and C\(_{16}\)H\(_{33}\) (V). \(^1\)H NMR spectra of these compounds (I - V) were measured in a chloroform (CDCl\(_3\)) solution at room temperature. As is shown in Fig.1(a), \(^1\)H NMR signals are very broad in all regions. Interestingly, the degree of the broadness in the signals of the glucose groups is very larger than that of the alkyl groups, whereas the latter is much larger than that of the signals in the unsubstituted γ-CD. These line-broadenings can be explained by considering the existence of strong aggregation of the N-alkylamino- γ-CD and the presence of isomers in different aggregation modes. The careful observation of the degree of the line broadenings in I clearly indicates that the molecular motion of γ-CD ring is very different from the motions of the eight N-butyl groups. The same tendency was also found in the spectra of II and