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Structural Studies on Molecular Complexes of Polyethers. 4 Deoxycholic Acid-Polyether Complexes

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Abstract. Complexes of deoxycholic acid with polyethers, $[-(CH_2)_{m-1}CHR-O-]_n$ ($R = H$, $m = 2$–4, 6 and $R = CH_3$, $m = 2$), were prepared. The crystals are orthorhombic and similar to those most commonly observed for complexes with low molecular weight molecules. Dimension a in the poly(propylene oxide) complex is about 1 Å longer than those in other polyether complexes, while b and c do not differ much in these DCA-polyether complexes.

Key words: Deoxycholic acid, polyether, complex, crystal structure.

1. Introduction

Deoxycholic acid (3α, 12α-dihydroxy-5β-cholan-24-oic acid) (DCA) is one of the steroid acids which are contained in the bile of vertebrates. This compound has the ability to form inclusion complexes with a wide variety of organic molecules such as alkanes, aliphatic acids, esters, ketones, and alcohols as well as alicyclic and aromatic compounds. Conjugated diene monomers can also be included in the DCA channel. They are converted to polymer inclusion compounds through polymerization by γ-ray irradiation [1]. But direct preparation of inclusion complexes from DCA and polymers has not yet been reported. Hence, the author tried complexing DCA with polymers using several polyethers.

2. Experimental

2.1. MATERIALS

Commercially available DCA was purified by recrystallization from ethanol. Polyethers used for the preparation of DCA complexes are listed in Table I. The poly-

Table I. Polyethers used for preparation of DCA complexes, $[-(CH_2)_{m-1}CHR-O-]_n$

Polyether	m	R
Poly(oxyethylene) (POE)	2	H
Poly(oxacyclobutane) (POCB)	3	H
Poly(tetrahydrofuran) (PTHF)	4	H
Poly(hexamethylene oxide) (PHMO)	6	H
Poly(propylene oxide) (PPO)	2	CH_3

ether samples, [—$(CH_2)_m$—O—]$_n$ with $m = 2 - 4$, are similar to those previously used for preparation of urea complexes [2]. The poly(propylene oxide) (PPO) sample is a liquid whose average molecular weight is 3000.

2.2. PREPARATION OF THE COMPLEXES

The complexes were obtained at room temperature by slow evaporation of solvent from ethanolic solutions of DCA and a little excess of polyethers. Uncomplexed polyethers were washed out with benzene.

2.3. MEASUREMENTS

X-ray diffraction patterns and differential scanning calorimetry curves were measured under the same conditions as reported previously [3].

3. Results and Discussion

The complexes between DCA and polyethers were obtained in the form of powder crystals. Surprisingly, despite its irregular atactic configuration, the liquid PPO crystallized with DCA. Table II shows the results of elemental analysis from which compositions of the complexes were determined. The calculated values are in good agreement with the observed values.

The melting points of the complexes are shown in Table III. The complexes of polyethers (with R = H) melt at a much higher temperature than DCA; the melting points of the former are 180 to 198 °C, whereas that of DCA is 173 to 174 °C. This indicates that DCA is stabilized by complexing with the polyethers, and decomposi-

Table II. Elemental analysis of DCA-polyether complexes

Polyether	[Monomer unit]/[DCA]	Elemental analysis			
		Found		Calcd.	
		%C	%H	%C	%H
POE	1.25	71.10	10.15	71.10	10.13
POCB	1.48	71.36	10.31	71.38	10.30
PTHF	1.06	72.33	10.39	72.32	10.42
PPO	1.41	71.48	10.25	71.46	10.29

Table III. Crystallographic data and melting points of DCA-polyether complexes

	POE	POCB	PTHF	PHMO	PPO
a/Å	26.20	26.13	26.03	25.68	27.19
b/Å	13.78	13.72	13.63	13.54	13.53
c/Å	7.23	7.41	7.24	7.36	7.2
Z	4	4	4	4	4
T_m/°C	180	183	198	196	174

tion of the complexes to the component liquids occurs on melting. However, the melting point of the complex of PPO is lower than those of the complexes with the linear polyethers. The resons for the low melting point of the DCA-PPO complex may be that the unit cell of the PPO complex is larger than the cells of the complexes of other linear polyethers, as mentioned later, and accordingly, cohesive forces between DCA molecules would be weaker.

X-ray diffraction patterns of the complexes of POE and PTHF are very similar (Figure 1). DCA complexes of POCB and PHMO also showed X-ray powder patterns similar to Figure 1, but the pattern of the PPO complex is somewhat different from those without side groups. The X-ray diffraction patterns of these complexes could be indexed with orthorhombic unit cells containing four DCA molecules. A number of X-ray analyses have been carried out for DCA complexes with low molecular weight molecules. The orthorhombic cell is the most commonly observed of the three crystal systems found in the DCA complexes. The crystallographic data are

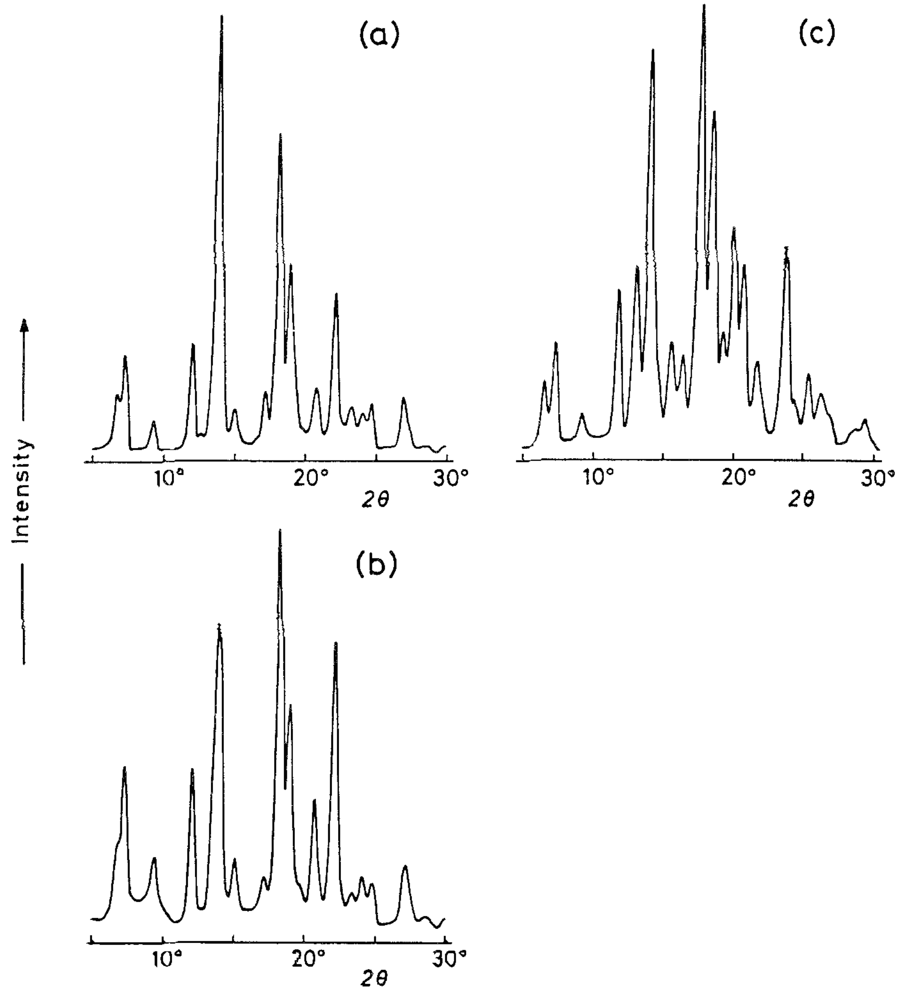

Fig. 1. X-ray diffraction patterns of DCA complexes with (a) poly(oxyethylene) POE, (b) poly(tetrahydrofuran) PTHF, and (c) poly(propylene oxide) PPO.

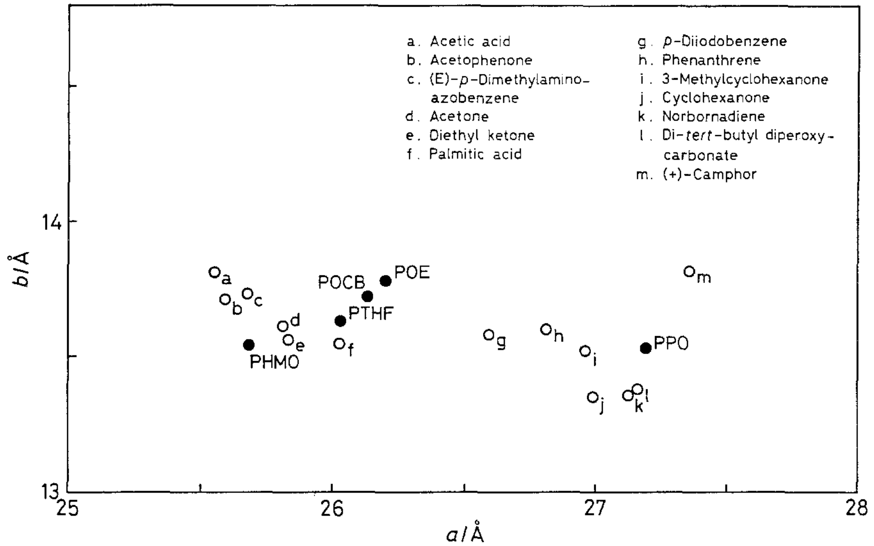

Fig. 2. Relation between dimensions *a* and *b* of the crystals of DCA complexes. Data for complexes between DCA and low molecular weight molecules were quoted from ref. [4].

listed in Table III. The cell dimensions of the DCA-polyether complexes which showed similar diffraction patterns are also similar. The length of the *a* axis of the PPO complex is about 1 Å longer than the *a* axis of complexes with other polyethers, while dimensions *b* and *c* do not differ much in these complexes. The dimensions of the *a* and *b* axes are compared in Figure 2, where the dimensions of the complexes with low molecular weight compounds [4] are also included. While the length of the *b* dimensions are within 0.5 Å, the lengths of the *a* axis cover a wide range and may be divided into two groups. Rather non-bulky molecules belong to the group with the shorter dimension of *a*, whereas bulky molecules belong to the longer *a* dimension group. The linear polyethers also fall within the shorter group. On the other

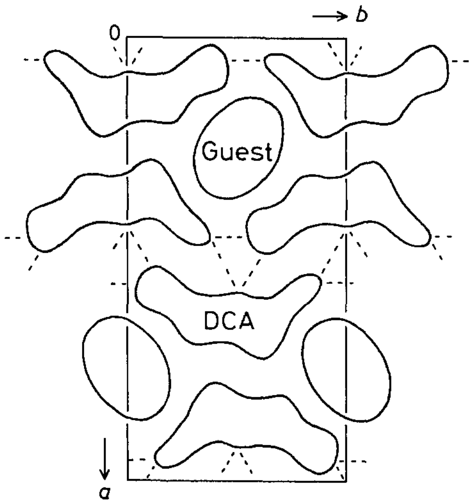

Fig. 3. Schematic crystal structure of DCA-polyether complexes.

hand PPO, having methyl side groups, falls within the longer dimension group.

The crystal structures of these polyether complexes have not been revealed in detail. By comparing X-ray diffraction patterns, it is inferred that the crystal packing of the polyether complexes is analogous to those of the orthorhombic complexes of low molecular weight molecules [5–7]. Thus, DCA molecules are linked by hydrogen bonds to form pleated bilayers extending into planes parallel to the *bc* plane. The polyether chains of the guest molecules are accommodated in the channels parallel to the *c* axis built up by the hydrogen bonded sheets stacking layer by layer in the *a* direction. These are schematically shown in Figure 3.

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