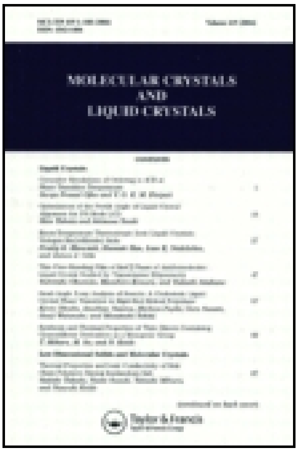

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STRUCTURES OF COMPLEX CRYSTALS OF ALKYLAMMONIUM SALTS WITH AROMATIC MOLECULES

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Abstract The complex crystal structures of dodecyltrimethylammonium chloride (DTAC) with catechol and hydroquinone were analysed by an X-ray diffraction method. Both complexes have isomorphous layered structures. The guest molecules locate between the interdigitated host molecules. Crystal structures are stabilized by mainly hydrogen bonds including water molecules. A cross-section balance between hydrophilic and hydrophobic parts is important for an energetically stable packing. DTAC can form the crystalline complexes with catechol and hydroquinone by both crystallizing from the solution and mixing host and guest powders in a mortar. In addition, DTAC can also make a complex with resorcinol. Powder diffraction pattern indicates that this complex has similar layered structure with complexes of DTAC / catechol and DTAC / hydroquinone. However, it is unstable in atmospheric condition.

INTRODUCTION

In some of cationic surfactant-aromatic compound systems, the solution exhibits a remarkable viscoelastic behavior even in very diluted state[1]. The solution of cetyltrimethylammonium bromide (CTAB) and salicylic acid is one of the most typical system[2]. In this system, the existence of elongated rod-like micelles which seem to cause the high viscoelaticity has been observed in electron micrographs[3,4]. In addition to this observation, the single crystals which are clearly different in shape and other features from crystals of CTAB and salicylic acid have been also found[5,6]. The electron diffraction pattern from these single crystals has suggested the formation of a complex between CTAB and salicylic acid.

Recently, it has been found that some amphiphile molecules such as ammonium salts, phosphonium salts and other onium salts have the specific abilities to form complexes with aromatic molecules. In some cases, the formation of complexes can be prepared simply by mixing both powders of amphiphiles and aromatic molecules in a mortar[7]. In order to clarify the structural details and interactions between host and guest molecules, we have been investigated the crystal structures of various

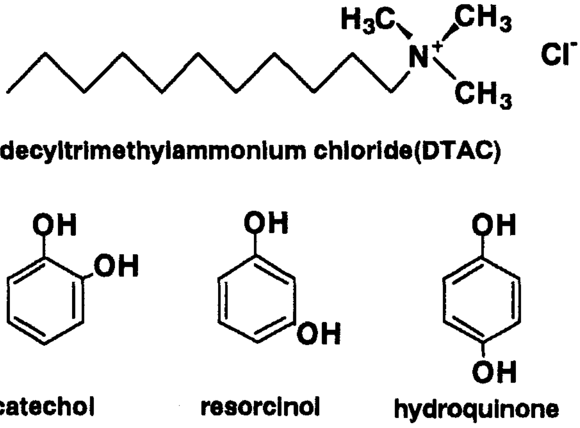


FIGURE 1 Chemical structures of host amphiphile and guest aromatic molecules.

amphiphiles and aromatic molecules. In the present study, crystal structures of dodecyltrimethyl-ammonium chloride (DTAC) / hydroquinone and DTAC / catechol complexes will be discussed (Figure 1).

EXPERIMENTAL

Single crystals of both complexes were grown by slow evaporation of an ethyl acetate / acetone mixture solution of host and guest compounds at 20°C. Collection of the diffraction intensities were carried out using a four-circle diffractometer (RASA 5R-II, Rigaku Co.) with graphite monochromatized CuKα radiation (λ = 1.5418 Å). The teXsan crystallographic software package (Molecular Structure Corporation)[8] was used for the solution of the phase problem and the refinement of parameters. The details of structure analyses were described elsewhere[9].

X-ray powder diffraction patterns were recorded on a Rigaku RAD-C diffractometer with scan speed of 10 ° / min.

RESULTS AND DISCUSSION

Crystal data for DTAC / catechol (**1**) and DTAC / hydroquinone (**2**) complexes are shown in Table 1. The packing structures of complexes **1** and **2** are isomorphous (Figure 2). The host / guest ratios of both complexes are 1 / 1. In addition, there are two water molecules per each host / guest unit in the crystal lattice.

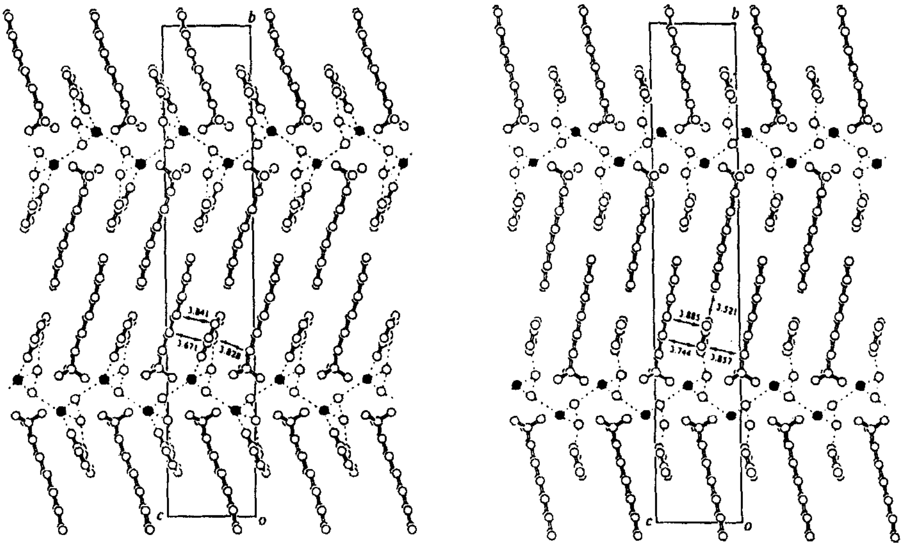
TABLE I Crystal data for dodecyltrimethylammonium chloride (DTAC) / catechol (**1**) and DTAC / hydroquinone (**2**) complexes

	DTAC / catechol	DTAC / hydroquinone
Molecular formula	$C_{15}H_{34}NCl / C_6H_6O_2 \cdot 2H_2O$	$C_{15}H_{34}NCl / C_6H_6O_2 \cdot 2H_2O$
Molecular weight	410.0	410.0
Crystal system	monoclinic	monoclinic
Space group	*P*21/n	*P*21/n
Cell dimension		
a / Å	7.084(4)	7.212(2)
b / Å	44.271(6)	45.099(5)
c / Å	8.415(2)	8.208(2)
β / deg	108.98(3)	108.96(2)
V / Å^3	2495(1)	2492.8(9)
Z value	4	4
Dx / g·cm^{-3}	1.092	1.093
Dm / g·cm^{-3}	1.08	1.10
$F(000)$	964	964
μ(CuKα)	15.3	15.3
No. of independent reflections	3771	3770
No. of independent reflections, with $F>3\sigma(F)$	2596	3274
Discrepancy factor		
R	0.057	0.036
Rw	0.069	0.037

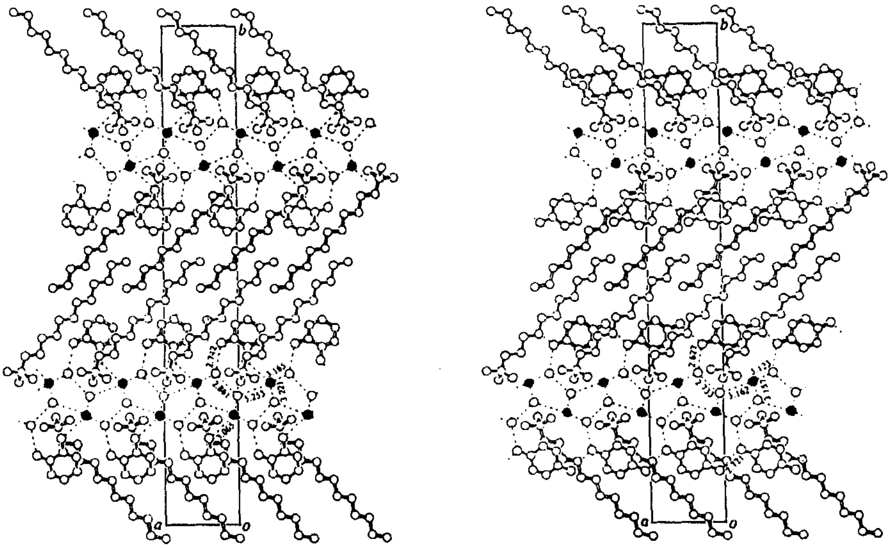
Although alkyl chains of the host molecules in **1** and **2** are nearly planar [the mean deviations of the least-square plane are 0.09 Å (**1**) and 0.04 Å (**2**), respectively], and the chain axes are somewhat bent. The carbon atoms at the end of the chain and adjacent to the nitrogen atom are out of plane on the one side (0.25 and 0.04 Å for **1**, and 0.12 and 0.02 Å for **2**, respectively) and the carbon atom of the middle of the chain is on the other side [-0.14 (**1**) and -0.07 (**2**), respectively].

The host molecules are arranged in the antiparallel fashion and mutually interdigitated within the smectic layer. The alkyl chains of host molecules in **1** and **2** are inclined 50° and 49° to the layer normal, respectively. The alkyl chains tilt in the opposite direction in the adjacent layer. The guest molecules locate between the interdigitated host molecules. The zigzag planes of alkyl chains and the ring planes of guest molecules are almost parallel to each other. The interplanar angles between these planes are 17° (**1**) and 9° (**2**), respectively.

In the hydrophilic part of complex **1**, a chloride ion is linked to three water molecules and one hydroxyl oxygen of guest molecule by hydrogen bonds. The other oxygen of the guest forms a hydrogen bond with water oxygen. On the other hand, a



a-projection



c-projection

DTAC / catechol **DTAC / hydroquinone**

FIGURE 2 Packing structures of DTAC / catechol (1) and DTAC / hydroquinone (2) complexes. Filled circles denote chloride ions. Broken lines indicate hydrogen bonds

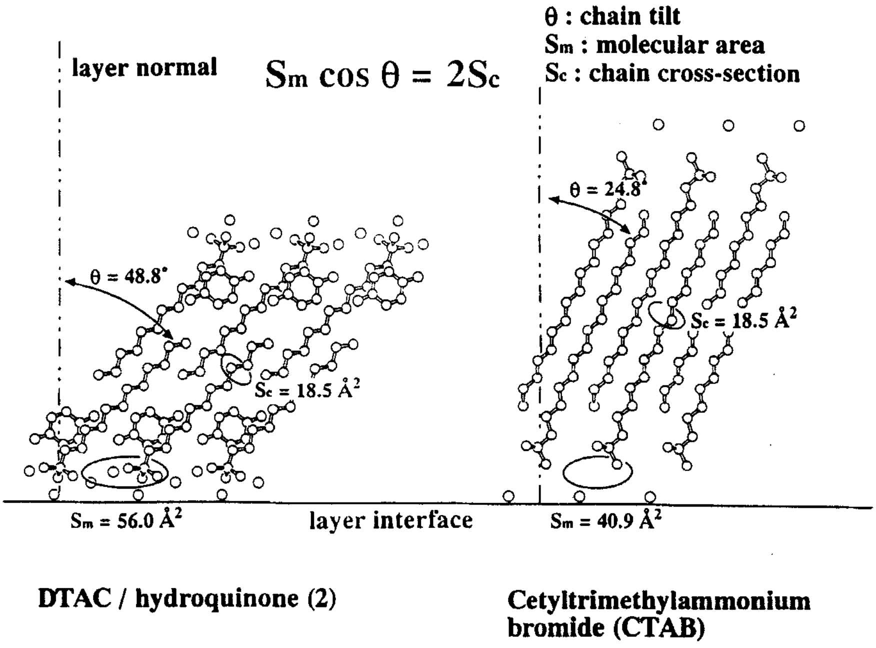


FIGURE 3 Cross-section balance between the hydrophilic and hydrophobic parts.

chloride ion in **2** has the same three hydrogen bonds with water oxygens as those of **1** But there is no hydrogen bond between the anion and guest molecules. The guest molecule of **2** is linked to the adjacent guest molecule along the *a*-axis and water molecule. The hydrogen bonds between water molecules are also observed in both complexes. In the hydrophilic region, the overlap region of the alkyl chains is small. The crystal structures of both complexes are stabilized mainly by hydrogen bonds in hydrophilic region.

So far, some crystal structures of the analogous compounds of the host molecules have been determined. In the crystal structure of CTAB[10], the alkyl chain is inclined 25° to the layer normal (Figure 3). On the other hand, the tilt angle of the alkyl chain in **1** and **2** are 50° and 49° mentioned above. Because of inclusion of guest molecules in the layered structure, the molecular area on the layer interface (Sm) of complexes **1** (56.4 Å^2) and **2** (56.0 Å^2) are larger than that of CTAB (40.9 Å^2). The molecular area can be calculated from lattice constants (Sm = $ac \sin \beta$). The cross-section of the hydrophilic part can be represented as Sm cos θ; here, θ is the tilt angle of the chain axis to the layer normal. In the interdigitated layered structure, the cross-section of the hydrophilic region corresponds to twice that of alkyl chain (Sc). The

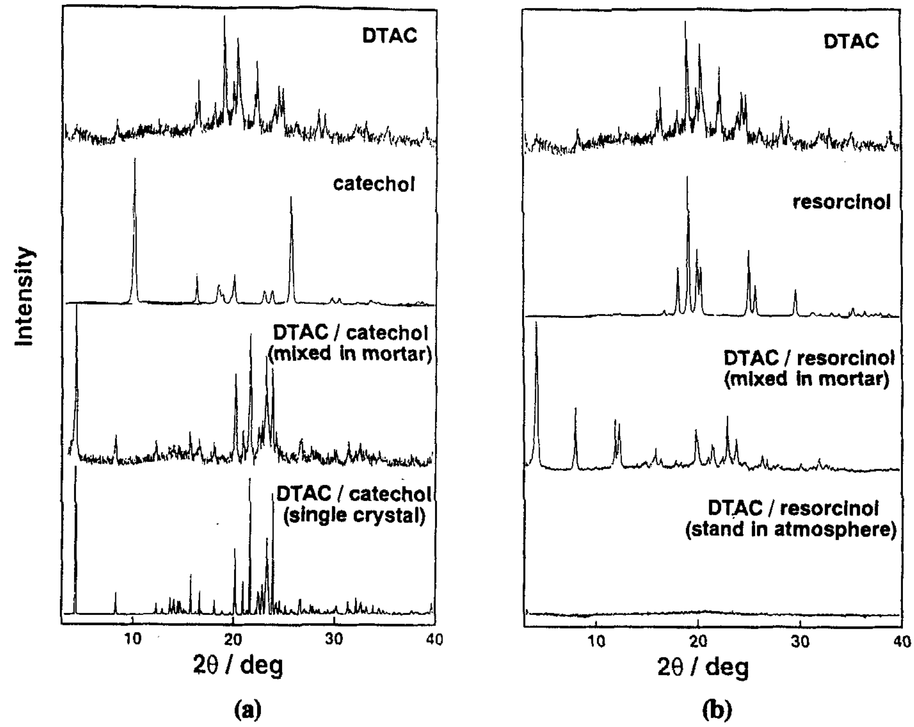


FIGURE 4 X-ray diffraction patterns of (a) DTAC / catechol (**1**) and (b) DTAC / resorcinol.

values Sm cos θ / 2 are 18.2 (**1**), 18.5 (**2**) and 18.5 (CTAB) Å^2. These are similar to that of the cross-section of an alkyl chain (18.3 Å^2). Therefore, it is important to balance the cross-section of hydrophilic part and that of hydrophobic part (Sm cos θ = 2Sc) in order to make an energetically stable structure.

From the results of X-ray measurements, it was found that the complexes **1** and **2** can be prepared by both mixing host and guest powder in a mortar and crystallizing from the solution. The X-ray diffraction pattern of the mixed powder of DTAC / catechol is different from that of each component, and essentially the same as the pattern calculated from thrre-dimensional intensity data of the complex single crystal (Figure 4). DTAC can also make complex with resorcinol molecules (Figures 4). Periodic peaks in the diffraction pattern of mixed powder of DTAC and resorcinol shows repeating period of *ca* 22 Å which seems to be a smectic layer thickness . This result suggests that the layered structure of DTAC / resorcinol complex is similar to those found in **1** and **2** . This complex, however, is unstable when it is allowed to stand in atmosphere. On the other hand, DTAC / hydroquinone and DTAC / catechol complexes are stable in the same condition.

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