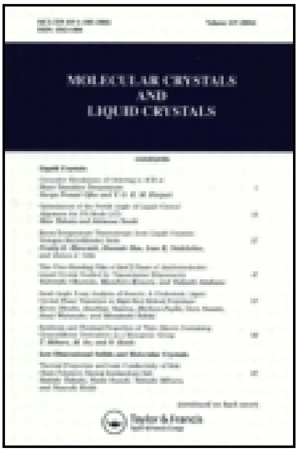

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Molecular Aggregation of Alkyltrimethylammonium Bromide and Alcohol in the Solid State

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MOLECULAR AGGREGATION OF ALKYLTRIMETHYLAMMONIUM BROMIDE AND ALCOHOL IN THE SOLID STATE

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Abstract Alkyltrimethylammonium bromide $C_nH_{2n+1}N^+Me_3Br^-$ (**1**, n =10, 12, 14, 16 and 18) and primary alcohol $C_mH_{2m+1}OH$ (**2**, m = 8-18) were found to form 1:1 crystalline complexes which show clear melting points. Separation of primary alcohol from a mixture with secondary alcohol was achieved very efficiently by complexation with ammonium salts.

INTRODUCTION

The molecular aggregation between alkylammonium salts and organic molecules is of importance in relation to the study of the role of membranes. Previously, we found that tetraalkylammonium halides aggregate to form a crystalline complexes with phenol derivatives through hydrogen bond formation between halide anion of the ammonium salt and hydroxy group of the phenol derivatives.[1] Since the complexation occurs selectively, separation of phenol isomers was accomplished very efficiently. When an optically active ammonium salt was used, optical resolution of phenol derivatives was also achieved very successfully. For example, bis-β-naphtol derivatives can be resolved efficiently by complexation with optically active *N*-alkylcinconidinium halide.[2] A hydrogen bond between OH group of bis-β-naphtol derivatives and Cl anion of the cinconidinium salt play an important role in the chiral recognition in the complex.[3]

Recently, we found that primary alcohol $C_mH_{2m+1}OH$ (**2**, m = 8~18) also aggregates with alkyltrimethylammonium bromide $C_nH_{2n+1}N^+Me_3Br^-$ (**1**, n =10, 12, 14, 16 and 18) in the solid state.[4] Separation of primary alcohol from a mixture with secondary alcohol is also found to proceed very efficiently by complex formation.

$C_nH_{2n+1}N^+Me_3Br^-$ (1)
a: $n = 10$ **b**: $n = 12$
c: $n = 14$ **d**: $n = 16$
e: $n = 18$

$C_mH_{2m+1}OH$ (2)
a: $m = 8$ **b**: $m = 9$ **c**: $m = 10$
d: $m = 11$ **e**: $m = 12$ **f**: $m = 13$
g: $m = 14$ **h**: $m = 15$ **i**: $m = 16$
j: $m = 17$ **k**: $m = 18$

RESULTS AND DISCUSSION

When a solution of hexadecyltrimethylammonium bromide (**1d**) (0.66 g, 2.7 mmol) and hexadecanol (**2i**) (1 g, 2.7 mmol) in acetone (10 ml) was kept at room temperature for 12 h, a 1:1 complex was formed as colorless plates (0.8 g, 48% yield, mp 98°C). The IR spectrum of the complex in a Nujol mull showed a sharp υOH absorption at high frequency, 3350 cm^{-1} whereas the υOH of **2i** itself is appeared at 3200 cm^{-1}(Fig. 1). This suggest that hydrogen bonding between the OH group of **2i** and the Br anion of **1d** is relatively week and that the hydrophobic interaction is more important. A strong υC-O absorption of **2i** at 1065 cm^{-1} became week absorption at 1050 cm^{-1} by complexation, probably due to the steric hindrance. This indicate that molecules of **1d** and **2i** are too tightly aggregated in the complex to stretch the C-O bond freely.

When the alkyl chain length, *n*, of the ammonium salt **1** is the same or close to that, *m*, of the alcohol **2**, their complex showed the highest melting point and was the most stable (Table 1). For example, **1d** (*m* = 16) formed 1:1 complexes of relatively high melting point with the alcohols **2g**~**2j** (*n* = 14~17) which have a similar alkyl chain length and the ΔH value of the complex of **1d** (*m* = 16) with **2j** (*n* = 17) was the highest (ΔH value of the complex of **1d** with **2c**, **2d**, **2e**, **2f**, **2g**, **2h**, **2i**, **2j** and **2k** was 53, 49, 54, 56, 50, 64, 67, 69 and 55 KJ/mol, respectively). Aggregation of molecules **1** and **2** of the same or similar alkyl chain length would be favorable for the crystal packing in the complex. Ammonium salts with a relatively long alkyl chain (**1c**~**1e**) did not form complex with an alcohol with a relatively short alkyl chain (**2a**~**2c**). Ammonium salts which have shorter alkyl chain than octyltrimethylammonium bromide also did not form complex with the alcohols **2a**~**2k**. It is also interesting that there was no correlation between melting point of the complex and whether the alkyl chain of **1** or **2** has an odd or even number.

Table 1 Melting point (°C)[a] of 1:1 complexes of **1** and **2**

Alcohol	**1a**	**1b**	**1c**	**1d**	**1e**
2a	78	79	b	b	b
2b	80	77	81	b	b
2c	81	87	87	80	b
2d	82	87	88	88	83
2e	81	88	91	92	89
2f	76	88	92	94	94
2g	75	87	93	100	98
2h	73	84	93	98	100
2i	72	82	93	98	103
2j	72	82	90	99	101
2k	75	83	89	96	102

[a] Measured by DSC. [b] No complexation occurred.

Since the ammomonium salts recognize the difference of the shape and size of the alcohol to form the 1:1 complex selectively, separation of alcohol isomers can be achieved efficiently by complexation. For example, when a solution of **1b** (0.4 g) and a mixture of **2e** (0.49 g) and octanol (0.4 g) in acetone (4 ml) was kept at room temperature for 1 h, a 1:1 complex of **1b** and **2e** (0.17 g, 31% yield) was formed as colorless prisms. Heating the complex in vacuo gave **2e** (97% purity, 0.07 g, 22% yield). Separation of primary and secondary alcohols is also found to proceed quite efficiently. For example, when a solution of **1b** (1.0 g) and a 1:1 mixture of **2g** and tetradecan-2-ol (0.7 g) in acetone (10 ml) was kept at room temperature for 12 h, a 1:1 complex of **1b** and **2g** was obtained as colorless prisms (0.8 g). Heating the complex in vacuo gave **2g** (96% purity, 0.22 g, 32% yield). The purity of **2e** and **2g** was determined by GC.

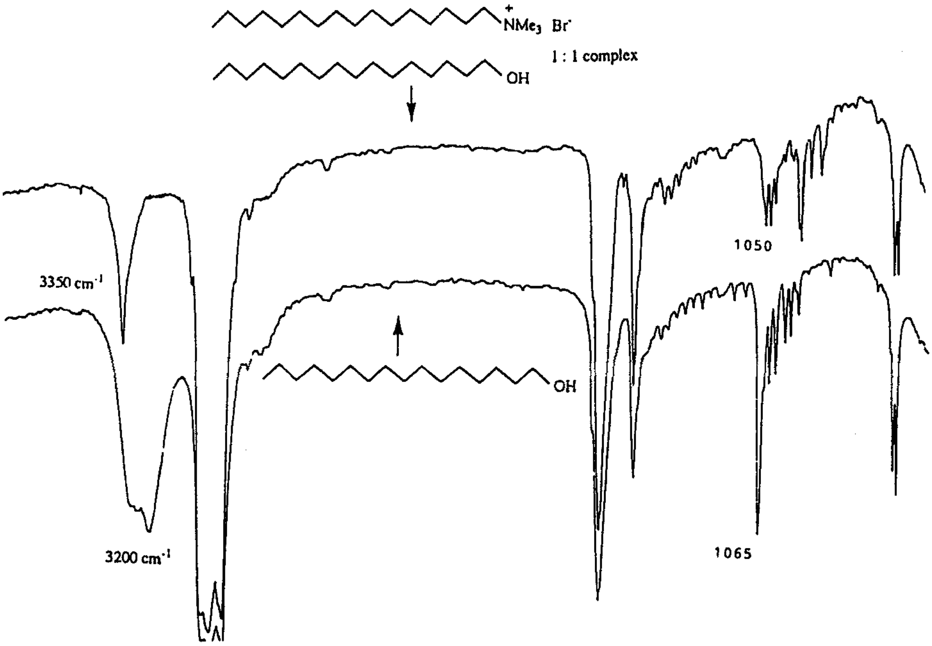

Fig. 1 IR spectra of hexadecanol (**2i**) and its 1:1 complex with **1d**.

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