Molecular aggregation of alkyltrimethylammonium bromide and alcohol. Discrimination of primary and secondary alcohols

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Alkyltrimethylammonium bromide (alkyl = decyl, dodecyl, tetradecyl, hexadecyl and octadecyl) and primary alcohol $C_nH_{2n+1}OH$ (n = 8–18) aggregated and formed 1:1 complex crystals which show clear melting points; an ammonium bromide and alcohol of similar alkyl chain length formed a complex with the highest melting point; since secondary alcohols did not complex with the ammonium bromide, the primary alcohol was isolated from a mixture.

Previously, we have reported that tetraalkylammonium halide and phenol derivatives aggregate and give a 1:1 complex through hydrogen bond formation between the halide ion of the ammonium salt and the OH group of the phenol.[1] In the complexation, molecular discrimination occurred and separation of a phenol isomer was accomplished.[1] When the ammonium salt was optically active, chiral discrimination occurred and optical resolution of the phenol derivative was achieved. For example, by complexation of *rac*-2,2′-dihydroxy-1,1′-binaphthyl with cinconidinium chloride, the former was resolved efficiently.[2] In this case, a hydrogen bond between the acidic OH group of the naphthol derivative and the Cl^- of the cinconidinium salt play an important role in the molecular aggregation.[3]

Recently, we found that primary alcohol $C_mH_{2m+1}OH$ (**2**) with a long alkyl chain (m = 8–18) also aggregates together with alkyltrimethylammonium bromide $C_nH_{2n+1}N^+Me_3{\cdot}Br^-$ (**1**) with a long alkyl chain (n = 10, 12, 14, 16, 18) and forms a 1:1 complex which shows a clear melting point (Table 1).

$C_nH_{2n+1}N^+Me_3{\cdot}Br^-$

a $n = 10$ **b** $n = 12$
c $n = 14$ **d** $n = 16$
e $n = 18$

$C_mH_{2m+1}OH$

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** $m = 18$

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

2	**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.

For example, when a solution of hexadecyltrimethylammonium bromide (**1d**) (0.66 g, 2.7 mmol) and hexadecanol (**2i**) (1 g, 2.7 mmol) in acetone (10 cm^3) was kept at room temperature for 12 h, a 1:1 complex of these was formed as colourless plates (0.8 g, 48% yield, mp 98 °C). The IR spectrum of the complex in a Nujol mull showed a sharp ν(OH) absorption at relatively high frequency, 3350 cm^{-1}. The data suggest that hydrogen bonding between the OH group of **2i** and the Br^- of **1d** is weak, if it exists at all, and that the hydrophobic interaction between alkyl groups of **1** and **2** is more important. A sharp and strong ν(C–O) absorption of **2i** itself at 1065 cm^{-1} (Nujol mull) became a weak absorption at 1050 cm^{-1} (Nujol mull) by the formation of the complex, probably due to a spacial restriction of the C–O stretch in the complex crystal. In other words, **1d** and **2i** molecules are too tightly aggregated in the complex crystal to stretch the C–O bond freely.

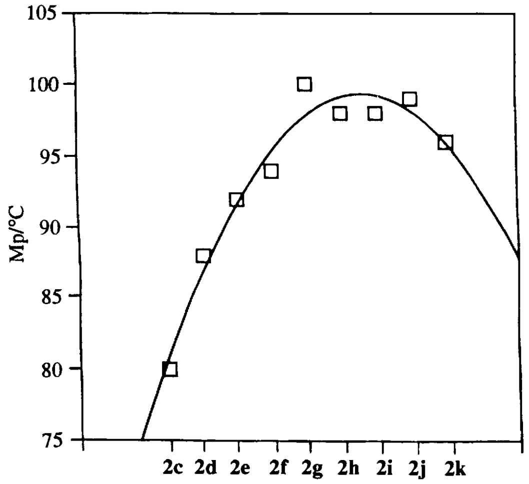

Fig. 1 Melting point (°C) of 1:1 complexes of **1d** and **2c–k**

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 (Table 1, Fig. 1) and was the most stable (Fig. 2). Ammonium salts with a relatively long alkyl chain, **1c–e**, did not complex with an alcohol with a relatively short alkyl chain, **2a–c**, respectively (Table 1). It is also interesting that octyltrimethylammonium bromide did not complex with **2a–k**. The ammonium salt **1d** (m = 16) formed complexes of relatively high melting point with an alcohol having a similar alkyl chain length **2g–j** (n = 14–17) (Fig. 1). Of the dissociation energy, ΔH, of 1:1 complexes of **1d** with **2c–k**, obtained from DSC data, that for the complex of **1d** (m = 16) with the alcohol **2j** (n = 17) which have similar alkyl chain lengths was the largest (Fig. 2). Mutual arrangement of molecules **1** and **2** of the same or similar alkyl chain length would form the most stable crystalline lattice of the complex.

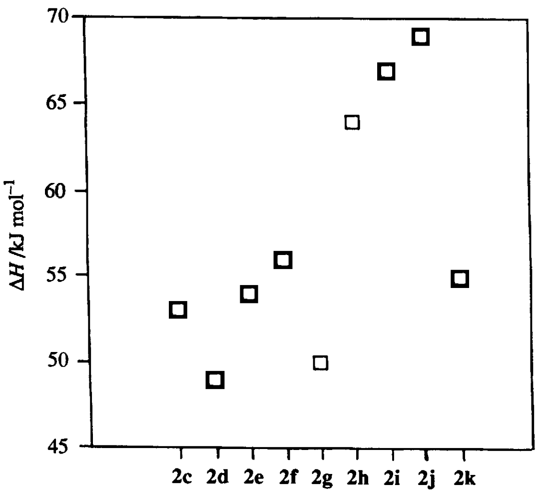

Fig. 2 Dissociation energy, ΔH, of 1 : 1 complexes of **1d** and **2c–k**

However, neither mp nor ΔH values of the complex are related to whether the alkyl chain of **1** or **2** has an odd or even number of methylene units.

By using the molecular recognition between **1** and **2**, separation of alcohol isomers can be achieved. When a solution of **1b** (404 mg) and a mixture of **2e** (494 mg) and heptanol (402 mg) in acetone (4 cm^3) was kept at room temperature for 1 h, a 1 : 1 complex of **1b** and **2e** (170 mg, 31% yield) was formed as colourless prisms. Heating the complex *in vacuo* gave **2e** (97% purity by distillation, 70 mg, 22% yield). Application of the molecular recognition to a separation of primary and secondary alcohols is also successful. When a solution **1b** (320 mg) and a 1 : 1 mixture of **2g** and tetradecan-2-ol (660 mg) in acetone (4 cm^3) was kept at room temperature for 1 h, a 1 : 1 complex of **1b** and **2g** was obtained as colourless prisms (170 mg, 31% yield). Heating the complex *in vacuo* gave **2g** (97% purity by distillation, 70 mg, 22% yield). The purity of **2e** and **2g** was determined by GC.

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