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Crystalline Molecular Complexes of 1-Alkylpyridinium Bromide with Aromatic Compounds

Nahoko Iimura,* Hirotaka Hirata, and Yuji Ohashi†

Department of Physical Chemistry, Niigata College of Pharmacy, 5-13-2 Kamishin'ei-cho, Niigata 950-2081

†Department of Chemistry and Materials Sciences, Tokyo Institute of Technology, Ookayama, Meguro-ku, Tokyo 152-8551

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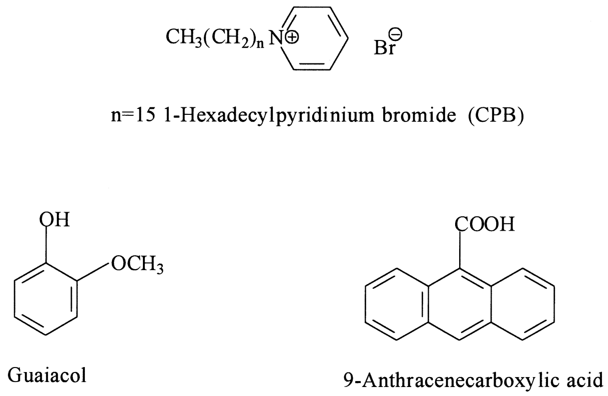
A surfactant, 1-alkylpyridinium salt, such as 1-hexadecylpyridinium bromide, formed complexes with aromatic compounds, such as phenolic derivatives and basic substances from an aqueous, alcohol, or acetone solution at low temperatures (< 10 °C). Fifteen complex crystals were obtained, of which two well-grown crystals, 1-hexadecylpyridinium/guaiacol and 1-hexadecylpyridinium/9-anthracenecarboxylic acid, were suitable for X-ray analysis. The structures, analyzed by X-rays, were shown to be very similar to each other, and have a common packing pattern, which has been observed in crystalline molecular complexes with surfactants contained as quaternary alkylammonium salts. The void space to accommodate the aromatic compounds in the 1-alkylpyridinium bromide complexes is greater than the corresponding one in the quaternary alkylammonium bromide complexes.

It is well known that surfactants from molecular aggregates in an aqueous solution with oily materials that are otherwise insoluble to water at certain concentrations above the critical micelle concentration (cmc). The aggregation is called a micelle.[1] A solution with a micelle shows high viscoelasticity.[2–5] We have reported that a variety of types of crystalline molecular complexes are provided between quaternary alkylammonium salts, such as hexadecyl-, tetradecyl-, dodecyl-, and decyltrimethylammonium bromides, and various aromatic compounds from their solubilized solution system.[6–10] The crystal structures of molecular complexes were determined by X-ray analysis. In complex crystals, a similar intermolecular interaction between the surfactant and aromatic compound was observed, which is called the "common packing pattern".[11] This common pattern is composed of two interactions, that is, the C–H···π interaction between the alkyl chain of the surfactant and the π electrons of an aromatic compound, and the hydrogen bond between the bromide ion of the surfactant and the aromatic compound if the aromatic compound has a donor group of the hydrogen bond. The molecular aggregation derived from the common packing pattern was proposed to be responsible for micelle formation and for the high viscoelasticity of the aqueous solution.[11]

The complex formation of surfactants and aromatic compounds gave two important characteristics: one is an enhancement of the solubility of insoluble drugs in water;[12] the other is an improvement in the thermal stability of unstable materials.[13] Surfactant molecular complexes will surely be useful for pharmaceutical and industrial chemistries.

Recently, we intended to form molecular complexes between surfactants of different type in a cationic surfactant, a 1-alkylpyridinium salt, such as 1-hexadecylpyridinium bromide (abbreviated as CPB), and various aromatic compounds. After many trials, we obtained about ten complex crystals, two of which are suitable for X-ray analysis (Scheme 1). One is a complex between CPB and guaiacol from an aqueous solution; the other is between CPB and 9-anthracenecarboxylic acid from a 1-butanol solution. In this paper, the structures of the two complexes are compared with each other and with those of the complexes analyzed so far.



Scheme 1. Surfactant and aromatic compounds.

Experimental

Preparation of the Complex Crystals: A cationic surfactant, CPB, was crystallized from a methanol solution, and then recrystallized from an aqueous solution. The aromatic compounds were purchased from Tokyo Kasei Co. Ltd. and purified by recrystallization. The complex crystals were isolated from the solubilized solution in which CPB and an aromatic compound were solved in a molar ratio of 1:1. Table 1 lists the complexes obtained as a sediment, the molar ratio and the solvent. The complex formation and its molar ratios were confirmed by ultraviolet

Table 1. Crystalline Molecular Complexes of CPB with Various Substances

Complexes	Molar composition ratio (CPB/aromatic compound)	Preparation medium
CPB/*o*-iodophenol	1/1	H_2O
CPB/*p*-iodophenol	1/1	H_2O
CPB/*p*-bromophenol	1/1	H_2O
CPB/*m*-cyanophenol	1/1	H_2O
CPB/1-naphthol	1/1	H_2O
CPB/2-naphthol	1/1	H_2O
CPB/*p*-nitrophenol	2/1	Methanol
CPB/*p*-ethoxyphenol	2/1	H_2O
CPB/guaiacol	2/1(2)*	H_2O
CPB/indole	3/2	H_2O
CPB/acridine	2/1	Acetone
CPB/diphenylamine	2/1	Acetone
CPB/carbazole	3/2	Acetone
CPB/1-naphthylamine	2/1	H_2O
CPB/9-anthracenecarboxylic acid	2/1	1-Butanol

*The number in parentheses gives that of the hydrated water molecules.

Table 2. Crystal Data and Experimental Details

		I	II
Formula		$2C_{21}H_{38}BrN/C_7H_8O_2/2H_2O$	$2C_{21}H_{38}BrN/C_{15}H_{10}O_2$
Molecular weight		929.03	991.10
Temperature/K		223	223
Wavelength/Å		0.71069	0.71069
Diffractometer		CCD	AFC-7R
Radiation		Mo$K\alpha$	Mo$K\alpha$
Crystal system		triclinic	triclinic
Space group		$P\bar{1}$	$P\bar{1}$
a/Å		8.4986(5)	9.5862(15)
b/Å		9.7298(5)	35.586(18)
c/Å		34.7830(19)	9.0601(15)
α/°		90.459(1)	91.37(3)
β/°		93.293(1)	117.683(11)
γ/°		115.251(1)	93.63(2)
Z		2	2
Volume/$Å^3$		2595.4(2)	2726.5(15)
D_{calc}/g cm^{-3}		1.189	1.207
Crystal dimensions/mm^3		0.25×0.20×0.03	0.30×0.28×0.11
Absorption correction		SADABS[19]	psi-scan[20]
2θmax/°		55	55
μ/mm^{-1}		1.602	1.527
$F(000)$		996	1056
Range of h		$-11 \rightarrow 8$	$-12 \rightarrow 12$
Range of k		$-10 \rightarrow 12$	$-46 \rightarrow 46$
Range of l		$-45 \rightarrow 45$	$-11 \rightarrow 11$
No. of observed reflections	total	18695	17226
	unique	11786	9629
	$(I > 2\sigma(I))$	9597	8673
No. of refined parameters		519	568
R(int)		0.027	0.055
$R(I > 2\sigma)$		0.042	0.048
$wR(F^2)$		0.091	0.127
Goodness-of fit on F^2		0.759	1.004
Weighting parameters			
a		0.0572	0.0854
b		0	0
$\delta\rho$/e$Å^{-3}$		+0.31, −0.49	+0.55, −0.44

spectroscopy and elemental analysis. The complexes of CPB/guaiacol (I) and CPB/9-anthracenecarboxylic acid (II) were plate-like crystals suitable for X-ray analysis.

Crystal Structure Analysis: The cell dimensions and intensity data of crystals (I) and (II) were measured with SMART-CCD and AFC-7R four-circle diffractometers, respectively, at 223 K using Rigaku low-temperature equipment. The crystal data are listed in Table 2. The structures of (I) and (II) were solved by a direct method with the programs SIR-92[14] and SHELXS-86,[15] respectively, and were refined by the full-matrix least-squares method with the program SHELXL-97.[16] The non-hydrogen atoms of the ordered surfactant and aromatic compound molecules were refined with anisotropic temperature factors. The C–C, C–OH, C–O, and O–CH_3 bonds and the C–C–C angels of guaiacol were constrained to 1.390, 1.362, 1.370, and 1.424 Å and 120°, respectively. The positions of hydrogen atoms were calculated geometrically and were fixed in the refinement. The atomic scattering factors were taken from International Tables for Crystallography.[17] The weighting scheme is $1/[\sigma^2(F_o^2)+(ap)^2+bp]$, where $P = (F_o^2+2F_c^2)/3$. The experimental details are also summarized in Table 2. The CIF data for the two crystals are deposited as Document No. 75003 at the Office of the Editor of Bull. Chem. Soc. Jpn. Crystallographic data have been deposited at the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK and copies can be obtained on request, free of charge, by quoting the publication citation and the deposition numbers 172592 and 172593.

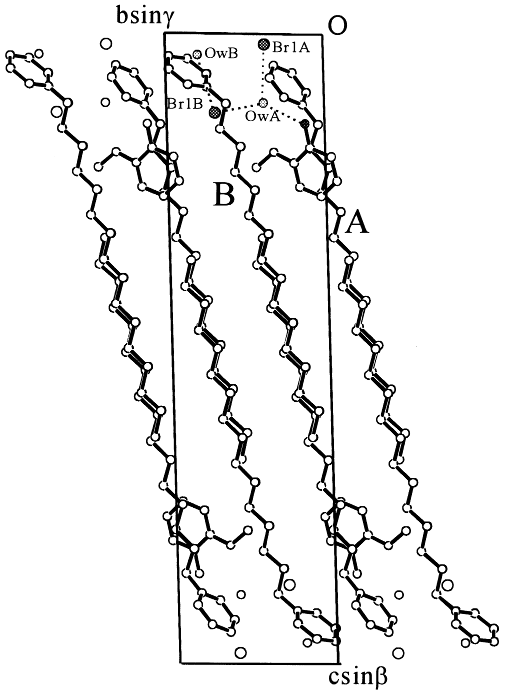


Fig. 1. Crystal structure of (I) viewed along the a axis.

Results and Discussion

Crystal and Molecular Structure of CPB/Guaiacol (I): The crystal structure viewed along the a axis is shown in Fig. 1. There are two 1-hexadecylpyridinium (CP) cations (A and B) and bromide anions (Br1A and Br1B), one guaiacol molecule and two solvent water molecules (OwA, OwB) in the asymmetric unit. The molecular structures with the atomic numbering are shown in Fig. 2. The A and B CP cations with all-trans conformation are packed in a head-to-tail way along the a axis. A guaiacol molecule is sandwiched by the alkyl chains of the CP cations, and is situated between the alkyl groups and the bromide anions and water molecules. Such a packing mode is substantially the same as the "common packing pattern", which we have observed in crystalline molecular complexes between surfactants, such as quaternary alkylammonium salts and aromatic compounds. The OH group of the guaiacol molecule makes a hydrogen bond with the solvent (OwA), which makes hydrogen bonds with the bromide anions, (Br1A and Br1B). Around an inversion center at (0, 1/2, 0), the hydrogen bonds are composed of OwA···Br1B···OwB···Br1A′···OwA′···Br1B′···Br1A···OwA make a ring. The distances are 2.623(3) Å (OwA···O2), 3.313(3) Å (OwA···Br1B), 3.355(3) Å (Br1B···OwB) and 3.351(4) Å (OwB···Br1A′) and 3.223(3) Å (Br1A···OwA).

Crystal and Molecular Structure of CPB/9-Anthracenecarboxylic Acid (II): A perspective view of the crystal structure is shown in Fig. 3. The crystal structure viewed along the c axis is very similar to that in Fig. 1. There are two 1-hexadecylpyridinium (CP) cations, (A and B), two bromide anions, (Br1A and Br1B), and one 9-anthracenecarboxylic acid molecule in the asymmetric unit. The molecular structures along with the atomic numbering are shown in Fig. 4. The CP cations with all-trans conformation are packed in a head-to-tail

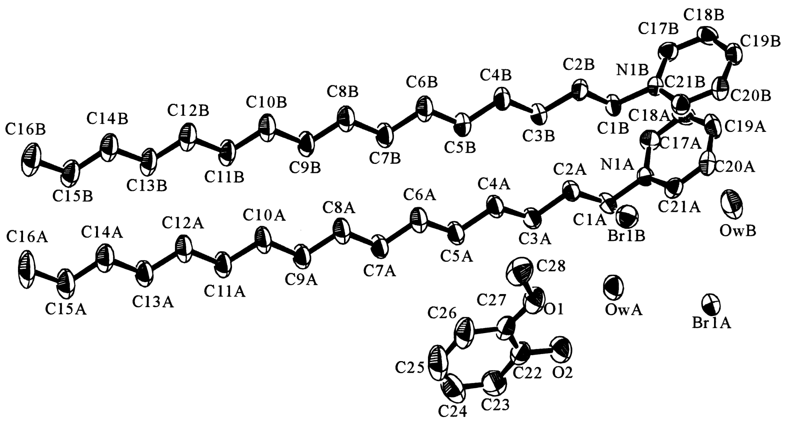


Fig. 2. Molecular structure of (I) with the atomic numbering. The displacement ellipsoids are shown with 50% probability.

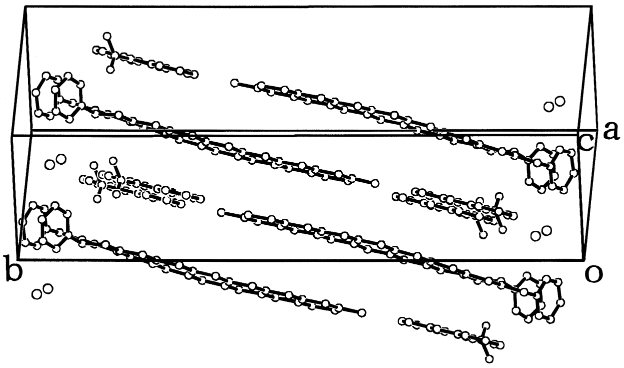


Fig. 3. Perspective view of the crystal structure of (II).

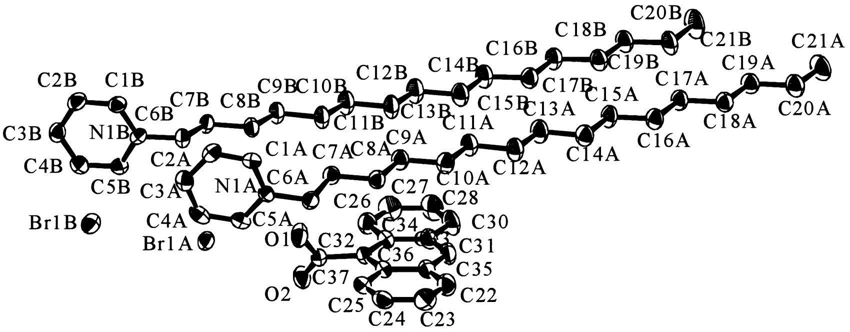


Fig. 4. Molecular structure of (II) with the atomic numbering. The displacement ellipsoids are shown with 50% probability.

manner along the c axis. The 9-anthracenecarboxylic acid molecule is sandwiched by the alkyl chains of the CP cations, and situated between the alkyl group and the bromide anion. The common packing pattern is also shown, which indicates the same interaction between the surfactant and the aromatic compound as those observed so far. The OH group of 9-anthracenecarboxylic acid makes a hydrogen bond with Br1A. The distance of Br1A···O1 is 3.106(3) Å.

Comparison of the Complex Structures of CPB with Those of CTAB: The crystal strucuture of CPB was reported by Ballirano et al.[18] If CPB alone and complex structures are compared, CPB complexes are made while the alkyl chains of CPB slide along the chain direction to form void apace between the alkyl chain and the bromide anion and between the neighboring alkyl chains and the aromatic molecules slip into the void space. Such structures are very similar to those of the common packing pattern which has been observed in crystalline molecular complexes with CTAB and aromatic compounds. The common packing pattern is shown in Fig. 5. Since only the head group of CPB is different from that of CTAB, the void spaces for the aromatic compounds are compared between CPB and CTAB in Table 3, in which the values of A, B, and C are defined as follows: A is the distance between the bromide anion and the methyl carbon atom of the neighboring alkyl chain; B and C are the distances between the two alkyl chains.

For the CTAB complexes, the A, B, and C values are less than 10.29, 7. 48, and 5.60 Å, respectively. Along the C direction, the void space is connected as a column. This means that the value of C corresponds to the molar ratio between the surfactant and the aromatic compound. On the other hand, the A and B values indicate the size of the molecule included in the

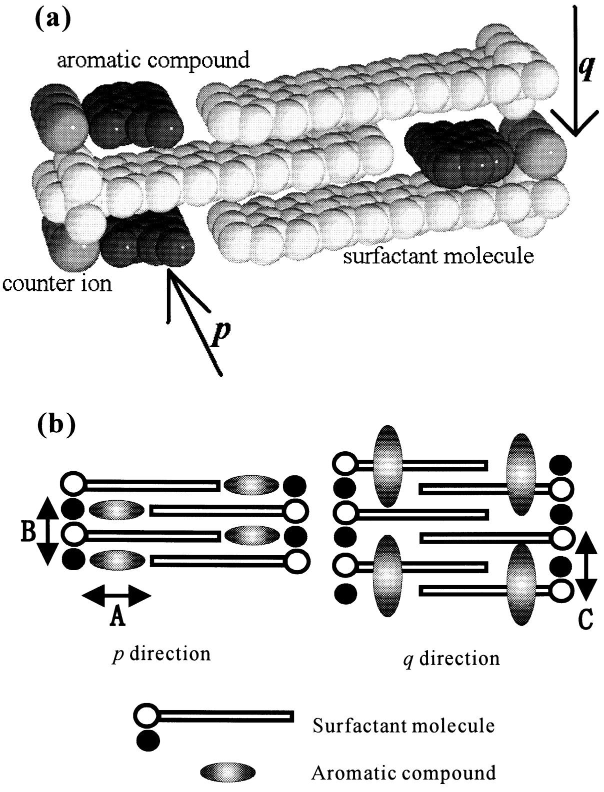


Fig. 5. (a) A perspective view of common packing pattern. The aromatic molecules form a column along the *p* direction and the *q* direction is normal to *p*.

(b) The definition of the distances A, B and C in the schematic drawing of common packing pattern. The left and right figures are along the *p* and *q* directions, respectively.

Table 3. The Values of A, B, and C of the Common Packing Pattern in Surfactant Complexes

Complexes	A/Å	B/Å	C/Å
CTAB/*p*-cresole	9.800	7.474	5.570
CTAB/*m*-cyanophenol	10.270	7.470	5.580
CTAB/guaiacol	9.913	7.427	5.512
CTAB/vanilline	9.931	7.351	5.597
CTAB/skatole	9.902	7.411	5.494
CTAB/2-methylindole	9.386	7.429	5.516
CTAB/acridine	9.640	7.401	5.590
CTAB/phenanthrene	10.285	7.385	5.520
CPB/guaiacol	10.926	8.499	9.730
CPB/9-anthracenecarboxylic acid	12.256	9.586	9.060

void space. The A and B values in the CPB complexes, especially in (**II**), are larger than the threshold values of the CTAB complexes. This indicates that CPB can accommodate bulkier aromatic compounds than CTAB. All of our efforts to make a complex between CTAB and 9-anthracenecarboxylic acid were in vain, although a guaiacol complex with CTAB was made. These results suggest that we can discriminate aromatic compounds by making complexes with different surfactants. Further studies are in progress.

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