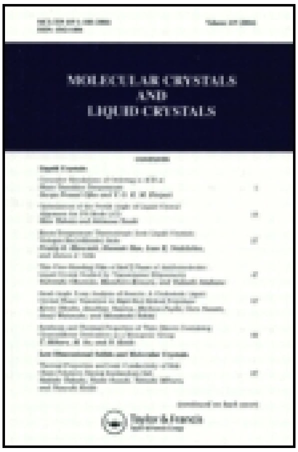

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Crystal Structure and Phase Transition Behavior of Dioctadecyldimethylammonium Chloride Monohydrate

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Crystal Structure and Phase Transition Behavior of Dioctadecyldimethylammonium Chloride Monohydrate

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Monohydrated single crystals of dioctadecyldimethylammonium chloride ($DC_{18}DA^+ Cl^- \cdot H_2O$) were prepared and the crystal structure was determined to elucidate the effects of water molecules on the crystalline to liquid-crystalline phase transition behavior. From the observation during the phase transition of as-prepared single crystals by polarizing optical microscopy and powder X-ray diffractometry, we demonstrated that the water molecules are firstly melted with increasing temperature and one-dimensional ionic chains, $[–\{Cl_2(H_2O)_2\}^{2-}–\{(N)_2\}^{2+}–]_n$, are merged into two-dimensional ionic layers by sliding on the (1 1 –5) planes. This rearrangement is accompanied by the formation of a smectic A like bilayer structure. In addition, the one-dimensional ionic chains are simultaneously stretched to the chain direction, and alkyl chains are interdigitated to reduce a free space within the hydrophobic unit.

Keywords Surfactant; ionic liquid crystal; hydrate; crystal structure; phase transition

1. Introduction

Alkylammonium halides with two methyl groups and two long *n*-alkyl chains have been well-known cationic surfactants, since Kunitake and Okahata first synthesized dioctadecyldimethylammonium bromide ($DC_{18}DA^+Br^-$) as a biomembrane model [1]. These surfactants aggregate to vesicles with biomembrane-like bilayer structures in an aqueous environment and exhibit lyotropic liquid crystallinity at higher concentrations of surfactants. In addition, the majority of such surfactants show thermotropic liquid-crystalline phases with an anisotropic structure self-assembled in a large monodomain due to the microsegregation between the hydrophobic unit of long alkyl chains and the hydrophilic unit of ionic groups [2]. These self-assembled structures are expected to serve as templates for mesoporous materials and nanomaterials, or as anisotropic ion-conductors [3].

Alkylammonium halides are very convenient materials to control their self-assembled structures because they can be stepwise prepared through the quaternization of amine, thus the molecular structure and the hydrophobic-hydrophilic balance can be easily designed by

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changing the alkyl chain lengths. The distance between segregated ionic domains can be also modified by the alkyl chain lengths. Moreover, halide anions can be exchanged for the other anions, for example metal-oxide anions [4–6]. Wide variety of alkylammonium halides has been synthesized so far, and tremendous efforts have been made to understand the basic principles governing their phase stabilities and self-assembled structures [7–9]. These compounds tend to incorporate water molecules, the content of which varies according to the sample preparation conditions. However, only few have paid attention how the water molecules presenting in the systems influence the phase transition behavior and the assembled structure [10,11]. In this study, therefore, we prepared single crystals of dioctadecyldimethylammonium chloride monohydrate, $DC_{18}DA^+Cl^-\cdot H_2O$ (Scheme 1), and observed its structures in crystalline and liquid-crystalline phases to clarify the effects of water molecules on its phase transition behavior as well as the structures.

2. Experimental

Preparation of Single Crystals

Thin platelike and colorless single crystals of $DC_{18}DA^+Cl^-\cdot H_2O$ were grown at an air-solution interface by slow cooling the solution of $DC_{18}DA^+Cl^-$ (100 mg, 0.17 mmol) in chlorobenzene (10 mL) with the presence of giant ring-shaped polyoxomolybdates [12]. The giant ring-shaped polyoxomolybdates might supply suitable amount of water to $DC_{18}DA^+Cl^-$ as crystal water, and it also can generate a density gradient in the solution. Single crystals of $DC_{18}DA^+Cl^-\cdot H_2O$ were obtained at the air-solution interface even without the polyoxomolybdates, and adopted the same crystal structure. Morphologies of crystals obtained from the solution without the polyoxomolybdates, however, tend to be twinned, which declined the quality of crystal structure analysis.

Crystal Structure Analysis

All measurements were carried out at the room temperature, 296(2) K, using a Rigaku AFC-5R diffractometer with graphite-monochromatized Cu Kα radiation ($\lambda = 1.54178$ Å). The intensity data were corrected for Lorentz and polarization effects. Numerical absorption corrections [13] and decay corrections were applied. Other details are summarized in Table 1, together with details of the software used. All nonhydrogen atoms were refined anisotropically. Isotropic displacement parameters of methylene-H atoms were set to be 1.2 U_{eq} of the parent atom, and for methyl-H atoms, they were set to be 1.5 U_{eq}. The methylene- and methyl-H atoms were located at idealized positions with C–H distances of 0.97 and 0.96 Å, respectively, and were allowed to ride on the parent carbon atoms. The H atoms of water molecules were located from a difference Fourier map, and the positional parameters were allowed to refine with the restrained O–H distance of 0.82 Å set to be 1.5 U_{eq} of the parent oxygen atom. The supplementary crystallographic data of this study, CCDC 846158, can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

Polarizing Optical Microscopy

The polarizing optical micrographs of a single crystal of $DC_{18}DA^+Cl^-\cdot H_2O$ were collected using an Olympus BX51 polarizing optical microscope equipped with Mettler FP82 hot

Table 1. Crystallographic data of $DC_{18}DA^+Cl^-\cdot H_2O$.[a]

Chemical formula moiety	$C_{38}H_{80}N^+Cl^-\cdot H_2O$
Molecular weight	604.50
Temperature (K)	296 (2)
Cell setting	Triclinic
Space group	*P*–1
a (Å)	8.227 (2)
b (Å)	8.347 (2)
c (Å)	33.552 (3)
α (°)	89.925 (14)
β (°)	83.180 (15)
γ (°)	62.966 (16)
V (Å^3)	2034.2 (8)
Z	2
Dx (Mg m^{-3})	0.987
$R[F^2 > 2\sigma(F^2)]$	0.080
$wR(F^2)$	0.284
S	1.02

[a] Numerical values in parentheses on the crystallographic data indicate standard deviations. Data collection and cell refinement, MSC/AFC Diffractometer Control Software [17]; data reduction, CrystalStructure [18]; program used to solve structure, SIR92 [19]; program used to refine structure, SHELXL97 [20]; molecular graphics, ORTEP-3 for Windows [21] and VESTA [22]; software used to prepare material for publication, WinGX [23].

stage and FP80 central processor. The textural changes were observed in the first heating process at a heating rate of 10°C min^{-1}, while the temperature was kept constant during the phase transition.

Powder X-Ray Diffractometry

A powdered sample of $DC_{18}DA^+Cl^-\cdot H_2O$ was sealed in a Lindemann capillary with an inner diameter of 0.3 mm. The powder X-ray diffraction image was recorded on a flat imaging-plate (IP) with an exposure time of 2 h using Ni-filtered Cu Kα radiation in a homemade vacuum camera equipped with a hot stage. Each measurement in the first heating process was performed at a constant temperature controlled within ± 1°C. The recorded image was read out using a Rigaku R-AXIS-DS3 IP-reader, and was converted to one dimensional powder X-ray diffraction pattern using XRD2DScan software [14]. The camera length from the sample to the IP-detector was calibrated on the powder X-ray diffraction pattern simulated from the single crystal data of $DC_{18}DA^+Cl^-\cdot H_2O$ using PLATON software [15].

3. Results and Discussion

Figure 1 shows the molecular structure of $DC_{18}DA^+Cl^-\cdot H_2O$. Two long *n*-alkyl chains were not fully extended as one long *n*-alkyl chain adopts double *gauche* conformations in which

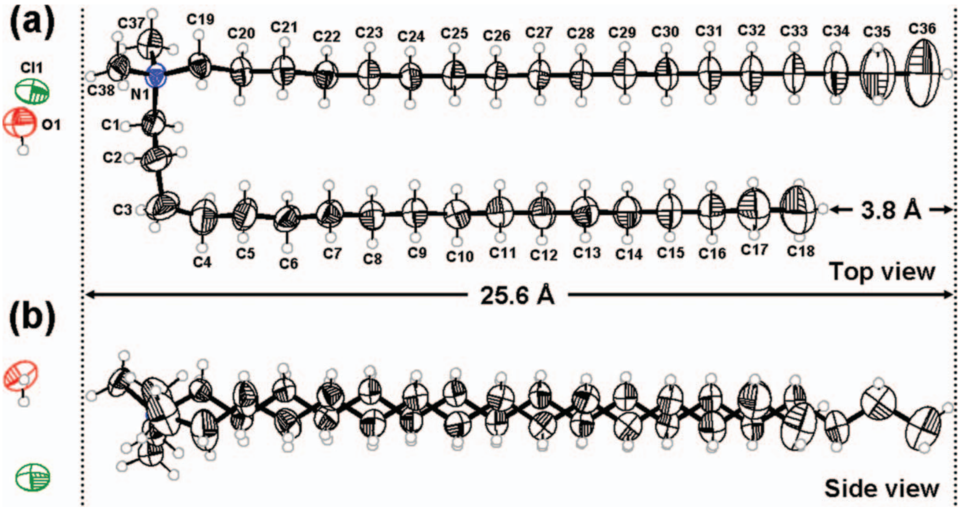

Figure 1. Molecular structure of $DC_{18}DA^{+}Cl^{-}\cdot H_2O$: (a), the top view with the crystallographic numbering scheme; (b), the side view. Displacement ellipsoids are drawn at the 50% probability level.

two torsion angles of C1–C2–C3–C4 and C2–C3–C4–C5 were 75.3 (8)° and 58.3 (9)°, respectively. In this way, two long *n*-alkyl chains were pairwise aligned parallel to their chain axes in one molecule, the length of which is 25.6 Å. These features are similar to those of the homologous compound substituted with bromide anion, dioctadecyldimethylammonium bromide monohydrate ($DC_{18}DA^{+}Br^{-}\cdot H_2O$), analyzed by Okuyama *et al.* [16].

In the crystal structure of $DC_{18}DA^{+}Cl^{-}\cdot H_2O$ (Fig. 2), the molecules form an interleaved layer structure with a thickness of 33.2 Å in which the hydrophilic units of the ionic groups (ammonium cations, chloride anions, and water molecules) and the hydrophobic units of long *n*-alkyl chains were segregated. The paired long *n*-alkyl chains in the hydrophobic unit were tilted by 49.9° with respect to the line normal to the hydrophilic layer in the *bc* plane, and accommodated a space to form a bilayer structure without interdigitation. In the hydrophilic layer of the ionic groups, two chloride anions and two water molecules were bridged by $Cl^{-}\cdots H\text{–}O$ hydrogen bonds, and form an isolated anionic cluster with a square shape, $\{Cl_2(H_2O)_2\}^{2-}$. In this anionic cluster, the distances between Cl^{-} anions and O atoms were 3.148 (4) and 3.201 (5) Å, and the angels of $Cl^{-}\cdots H\text{–}O$ were 175 (6) and 163 (6)°. From those results, we conclude that the $Cl^{-}\cdots H\text{–}O$ hydrogen bonds exist in the hydrophilic layer. In addition, as shown in Fig. 2, the $\{Cl_2(H_2O)_2\}^{2-}$ cluster showed ordered structure; in $\{Cl_2(H_2O)_2\}^{2-}$, the distance between the two chloride anions was 5.120 (3) Å, and angles of $Cl^{-}\cdots O\cdots Cl^{-}$ and $O\cdots Cl^{-}\cdots O$ were 107.48 (12) and 72.52 (12)°, respectively. On the other hand, in the crystal structure of $DC_{18}DA^{+}Br^{-}\cdot H_2O$ reported so far, two water molecules with half occupancy were accommodated in an asymmetric unit, and the hydrogen bonding scheme between bromide anions and water molecules was disordered [16]. Therefore, we consider that the hydration interaction of chloride anions is stronger than that of bromide anions in the system of dioctadecyldimethylammonium halide monohydrate.

The isolated anionic clusters of $\{Cl_2(H_2O)_2\}^{2-}$ were stacked along the *a* axis, and were bridged by the electrostatic interaction with two ammonium cations astride the (0 1 –1) planes (Fig. 2c). The $Cl^{-}\cdots N^{+}$ distances were 4.174 (4) and 4.184 (3) Å. In this way,

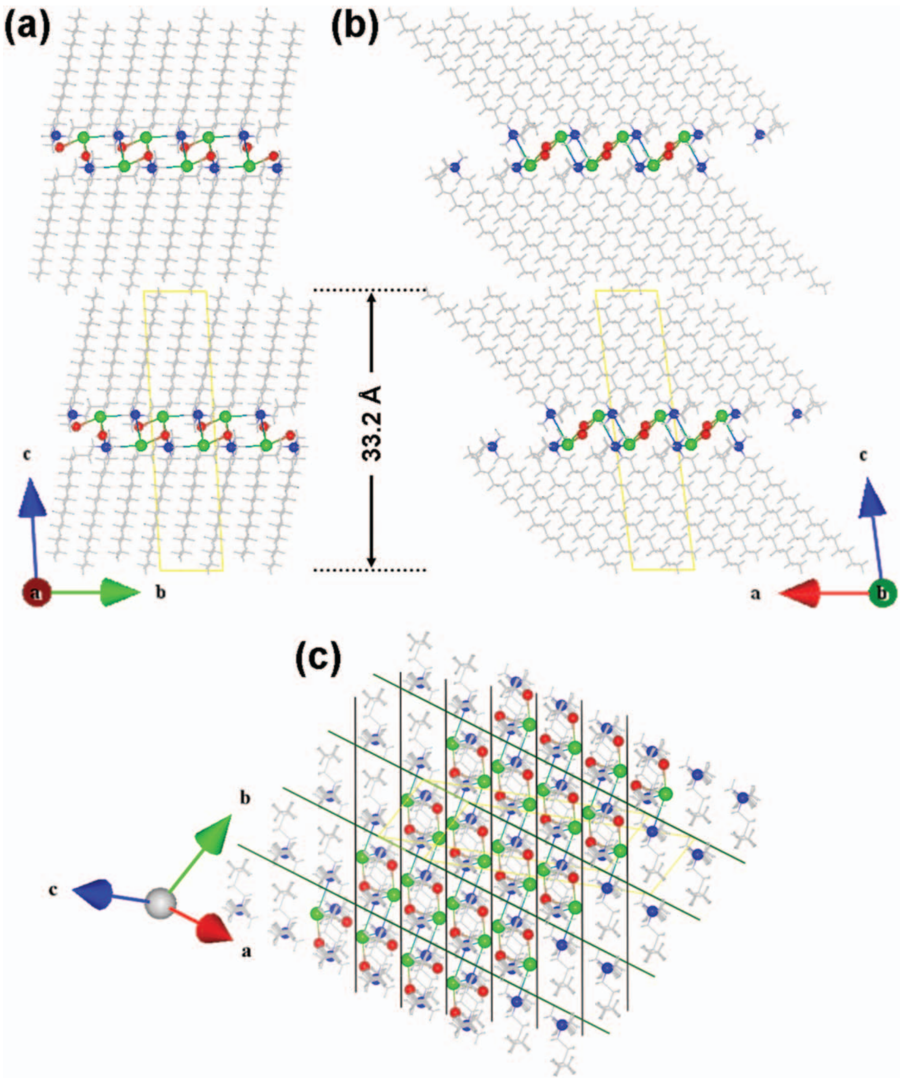

Figure 2. Projections of the crystal structure of $DC_{18}DA^{+}Cl^{-}{\cdot}H_2O$: (a), along the *a* axis; (b), along the *b* axis; (c), along the alkyl chain axes. Legends: Cl^{-}, green; O, red; N^{+}, blue; hydrocarbon chain, light gray lines; unit cell, yellow lines; (0 1 –1) plane, green lines; (1 1 –5) plane, black lines.

one-dimensional ionic chains, $[-\{Cl_2(H_2O)_2\}^{2-}-\{(N)_2\}^{2+}-]_n$, were formed on the (1 1 –5) planes, between which $\{Cl_2(H_2O)_2\}^{2-}$ clusters were weakly interacted with ammonium cations (the $Cl^{-}\cdots N^{+}$ distance is 4.822 (4) Å), totally forming two-dimensional ionic layers.

Figure 3a shows polarizing optical micrographs of a single crystal of $DC_{18}DA^{+}Cl^{-}{\cdot}H_2O$. The most developed facet was the (0 0 1) plane (parallel to the glass surface) formed by interleaving the hydrophilic and the hydrophobic units. The fastest crystal-growth direction was along the *a* axis, which corresponds to the stacking direction of $\{Cl_2(H_2O)_2\}^{2-}$ clusters. During the heating process, the single crystal of

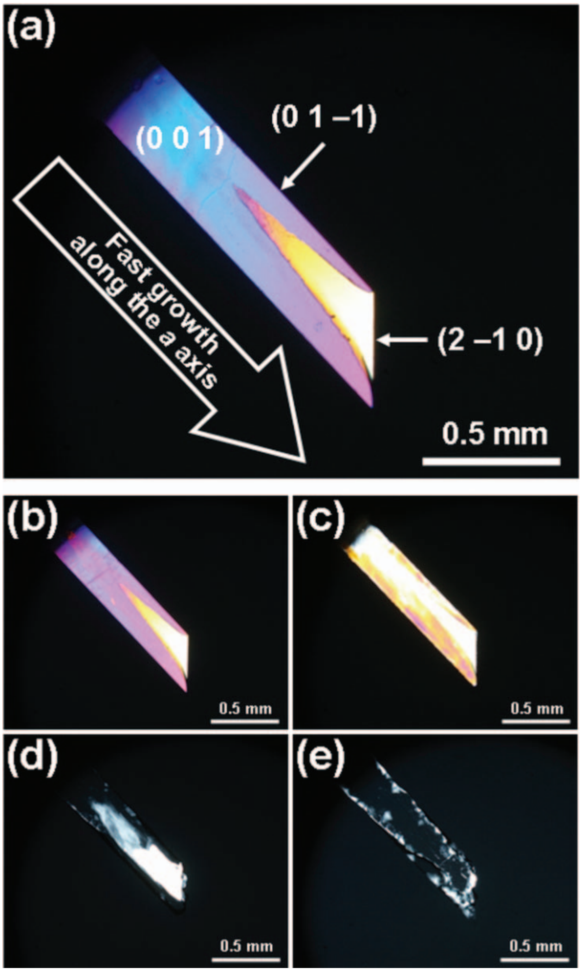

Figure 3. Polarizing optical micrographs of a single crystal of $DC_{18}DA^+Cl^-\cdot H_2O$ and the crystal habit: (a), at 25°C in the crystalline phase; (b–e), at 70°C during the phase transition from crystalline phase to smectic A phase with a homeotropic alignment.

$DC_{18}DA^+Cl^-\cdot H_2O$ exhibited a phase transition around 70°C with changing the optical texture to a dark field (Fig. 3b–e). In this state, the molecules were therefore spontaneously self-assembled to a homeotropic alignment with a monodomain of smectic A phase on the glass surface. It have been reported that completely dehydrated samples of $DC_{18}DA^+Cl^-$ exhibits a phase transition at 96.7°C, while the samples with the water content of about 2.5 wt% show at about 70°C [10] in accordance with the single crystal of $DC_{18}DA^+Cl^-\cdot H_2O$ including water molecules of 3.0 wt%. Enhancement of the temperature range of liquid-crystalline phase in hydrated samples can be achieved via hydrogen bonding between chloride anions and water molecules as observed in the crystal structure of $DC_{18}DA^+Cl^-\cdot H_2O$.

The phase transition behavior of $DC_{18}DA^+Cl^-\cdot H_2O$ was also observed by the powder X-ray diffraction experiments (Fig. 4). The X-ray diffraction pattern at 25°C was entirely consistent with the simulation from the single crystal data. At 65°C, the X-ray

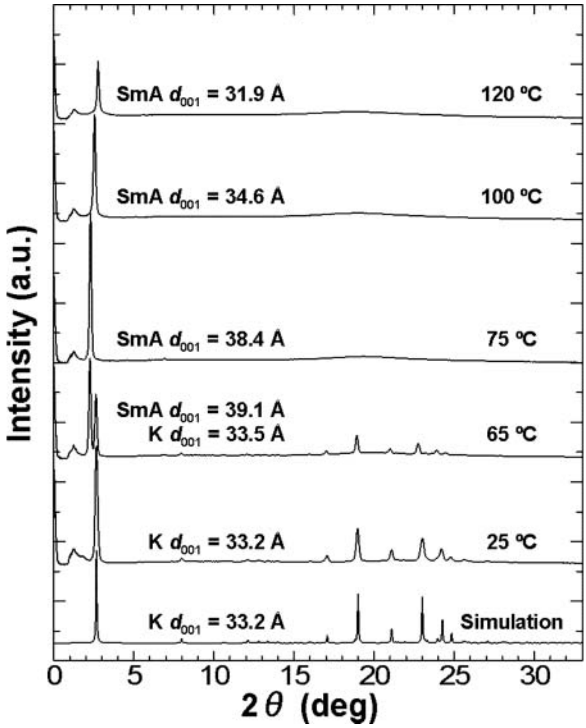

Figure 4. Powder X-ray diffraction patterns of $DC_{18}DA^+Cl^-·H_2O$ in the first heating process and the simulated diffraction pattern from the single crystal data (K, crystalline phase; SmA, smectic A phase). The numerical value of d_{001} indicates the long period in each phase.

diffraction pattern was assigned to two phases: the crystalline phase same as the above structure and a smectic A phase with $d_{001} = 39.1$ Å. The X-ray diffraction peaks derived from the crystalline phase were disappeared in further elevated temperature, and the X-ray diffraction patterns of a smectic A phase contain a diffused halo in the wide angle region revealing the molten state of the alkyl chains. The long period in a smectic A phase decreased with increasing temperature, which can be estimated by the shrinkage of alkyl chain length along the chain direction due to the introduction of *gauche* conformations with the thermal fluctuation. Based on these results, we deduce the mechanism on the phase transition behavior of $DC_{18}DA^+Cl^-·H_2O$ as follows: water molecules melted firstly with increasing temperature and one-dimensional ionic chains, $[–\{Cl_2(H_2O)_2\}^{2-}–\{(N)_2\}^{2+}–]_n$, are merged into two-dimensional ionic layers by sliding on the (1 1 –5) planes (Fig. 5a). This rearrangement is accompanied by the formation of a smectic A bilayer structure. According to estimation from the molecular length of $DC_{18}DA^+Cl^-$ obtained from the single-crystal experiment and the thickness of the two-dimensional ionic layer, a long period of the smectic A phase should be 52.8 Å. However, the long period observed by the powder X-ray diffraction experiment was 39.1 Å in the smectic A phase. Therefore, one-dimensional ionic chains are simultaneously stretched to the chain direction, and alkyl chains are interdigitated to reduce a free space within the hydrophobic unit (Fig. 5b).

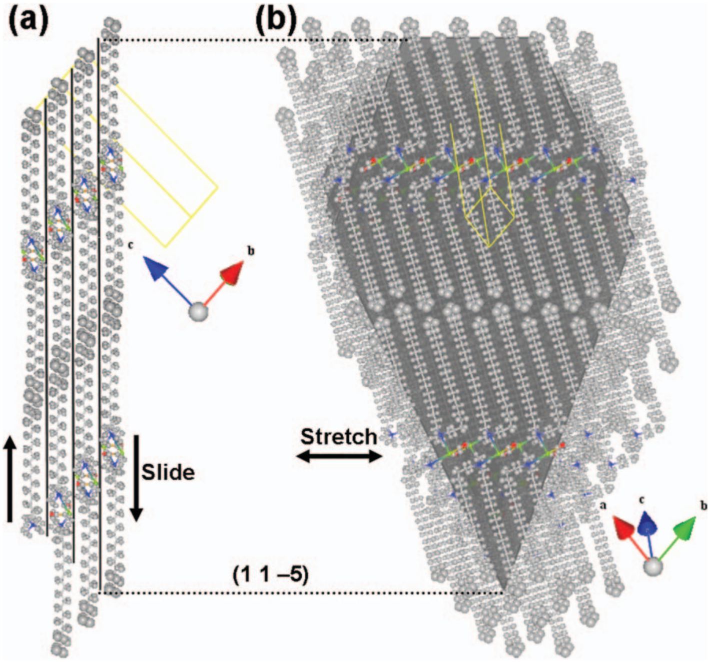

Figure 5. Cut-out views parallel and perpendicular to the (1 1 –5) plane in the crystal structure of $DC_{18}DA^+Cl^-\cdot H_2O$ (Cl^-, green spheres; O, red spheres; N^+, blue spheres; C and H, light gray spheres; unit cell, yellow lines; (1 1 –5) plane, black lines and gray planes). (a): parallel to the (1 1 –5) plane, (b): perpendicular to the (1 1 –5) plane.

Conclusion

We discussed the structures and mechanism of the crystalline to liquid crystalline phase transition of $DC_{18}DA^+Cl^-\cdot H_2O$. In the phase transition process, we found that the water molecules are firstly melted with increasing temperature and one-dimensional ionic chains, $[-\{Cl_2(H_2O)_2\}^{2-}-\{(N)_2\}^{2+}-]_n$, are merged into two-dimensional ionic layers by sliding on the (1 1 –5) planes. This rearrangement is accompanied by the formation of a smectic A like bilayer structure. In addition, the one-dimensional ionic chains are simultaneously stretched to the chain direction, and alkyl chains are interdigitated to reduce a free space within the hydrophobic unit.

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